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CHAPTER 340
DEPARTMENT OF ENVIRONMENTAL QUALITY

FILING CAPTION: Low Emission Vehicle Rules – 2018 Update

EFFECTIVE DATE: 11/15/2018

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RULES:
340-257-0030, 340-257-0050, 340-257-0090

AMEND: 340-257-0030

RULE TITLE: Definitions and Abbreviations

NOTICE FILED DATE: 08/30/2018

RULE SUMMARY: Added: (23) “TZEV” means transitional zero emission vehicle as defined in CCR Title 13, section 1962.1(j)

RULE TEXT:
The definitions in OAR 340-200-0020, the definitions in CCR, Title 13, sections incorporated by reference in OAR 340-257-0050, and the definitions in this division apply to this division. If the same term is defined in different passages, the definitions in this division apply first, followed by definitions in CCR Title 13 sections incorporated by reference, and finally the definitions in OAR 340-200-0020.
(1) "Assembled vehicle" means a motor vehicle that:
(a) Is an assembled vehicle under ORS 801.130; or
(b) Is a replica vehicle under ORS 801.425.
(c) Will be used for occasional transportation, exhibitions, club activities, parades, tours, testing its operation, repairs or maintenance and similar uses; and
(d) Will not be used for general daily transportation.
(2) "ATPZEV" means advanced technology partial zero emission vehicle as defined in CCR, Title 13, section 1962.1(i).
(3) "CARB" means California Air Resources Board.
(4) "CCR" means California Code of Regulations.
(5) "Custom vehicle" means a motor vehicle that:
(a) Is a street rod under ORS 801.513; or
(b) Was manufactured to resemble a vehicle at least twenty-five (25) years old and of a model year after 1948; and
(A) Has been altered from the manufacturer's original design; or
(B) Has a body constructed from non-original materials.
(6) “Emergency vehicle” means a vehicle as defined in ORS 801.260 that is equipped with lights and sirens as required

under ORS 820.350 and 820.370 and that is any of the following:

(a) Operated by public police, fire or airport security agencies.

(b) Designated as an emergency vehicle by a federal agency.

(c) Designated as an emergency vehicle by the Director of Transportation.

(7) "Emission credits" are earned when a manufacturer's reported fleet average is less than the required fleet average. Credits are calculated according to formulas contained in CCR, Title 13, section 1961(c) and 1961.1(b).

(8) "Emission debits" are earned when a manufacturer's reported fleet average exceeds the required fleet average. Debits are calculated according to formulas contained in CCR, Title 13, section 1961(c) and 1961.1(b).

(9) "Fleet average greenhouse gas emission requirements" are generally referred to as limitations on greenhouse gas exhaust mass emission values from passenger cars, light-duty trucks and medium-duty passenger vehicles. The fleet average greenhouse gas emission requirements are set forth in CCR, Title 13, section 1961.1(b).

(10) "Gross vehicle weight rating" or "GVWR" is the value specified by the manufacturer as the loaded weight of a single vehicle.

(11) "Independent low volume manufacturer" is defined in CCR, Title 13, section 1900(b)(8).

(12) "Intermediate volume manufacturer" is defined in CCR, Title 13, section 1900(b)(9)..

(13) "Large volume manufacturer" is defined in CCR, Title 13, section 1900(b)(10).

(14) "Light-duty truck" is any 2000 and subsequent model year motor vehicle certified to the standards in CCR, Title 13, section 1961(a)(1), rated at 8,500 pounds gross vehicle weight or less, and any other motor vehicle rated at 6,000 pounds gross vehicle weight or less, which is designed primarily for the purposes of transportation of property, is a derivative of such vehicle, or is available with special features enabling off-street or off-highway operation and use.

(15) "Medium duty-passenger vehicle" (MDPV) is any medium-duty vehicle with a gross vehicle weight rating of less than 10,000 pounds that is designed primarily for the transportation of persons. The medium-duty passenger vehicle definition does not include any vehicle which

(a) Is an "incomplete truck" i.e., is a truck that does not have the primary load carrying device or container attached; or

(b) Has a seating capacity of more than 12 persons; or

(c) Is designed for more than 9 persons in seating rearward of the driver’s seat; or

(d) Is equipped with an open cargo area of 72.0 inches in interior length or more. A covered box not readily accessible from the passenger compartment will be considered an open cargo area for the purpose of this definition.

(16) "Medium duty vehicle" means any pre-1995 model year heavy-duty vehicle having a manufacturer's gross vehicle weight rating of 8,500 pounds or less; any 1992 through 2006 model-year heavy-duty low-emission, ultra-low-emission, super-ultra-low-emission or zero-emission vehicle certified to the standards in section 1960.1(h)(2) having a manufacturer's gross vehicle weight rating of 14,000 pounds or less; and any 2000 and subsequent model heavy-duty low-emission, ultra-low-emission, super-ultra-low-emission or zero-emission vehicle certified to the standards in Section 1961(a)(1) or 1962.1 having a manufacturer's gross vehicle weight rating between 8,501 and 14,000 pounds.

(17) "Model year" is the manufacturer's annual production period which includes January 1 of a calendar year or, if the manufacturer has no annual production period, the calendar year. In the case of any vehicle manufactured in two or more stages, the time of manufacture is the date of completion of the chassis.

(18) "Non-methane organic gas" (NMOG) is the sum of non-oxygenated and oxygenated hydrocarbons contained in a gas sample as measured in accordance with the "California Non-Methane Organic Gas Test Procedures," which is incorporated herein by reference.

(19) "NMOG fleet average emissions" is a motor vehicle manufacturer's average vehicle emissions of all non-methane organic gases from passenger cars and light duty trucks in any model year subject to this regulation delivered for sale in Oregon.

(20) "Passenger car" is any motor vehicle designed primarily for transportation of persons and having a design capacity of twelve persons or less.

(21) "PZEV" means partial zero emission vehicle as defined in CCR, Title 13, section 1962.1(j).

(22) "Small volume manufacturer" is defined as set forth in CCR, Title 13, section 1900(b)(22), and incorporated herein

by reference.

(23) “TZEV” means transitional zero emission vehicle as defined in CCR Title 13, section 1962.1(j)

(24) "ZEV" means zero emission vehicle as defined in CCR Title 13, section 1962.1(j).

Note: A copy of the California Non-Methane Organic Gas Test Procedures is available through the link below.

STATUTORY/OTHER AUTHORITY: ORS 468.020, 468A.025, 468A.360

STATUTES/OTHER IMPLEMENTED: ORS 468.010, 468A.015, 468A.025, 468A.360

California Environmental Protection Agency
AIR RESOURCES BOARD

CALIFORNIA NON-METHANE ORGANIC GAS TEST PROCEDURES

Adopted:	July 12, 1991
Amended:	September 22, 1993
Amended:	June 24, 1996
Amended:	August 5, 1999
Amended:	July 30, 2002

Monitoring and Laboratory Division, Southern Laboratory Branch
Mobile Source Division
9528 Telstar Avenue
El Monte, California 91731

NOTE: Mention of any trade name or commercial product does not constitute endorsement or recommendation of this product by the Air Resources Board.

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APPENDICES

Part A

GENERAL APPLICABILITY AND REQUIREMENTS

1. These test procedures shall apply to all 1993 and subsequent model-year transitional low-emission vehicles (TLEV), low-emission vehicles (LEV), ultra-low-emission vehicles (ULEV), and super-ultra-low-emission vehicles (SULEV) certifying to non-methane organic gas (NMOG) emission standards.

2. This document sets forth the analysis and calculation procedures that shall be performed to determine NMOG mass emissions. The document consists of the following parts:

   A. General Applicability and Requirements
   B. Determination of Non-Methane Hydrocarbon Mass Emissions by Flame Ionization Detection
   C. Determination of Alcohols in Automotive Source Samples by Gas Chromatography (Method No. 1001)
   D. Determination of C_2 to C_5 Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1002)
   E. Determination of C_6 to C_{12} Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1003)
   F. Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography (Method No. 1004).
   G. Determination of NMOG Mass Emissions

   Appendix 1 List of Light-End and Mid-Range Hydrocarbons
   Appendix 2 Definitions and Commonly Used Abbreviations
   Appendix 3 References

Alternative procedures may be used if shown to yield equivalent results and if approved in advance by the Executive Officer of the Air Resources Board.

3. The analyses specified in the table below shall be performed to determine mass emission rates of NMOG in grams per mile (g/mi) or milligrams per mile (mg/mi) for vehicles operated on the listed fuel:

Fuel	NMHC by FID	NMHC by GC	Alcohols	Carbonyls
Alcohol	X		X	X
CNG		X		X
Diesel	X			X
Gasoline	X			X
LPG	X			X

The specified analyses shall be performed in accordance with the following parts of this document:

NMHC by FID--	Part B.	Determination of Non-Methane Hydrocarbon Mass Emissions by Flame Ionization Detection
NMHC by GC--	Part D.	Determination of C_2 to C_5 Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1002); and
	Part E.	Determination of C_6 to C_{12} Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1003)
CARBONYLS--	Part F.	Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography (Method No. 1004)
ALCOHOLS --	Part C.	Determination of Alcohols in Automotive Source Samples by Gas Chromatography (Method No. 1001)

4. For those manufacturers that choose to develop reactivity adjustment factors unique to a specific engine family, exhaust NMOG emissions shall be fully speciated. NMHC emissions shall be analyzed in accordance with parts D and E (Method Nos. 1002 and 1003). In addition, aldehydes and ketones, alcohols, and ethers shall be analyzed according to parts F, C, and E (Method Nos. 1004, 1001, and 1003). Analysis for alcohols shall be required only for vehicles that are operated on fuels containing alcohols.

5. For natural gas-fueled vehicles, the methane concentration in the exhaust sample shall be measured with a methane analyzer. A GC combined with a FID is used for direct measurement of methane concentrations. SAE Recommended Practice J1151 is a reference on generally accepted GC principles and analytical techniques for this application. A density of 18.89 g/ft^3 shall be used to determine the methane mass emissions. The methane mass emissions shall be multiplied by the appropriate methane reactivity adjustment factor and then added to the reactivity-adjusted NMOG emissions as specified in the "California Exhaust Emission Standards and Test Procedures for 1988-2000 Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles" and in the "California Exhaust Emission Standards and Test Procedures for 2001 and Subsequent Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles."

6. The mass of NMOG emissions shall be calculated in accordance with part G, "Determination of NMOG Mass Emissions". The mass of NMOG emissions in g/mile or mg/mile shall be calculated by summing the mass of NMHC determined by the FID, the mass of aldehydes and ketones, and the mass of alcohols.

PART B

DETERMINATION OF NON-METHANE HYDROCARBON MASS EMISSIONS BY FLAME IONIZATION DETECTION

1. INTRODUCTION

1.1 This procedure describes a method for determining NMHC exhaust mass emissions from motor vehicles. Other applicable forms of instrumentation and analytical techniques which prove to yield equivalent results to those specified in this procedure may be used subject to the approval of the Executive Officer of the Air Resources Board.

1.2 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. TOTAL HYDROCARBON MEASUREMENT

2.1 A FID is used to measure total hydrocarbon concentration in vehicle exhaust in accordance with the Code of Federal Regulations [Ref.1]. SAE Recommended Practices J254 [Ref. 2] and J1094a [Ref. 3] are references on generally accepted gas analysis and constant volume sampling techniques. For Beckman 400 FIDs only, implementation of the recommendations outlined in SAE paper 770141[Ref. 4] shall be required. Other FID analyzer models shall be checked and adjusted, if necessary, to minimize any non-uniformity of relative response to different hydrocarbons.

3. METHANE MEASUREMENT

3.1 A GC combined with a FID constitute a methane analyzer and shall be used for direct measurement of methane concentrations. The SAE Recommended Practice J1151[Ref. 5] is a reference on generally accepted GC principles and analytical techniques for this specific application.

4. TOTAL HC FID RESPONSE TO METHANE

4.1 The FID is calibrated to propane and therefore tends to over respond to the methane portion of the vehicle exhaust sample during hydrocarbon analysis. In order to calculate the NMHC concentration, a methane response factor must be applied to the methane concentration (as measured by the methane analyzer) before it can be deducted from the total hydrocarbon concentration. To determine the total hydrocarbon FID response to methane, known methane in air concentrations traceable to NIST shall be analyzed by the FID. Several methane concentrations shall be analyzed by the FID in the range of the exhaust sample concentration. The total hydrocarbon FID response to methane is calculated as follows:

$$r_{CH_4} \quad = \quad FID_{ppm}/SAM_{ppm}$$

where:

r_{CH_4} = FID methane response factor.
FID_{ppm} = FID reading in ppmC.
SAM_{ppm} = the known methane concentration in ppmC.

The FID response to methane shall be checked at each calibration interval.

5. NMHC MASS EMISSION PER TEST PHASE

5.1 The following calculations shall be used to determine the NMHC mass emissions for each phase of the Federal Test Procedure [Ref. 1].

5.2 Non-Alcohol Fueled Vehicles

5.2.1 $NMHC_e = FID\ THC_e - (r_{CH_4} * CH_{4e})$

NOTE: If $NMHC_e$ is calculated to be less than zero, then $NMHC_e = 0$.

5.2.2 $NMHC_d = FID\ THC_d - (r_{CH_4} * CH_{4d})$

NOTE: If $NMHC_d$ is calculated to be less than zero, then $NMHC_d = 0$.

5.2.3 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

a) For gasoline, $CH_{1.85}$, where HCR = 1.85:
$CO_e = (1 - 0.01925 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

b) For Phase 2 gasoline, $CH_{1.94}$, where HCR = 1.94:
$CO_e = (1 - 0.01970 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

c) For LPG, $CH_{2.64}$, where HCR = 2.64:
$CO_e = (1 - 0.02320 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

d) For CNG, $CH_{3.78}$, where HCR = 3.78:
$CO_e = (1 - 0.02890 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

5.2.4 $$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * \left(x + y/4 - z/2\right)} \right)}{CO_{2e} + \left(NMHC_e + CH_{4e} + CO_e\right) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

a) For gasoline, $CH_{1.85}$, where x = 1, y = 1.85, and z = 0:
$DF = 13.47 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$

b) For Phase 2 gasoline, $CH_{1.94}$, x = 1, y = 1.94 and z = 0.017:
$DF = 13.29 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$

c) For LPG, $CH_{2.64}$, where x = 1, y = 2.64, and z = 0:
$DF = 11.68 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$

d) For CNG, $CH_{3.78}$, where x = 1, y = 3.78, and z = 0.016:
$DF = 9.83 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$

5.3 Vehicles Operating on Fuels Containing Methanol

5.3.1 $NMHC_e = FID\ THC_e - (r_{CH_4} * CH_{4e}) - (r_{CH_3OH} * CH_3OH_e)$
NOTE: If $NMHC_e$ is calculated to be less than zero, then $NMHC_e = 0$.

5.3.2 $NMHC_d = FID\ THC_d - (r_{CH_4} * CH_{4d}) - (r_{CH_3OH} * CH_3OH_d)$
NOTE: If $NMHC_d$ is calculated to be less than zero, then $NMHC_d = 0$.

5.3.3 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$
NOTE: If a CO instrument which meets the criteria specified in CFR 40 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

a) For M100 (100% methanol), CH_3OH, where HCR = 4:
$CO_e = (1 - 0.03000 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

b) For M85 (85% methanol, 15% indolene), $CH_{3.41}O_{0.72}$, where HCR = 3.41:
$CO_e = (1 - 0.02705 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

5.3.4 $$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)} \right)}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e + CH_3OH_e + HCHO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

a) For M100 (100% methanol), CH_3OH, where x = 1, y = 4, and z = 1:
$DF = 11.57 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + CH_3OH_e + HCHO_e) * 10^{-4}]$

b) For M85 (85% methanol, 15% Indolene), $CH_{3.41}O_{0.72}$, where x = 1, y = 3.41, and z = 0.72:
$DF = 12.02 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + CH_3OH_e + HCHO_e) * 10^{-4}]$

5.4 Vehicles Operating on Fuels Containing Ethanol

5.4.1 $NMHC_e = FID\ THC_e - (r_{CH_4} * CH_{4e}) - (r_{C_2H_5OH} * C_2H_5OH_e)$
NOTE: If $NMHC_e$ is calculated to be less than zero, then $NMHC_e = 0$

5.4.2 $NMHC_d = FID\ THC_d - (r_{CH_4} * CH_{4d}) - (r_{C_2H_5OH} * C_2H_5OH_d)$
NOTE: If $NMHC_d$ is calculated to be less than zero, then $NMHC_d = 0$

5.4.3 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

a) For E100 (100% ethanol), C_2H_5OH, where HCR = 3:
$CO_e = (1 - 0.02500 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

5.4.4 $$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)} \right)}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e + C_2H_5OH_e + HCHO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

a) For E100 (100% ethanol), C_2H_5OH, where x = 1, y = 3, and z = 0.5:
$DF = 12.29 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + C_2H_5OH_e + HCHO_e) * 10^{-4}]$

5.5 All Vehicles

5.5.1 $NMHC_{conc} = NMHC_e - NMHC_d * [1 - (1 / DF)]$
NOTE: If $NMHC_{conc}$ is calculated to be less than zero, then $NMHC_{conc} = 0$

5.5.2 $NMHC_{mass_n} = NMHC_{conc} * NMHC_{dens} * VMIX * 10^{-6}$

6. TOTAL WEIGHTED NMHC MASS EMISSIONS

6.1 All Vehicles

6.1.1 $$NMHC_{wm} = 0.43 * \left(\frac{NMHC_{mass1} + NMHC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{NMHC_{mass3} + NMHC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

7. SAMPLE CALCULATIONS

7.1 Given the following data for a gasoline vehicle, calculate the weighted NMHC mass emission.

Test Phase	FID THC_e (ppmC)	FID THC_d (ppmC)	CH_{4e} (ppmC)	CH_{4d} (ppmC)	CO_{em} (ppm)	CO_{2e} (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)	R_a (%)
1	41.8	8.6	7.53	5.27	147.2	1.19	2846	3.583	38
2	13.0	8.4	5.68	5.10	20.8	0.80	4856	3.848	38
3	15.4	8.9	6.16	5.20	36.7	1.04	2839	3.586	38

For Phase 1:

$NMHC_e$ = FID THC_e - (r_{CH_4} * CH_{4e})
= 41.8 ppmC - (1.04 * 7.53 ppmC)
= 33.97 ppmC

$NMHC_d$ = FID THC_d - (r_{CH_4} * CH_{4d})
= 8.6 ppmC - (1.04 * 5.27 ppmC)
= 3.12 ppmC

CO_e = (1 - 0.01925 * CO_{2e} - 0.000323 * R_a) * CO_{em}

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

= (1 - 0.01925 * 1.19% - 0.000323 * 38%) * 147.18 ppm
= 142.0 ppm

DF = 13.47 ÷ [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}]

$$DF = \frac{13.47}{1.19\% + (33.97\ ppmC + 7.53\ ppmC + 142.0\ ppmC) * 10^{-4}}$$

= 11.15

$NMHC_{conc}$ = $NMHC_e$ - $NMHC_d$ * [1 - (1 ÷ DF)]

$$= 33.97 \text{ ppmC} - 3.12 \text{ ppmC} * [1- (1 \div 11.15)]$$
$$= 31.13 \text{ ppmC}$$

$$NMHC_{mass\ n} = NMHC_{conc} * NMHC_{dens} * VMIX * 10^{-6}$$
$$= 31.13 \text{ ppmC} * 16.33 \text{ g/ft}^3 * 2846 \text{ ft}^3 * 10^{-6}$$

$$NMHC_{mass\ 1} = 1.45 \text{ g}$$

Similarly, for Phase 2: $NMHC_{mass\ 2} = 0.33$ g
and for Phase 3: $NMHC_{mass\ 3} = 0.27$ g

Therefore,

$$NMHC_{wm} = 0.43 * \left(\frac{NMHC_{mass1} + NMHC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{NMHC_{mass3} + NMHC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

$$NMHC_{wm} = 0.43 * \left(\frac{1.45\,g + 0.33\,g}{3.583 \text{ miles} + 3.848 \text{ miles}} \right) + 0.57 * \left(\frac{0.27\,g + 0.33\,g}{3.586 \text{ miles} + 3.848 \text{ miles}} \right)$$

$$NMHC_{wm} = 0.15 \text{ g/mile}$$

7.2 Given the following data for a vehicle operating on 85% methanol and 15% gasoline (M85), calculate the weighted NMHC mass emission.

Test Phase	FID THC_e (ppmC)	FID THC_d (ppmC)	CH_{4e} (ppmC)	CH_{4d} (ppmc)	CH_3OH_e (ppm)	CO_{em} (ppm)	CO_{2e} (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)	R_a (%)	$HCHO_e$ (ppm)
1	88.5	5.5	17.76	2.82	72.9	303.2	1.28	2832	3.570	32	0.96
2	14.5	7.0	8.01	2.82	5.1	9.7	0.83	4827	3.850	32	0.10
3	21.8	7.7	10.13	2.93	7.4	18.2	1.13	2825	3.586	32	0.12

[For this example, CH_3OH_d was assumed to be 0.0 ppmC for all three background bag samples.]

For Phase 1:

$$NMHC_e = \text{FID } THC_e - (r_{CH_4} * CH_{4e}) - (r_{CH_3OH} * CH_3OH_e)$$
$$= 88.5 \text{ ppmC} - (1.04*17.76 \text{ ppmC}) - (0.66*72.9 \text{ ppmC})$$
$$= 21.92 \text{ ppmC}$$

$NMHC_d$ = FID THC_d - (r_{CH_4} * CH_{4d}) - (r_{CH_3OH} * CH_3OH_d)
= 5.5 ppmC - (1.04*2.82 ppmC) - (0.66*0.0 ppmC)
= 2.57 ppmC

CO_e = (1 - 0.02705 * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e
.

= (1 - 0.02705 * 1.28% - 0.000323 * 32%) * 303.2 ppm
= 289.6 ppm

DF = 12.02 ÷ [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e + CH_3OH_e + $HCHO_e$) * 10^{-4}]

$$= \frac{12.02}{1.28\% + \left(21.92\,\text{ppmC} + 17.76\,\text{ppmC} + 289.6\,\text{ppmC} + 72.9\,\text{ppmC} + 0.96\,\text{ppmC}\right) * 10^{-4}}$$

= 9.10

$NMHC_{conc}$ = $NMHC_e$ - $NMHC_d$ * [1 - (1 / DF)]
= 21.92 ppmC - 2.57 ppmC * [1 - (1 / 9.10)]
= 19.63 ppmC

$NMHC_{mass\ n}$ = $NMHC_{conc}$ * $NMHC_{dens}$ * VMIX * 10^{-6}

$NMHC_{mass\ 1}$ = 0.91 g

Similarly, Phase 2: $NMHC_{mass\ 2}$ = 0.0 g
and for Phase 3: $NMHC_{mass\ 3}$ = 0.10 g

Therefore,

$$NMHC_{wm} = 0.43 * \left(\frac{NMHC_{mass1} + NMHC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{NMHC_{mass3} + NMHC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

$$NMHC_{wm} = 0.43 * \left(\frac{0.91\,\text{g} + 0.00\,\text{g}}{3.570\ \text{miles} + 3.850\ \text{miles}} \right) + 0.57 * \left(\frac{0.10\,\text{g} + 0.00\,\text{g}}{3.586\ \text{miles} + 3.850\ \text{miles}} \right)$$

$NMHC_{wm}$ = 0.06 g/mile

Part C

DETERMINATION OF ALCOHOLS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1001

1. INTRODUCTION

1.1 This document describes a method of sampling and analyzing automotive exhaust for alcohols in the range of 1 to 1200 µg per 15 mL of solution. The "target" alcohols that shall be analyzed and reported by this method are methanol and ethanol. These alcohols, when measured in concentrations above the LOD, shall be reported.

1.2 This procedure is based on a method developed by the U. S. Environmental Protection Agency, (U.S. EPA) [Ref 6] which involves flowing diluted engine exhaust through deionized or purified water contained in glass impingers and analyzing this solution by gas chromatography .

1.3 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

2.1 The samples are received by the laboratory in impingers. Compound separation and analysis are performed using a GC. The sample is injected into the GC by means of a liquid autosampler. Separation of the sample mixture into its components is performed by a temperature-programmed capillary column. A FID is used for alcohol detection and quantification.

2.2 The computerized GC data system identifies the alcohol associated with each peak. The alcohol concentrations are determined by integrating the peak areas and using response factors determined from external standards.

3. INTERFERENCES AND LIMITATIONS

3.1 An interferent is any component present in the sample with a retention time similar to that of any target alcohol described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method and/or instrumentation, e.g., GC/MS.

3.2 The concentration of the alcohols in the range of interest is stable for up to six days as long as the samples are sealed and refrigerated at a temperature below 40°F.

4. INSTRUMENTATION AND APPARATUS

4.1 For each mode of the CVS test, two sampling impingers, each containing a known amount of deionized or purified water (e.g. 15 mL for this procedure), are used to contain the sample.

4.1.1 A temperature-programmable GC, equipped with a DB-Wax Megabore column (30 m, 0.53 mm ID, 1.0 µ film thickness) and FID, is used. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all the target alcohols.

4.1.2 A liquid autosampler is required.

4.1.3 A PC-controlled data acquisition system for quantifying peak areas is required.

5. REAGENTS AND MATERIALS

5.1 Methanol shall have a purity of 99.9 percent, or be high performance liquid chromatography grade, EM Science or equivalent.

5.2 Ethanol shall be absolute, ACS reagent grade.

5.3 ASTM Type I purified or Type II deionized water shall be used.

5.4 Stock solutions are prepared gravimetrically or volumetrically by diluting methanol and ethanol with deionized or purified water, e.g., for this method a typical stock solution contains approximately 10 mg/mL of each target alcohol. Stock solutions must be replaced at least every six months.

5.4.1 A **calibration standard** within the expected concentration range of the samples is prepared by successive dilutions of the stock solution with deionized or purified water; 3 to 50 µg/mL is typical, depending on fuel type. Calibration standards must be replaced at least every week.

5.4.2 A **control standard** containing all target alcohols is prepared by successive dilutions of a stock solution different from that of Section 5.4.1. This standard, at an approximate concentration of the samples, is used to monitor the precision of the analysis of each target alcohol. Control standards must be replaced at least every week.

5.4.3 Standards used for linearity and LOD determinations (Section 8) are also prepared by successive dilutions of an appropriate level stock solution.

5.4.4 All standards should be refrigerated at a temperature below 40°F during storage.

5.5 Gas requirements.

5.5.1 Air shall be “Zero” grade (<1 ppmC total hydrocarbon contamination) or better.

5.5.2 Nitrogen shall have a minimum purity of 99.998 percent.

5.5.3 Helium shall have a minimum purity of 99.995 percent.

5.5.4 Hydrogen shall have a minimum purity of 99.995 percent.

6. PROCEDURE

6.1 Each of the graduated sampling impingers is filled with 15 mL of deionized or purified water.

6.2 The impingers are placed in an ice bath during the sample collection.

6.3 After sampling, the solution contained in each impinger is transferred to a vial and sealed.

6.3.1 Samples shall be refrigerated at a temperature below 40°F if immediate analysis is not feasible, or if reanalysis at a later date may be required.

6.4 One microliter aliquots of unmodified samples are injected via autosampler into a GC. Suggested standard operating conditions for the GC are:

Column:	DB-Wax, 30 m, 0.53 mm ID, 1.0μ film thickness
Carrier gas flow:	Helium at 5 mL/min
Make-up gas flow:	Nitrogen at 25 mL/min
Detector:	FID, hydrogen at 30 mL/min and air at 300 mL/min
Injector:	Packed column injector with Megabore adapter insert; on-column injection
Column temperature:	50°C (1 min), 50°C to 70°C (5°C/min), 70°C to 110°C (15°C/min), 110°C (4 min)
Data system:	PC-based data acquisition system

6.5 Samples containing compounds having concentrations above the documented range of instrument linearity must be diluted and reanalyzed.

6.6 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.

6.7 The peak identifications provided by the computer are checked and corrected if necessary.

7. CALCULATIONS

7.1 The concentration of each target alcohol, in µg/mL, is determined by the following calculation that compares the sample peak area with that of an external standard:

$$\text{Concentration } (\mu g/mL)_{sample} = \text{ Peak Area}_{sample} \times \text{ Response Factor}$$

where the response factor (RF) is calculated during the calibration by:

$$RF = \frac{\text{Concentration}_{\text{standard}\,(\mu g/mL)}}{\text{Peak Area}_{\text{standard}}}$$

7.2 This concentration is then used to calculate the total amount of alcohol in each impinger:

$$\text{Mass } (\mu g) = \text{Concentration } (\mu g/mL) \times \text{ Impinger volume (mL)}$$

7.3 An internal standard method may also be used.

8. QUALITY CONTROL

8.1 Blank Run - A deionized or purified water blank is run each analysis day. All target alcohol concentrations from the blank analysis must be below the LOD before the analysis may proceed.

8.1.1 If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of the contamination must be investigated and remedied.

8.2 Calibration Run - The calibration standard is analyzed each analysis day to generate the response factor used to quantify the sample concentrations.

8.3 Control Standard Run - The quality control standard is analyzed at least once each analysis day. Measurements of all target alcohols in the control standard must fall within the control limits to ensure the validity of the sample analyses that day. To meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.

8.4 Control Charts - A quality control chart is maintained for each analyte in the control standard. The control charts, used on a daily basis, establish that the method is "in-control". The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard results;
2. Calculate the control standard mean concentration and standard deviation for the target analyte; and
3. Create a control chart for the target analyte by placing the concentration on the Y-axis and the date on the X-axis. Establish upper and lower warning limits at either two standard deviations (2s) or 5 percent, whichever is greater, above and below the average concentration. Establish upper and lower control limits at either three standard deviations (3s) or 5 percent, whichever is greater, above and below the average concentration.
4. A control standard measurement is considered to be out-of-control when the analyzed value exceeds the control limit or two successive control standard measurements of the same analyte exceed the warning limit.
5. If 20 control standard results are not yet available to create a control chart (e.g., the control standard was expended and replaced with a different concentration standard prior to obtaining 20 points with the new standard), measurements must be within 10% of the theoretical concentration.

The measured concentrations of all target analytes contained in the control standard must be within the control limits ("in-control") for the sample results to be considered acceptable.

8.5 Duplicates - A duplicate analysis of one sample is performed at least once per analysis day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\mathrm{RPD}(\%) = \frac{|\text{Difference between duplicate and original measurements}|}{\text{Average of duplicate and original measurements}} * 100$$

For each compound, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

Average Measurement for Duplicate Runs		Allowable RPD (%)
1 to 10	times LOD	100
10 to 20	" "	30
20 to 50	" "	20
Greater than 50	" "	15

If the results of the duplicate analyses do not meet these criteria for all target alcohols, the sample may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

8.6 Linearity - A multipoint calibration to confirm instrument linearity is performed for all target alcohols for new instruments, after making instrument modifications that can affect linearity, and at least once every year. The multipoint calibration consists of at least five concentration or mass loading levels, each above the LOD, distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one point calibrations.

8.7 Limit of Detection - The LOD for the target alcohols must be determined for new instruments, after making instrument modifications that can affect the LOD and at least once every year. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the expected LOD, with at least five replicate determinations of the lowest concentration standard. A linear regression is performed and the standard deviation (in area counts) of the lowest concentration standard determined. The standard deviation is converted to concentration units using the slope of the linear regression:

$$s = s_a \div m$$

where m is the slope of the linear regression, s is the standard deviation (in concentration units) of the lowest concentration standard and s_a is the standard deviation (in area counts) of the lowest concentration standard.

The LOD must be calculated using the following equation [Ref. 12]:

$$\mathrm{LOD} = t * s$$

where s is the standard deviation (in concentration units) of at least five replicate determinations of the lowest concentration standard and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t–table is:

Degrees of Freedom	t-value
4	3.7
5	3.4
6	3.1
7	3.0

The lowest standard must be of a concentration of one to five times the estimated LOD.

8.7.1 The maximum allowable LOD for each alcohol is 0.10 µg/mL. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.7.2 For the purpose of calculating the total mass of all species, the concentrations of the compounds below the LOD are considered to be zero.

Part D

DETERMINATION OF C_2 TO C_5 HYDROCARBONS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1002

1. INTRODUCTION

1.1 This document describes a gas chromatographic method of analyzing C_2 to C_5 hydrocarbons (light-end hydrocarbons) in the ppbC range from automotive source samples. This method does not include sample collection procedures [Ref. 8]. The "target" hydrocarbons that shall be analyzed and reported by this method and Method 1003 are listed in Appendix 1. All compounds on this list, when measured in concentrations above the LOD, shall be measured and reported ("targeted") by either Method 1002 or Method 1003. Each laboratory should divide the list into light-end (Method 1002) and mid-range (Method 1003) hydrocarbons in the manner that best suits the laboratory instrumentation. All compounds on the list not targeted by Method 1002 must be targeted by Method 1003.

1.2 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

2.1 This is a method intended for routine analysis.

2.2 The samples are received by the laboratory in Tedlar bags, which are sub-sampled into a GC for separation and analysis.

2.3 The gas chromatographic analysis is performed on an Alumina (Al_20_3) PLOT column temperature programmed from 0^oC to 200^oC. An FID is used for detection and quantification.

2.4 The sample is injected into the GC by means of gas sampling valves. Separation of the sample hydrocarbon mixture into its components takes place in the chromatographic column. The chromatographic column and the corresponding operating parameters described in this method normally provide complete resolution of most target compounds.

2.5 The computerized GC data acquisition system identifies the hydrocarbons associated with each peak. The hydrocarbon concentrations are determined by integrating the peak areas and using response factors determined from NIST-traceable standards.

3. INTERFERENCES AND LIMITATIONS

3.1 An interferent is any component present in the sample with a retention time very similar to that of any target hydrocarbon described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method and/or instrumentation, e.g., GC/MS, PID, different column, etc.

3.2 To maximize sample integrity, sample bags should not leak or be exposed to bright light or excessive heat. Sampling bags must be shielded from direct sunlight to avoid photochemically induced reactions of any reactive hydrocarbons. The compound 1,3-butadiene, resulting mostly during cold-start testing is unstable. Therefore all cold-start samples must be analyzed within 8 hours; all other samples must be analyzed within 24 hours, although analysis within 8 hours is recommended.

4. INSTRUMENTS AND APPARATUS

4.1 Tedlar bags, 2 mil in thickness, nominally 5 to 10 liters in capacity and equipped with quick-connect fittings, are used to contain the samples.

4.2 For manual sub-sampling into a GC, a ground glass syringe is used to transfer gaseous samples from Tedlar bags to the GC sample inlet. For automated systems, a sample loop is used to transfer gaseous samples from the Tedlar bag to the sample inlet of the GC. Sample aliquot size is chosen based on considerations of instrument sensitivity and/or linearity.

4.3 A temperature-programmable GC equipped with a gas sampling valve system, a FID, and accessories is required.

4.4 An Alumina PLOT column (50 m x 0.32 mm) is used. A wax precolumn is recommended to prevent water damage to the PLOT column. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all the target hydrocarbons.

4.5 A sample trap capable of being cryogenically cooled may be used.

4.6 Data acquisition software is used to integrate peak areas to determine hydrocarbon concentrations.

5. REAGENTS AND MATERIALS

5.1 Helium shall have a minimum purity of 99.995 percent. Higher purity helium may be required to achieve the LOD required by Section 8.7.1.

5.2 Hydrogen shall have a minimum purity of 99.995 percent.

5.3 Air shall be “Zero” grade (<1 ppmC total hydrocarbon contamination) or better.

5.4 Nitrogen shall have a minimum purity of 99.998 percent.

5.5 Calibration Standard - The quantitative calibration standard for all target hydrocarbons shall be propane at a concentration level between 0.25 and 1 ppm-mole and within the calculated linearity of the method. (See Section 8.6.) This propane standard must be a NIST-certified SRM or secondary NIST-traceable standard. A secondary standard is obtained by a comparison between a SRM and a candidate standard.

5.6 Control Standard - A quality control standard, containing at least ethene, propane, n-butane, and 2-methylpropene with concentrations between 0.2 and 3 ppmC based on a propane standard, is used for the following purposes:

1. Daily update of control charts, and
2. Daily determination of marker retention time windows.

5.7 A high concentration standard (higher than the calibration standard), containing the target hydrocarbons listed in Section 5.6, is used for linearity determinations. The high concentration standard must have concentrations verified against a NIST-traceable propane standard. (See Section 5.5 for the definition of NIST-traceable.) This verification can be performed at the laboratory performing the analysis.

5.8 A low concentration standard (one to five times the estimated LOD), containing the target hydrocarbons listed in Section 5.6, is used for LOD determinations. The low concentration standard must have concentrations verified against a NIST-traceable propane standard. (See Section 5.5 for the definition of NIST-traceable.) This verification can be performed at the laboratory performing the analysis.

5.8.1 In lieu of a low concentration standard, a higher concentration standard may be diluted.

5.9 Liquid nitrogen may be required to cool the cryogenic sample trap and column oven where applicable.

6. PROCEDURE

6.1 The gaseous sample is analyzed for the target hydrocarbons C_2 through C_5.

6.2 Suggested standard operating conditions for the gas chromatograph are:

Helium carrier gas velocity:	30 cm/sec at 200^{0}C
Nitrogen make-up gas flow:	sufficient such that the total flow of helium plus nitrogen is 30 mL/min
Hydrogen gas flow:	30 mL/min
Air flow:	300 mL/min
Sample valve temperature:	150^{0}C (PLOT column)
Column temperature:	0^{0}C (hold 7 min), 10^{0}C/min to 200^{0}C (hold 15 min)
Detector temperature:	250^{0}C
Injector temperature:	150^{0}C

6.3 For automated systems, connect the samples to the GC and begin the analytical process.

6.4 Introduce the sample into the carrier gas stream through the injection valve.

6.5 Each separated component exits from the column into the FID where a response is generated.

6.6 Concentrations of hydrocarbons are calculated using data acquisition/ processing software that uses calibration data from the NIST-traceable propane calibration standard.

6.7 For compounds having concentrations above the documented range of instrument linearity, a smaller aliquot must be taken (for manual systems, a smaller syringe or smaller loop; for automated systems, a smaller loop) or the sample must be diluted.

6.8 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.

6.9 The peak identifications provided by the computer are checked and corrected if necessary.

6.10 Target compounds that coelute are reported as the major component, as determined by the analysis of several samples by GC/MS or other methods. An exception to this is m- and p-xylene, where GC/MS data and fuel profiles are used to determine the relative contribution of each component to the peak. This method was used to determine the m- and p-xylene MIR value given in Appendix 1.

6.11 The Alumina PLOT column is programmed to 200°C to assure all compounds are eluted before the next run.

7. CALCULATIONS

7.1 The target hydrocarbon concentrations, in ppbC, are calculated by the data system using propane as an external standard.

$$\text{Concentration}_{\text{sample}}\ (\text{ppbC}) = \text{Peak Area}_{\text{sample}} \times \text{Response Factor}$$

where the response factor (RF) is calculated during daily calibration by:

$$\text{RF} = \frac{\text{Concentration of NIST-traceable propane standard, ppbC}}{\text{Area of propane peak}}$$

8. QUALITY CONTROL

8.1 Blank Run - A blank (pure nitrogen or helium) is run each analysis day. All target hydrocarbon concentrations from the blank analysis must be below the LOD before the analysis may proceed. As an alternative to a daily blank run, a daily partial blank check in tandem with a weekly blank run may be used. A partial blank check is defined as a check of the calibration standard run for contamination over all but the propane region of the chromatograph. The calibration standard must consist of only propane and make-up gas, with the concentration of all organic compounds except methane and propane below 2 percent of the propane standard concentration. The weekly blank run will provide a check on contamination in the propane region of the chromatograph.

8.1.1 If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of contamination must be investigated and remedied.

8.2 Calibration Run - The calibration standard is analyzed each analysis day to generate the response factor used to quantify the sample concentrations.

8.3 Control Standard Run - The quality control standard is analyzed at least once each analysis day. Measurements of all compounds specified in Section 5.6 must fall within the control limits to ensure the validity of the sample analyses that day. To meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.

8.4 Control Charts - A quality control chart is maintained for each component of the control standard listed in Section 5.6. The control charts, used on a daily basis, establish that the method is "in- control." The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard results;
2. Calculate the control standard mean concentration and standard deviation for the target hydrocarbon; and
3. Create a control chart for the target hydrocarbon by placing the concentration on the Y-axis and the date on the X-axis. Establish upper and lower warning limits at either two standard deviations (2s) or 5 percent, whichever is greater, above and below the average concentration. Establish upper and lower control limits at either three standard deviations (3s) or 5 percent, whichever is greater, above and below the average concentration.
4. A control standard measurement is considered to be out-of-control when the analyzed value exceeds the control limit or two successive control standard measurements of the same analyte exceed the warning limit.
5. If 20 control standard measurements are not yet available to create a control chart (e.g., the control standard was expended and replaced prior to obtaining 20 points with the new standard), measurements must be within 10% of the certified concentration. If the control standard is not a NIST standard, the cylinder should be certified by the laboratory against a NIST standard.

The measured concentrations of all target hydrocarbons contained in the control standard must be within the control limits (in-control) for the sample results to be considered acceptable.

8.5 Duplicates - A duplicate analysis of one sample is performed at least once per analysis day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\text{RPD (\%)} = \frac{|\text{Difference between duplicate and original measurements}|}{\text{Average of duplicate and original measurements}} \times 100$$

For each compound specified in Section 5.6, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

Average Measurement for the Duplicate Runs			Allowable RPD (%)
1 to 10	times	LOD	100
10 to 20	“	“	30
20 to 50	“	“	20
Greater than 50	“	“	15

If the results of the duplicate analyses do not meet these criteria for all compounds specified in Section 5.6, the sample may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

8.6 Linearity - A multipoint calibration to confirm instrument linearity is performed for the target hydrocarbons in the control standard for new instruments, after making instrument modifications that can affect linearity, and at least once every year unless a daily check of the instrument response indicates that the linearity has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in Section 8.4, except using calibration standard area counts rather than control standard concentrations. When the standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), each above the LOD, distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one-point calibrations.

8.7 Limit of Detection – The LOD for the target hydrocarbons in the control standard must be determined must be determined for new instruments and after making instrument modifications that can affect linearity and/or sensitivity and at least once every year unless a daily check of the instrument response indicates that the LOD has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in Section 8.4, except using calibration standard area counts rather than control standard concentrations. When the calibration standard area counts are out-of-control, investigation and/or corrective action(s) must be taken. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four “low” concentration levels, each above the LOD, with at least five replicate determinations of the lowest concentration standard. A linear regression is performed and the standard deviation is converted to concentration units using the slope of the linear regression:

$$s = s_a \div m$$

where m is the slope of the linear regression, s is the standard deviation (in concentration units) of the lowest concentration standard and s_a is the standard deviation (in area counts) of the lowest concentration standard.

The LOD must be calculated using the following equation [Ref. 12]:

$$\text{LOD} = t * s$$

where s is the standard deviation (in concentration units) of at least five replicate determinations of the lowest concentration standard and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

Degrees of Freedom	t-value
4	3.7
5	3.4
6	3.1
7	3.0

The lowest standard must be of a concentration of one to five times the estimated LOD.

8.7.1 The maximum allowable LOD for each compound is 5 ppbC. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.7.2 For the purpose of calculating the total mass of all species, the concentrations of all compounds below the LOD are considered to be zero.

8.8 Method No. 1002/Method No. 1003 Crossover Check - For each sample, a compound shall be measured by both Method No. 1002 and Method No. 1003. The crossover compound shall be a compound that can reasonably be expected to be found and measured by both methods in the laboratory performing the analysis. The results obtained by the two methods should be compared and an acceptance criteria set for the relative percent difference.

Part E

DETERMINATION OF C_6 TO C_{12} HYDROCARBONS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1003

1. INTRODUCTION

1.1 This document describes a gas chromatographic method of analyzing C_6 to C_{12} hydrocarbons (mid-range hydrocarbons) in the ppbC range from automotive source samples. This method does not include sample collection procedures [Ref. 7]. The target hydrocarbons that shall be analyzed and reported by this method and Method 1002 are listed in Appendix 1. All compounds on this list, when measured in concentrations above the LOD, shall be measured and reported ("targeted") by either Method 1002 or Method 1003. Each laboratory should divide the list into light-end (Method 1002) and mid-range (Method 1003) hydrocarbons in the manner that best suits the laboratory instrumentation. All compounds on the list not targeted by Method 1003 must be targeted by Method 1002.

1.2 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

2.1 This is a method intended for routine analysis.

2.2 The samples are received by the laboratory in Tedlar bags, which are sub-sampled into a GC for separation and analysis.

2.3 The gas chromatographic analysis is performed through a temperature-programmed capillary column. A FID is used for detection.

2.4 The sample is injected into the GC by means of gas sampling valves. Separation of the sample hydrocarbon mixture into its components takes place in the chromatographic column. The chromatographic column and the corresponding operating parameters described in this method normally provide complete resolution of most target hydrocarbons.

2.5 The computerized GC data acquisition system identifies the hydrocarbons associated with each peak. The hydrocarbon concentrations are determined by integrating the peak areas and using a response factor determined from NIST-traceable standards.

3. INTERFERENCES AND LIMITATIONS

3.1 An interferent is any component present in the sample with a retention time similar to that of any target hydrocarbon described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method and/or instrumentation, e.g., GC/MS, PID, different column, etc.

3.2 The concentration of hydrocarbons in the range of interest is stable for at least 24 hours in the Tedlar sampling bags, provided the sample bags do not leak and are not exposed to bright light or excessive heat. Sampling bags must be shielded from direct sunlight to avoid photochemically induced reactions of any reactive hydrocarbons. Samples must be analyzed within 24 hours.

4. INSTRUMENTATION AND APPARATUS

4.1 Tedlar bags, 2 mil in thickness, nominally 5 to 10 liters in capacity and equipped with quick-connect fittings, are used to contain the samples.

4.2 For manual sub-sampling into a GC, a ground glass syringe is used to transfer gaseous samples from Tedlar bags to the GC sample inlet. For automated systems, a sample loop is used to transfer gaseous samples from the Tedlar bag to the sample inlet of the GC. Sample aliquot size is chosen based on considerations of instrument sensitivity and/or linearity.

4.3 The GC is equipped with a FID, and a gas sampling valve system.

4.4 A non-polar capillary column [e.g., J&W DB-1, 60 m x 0.32 mm ID, film thickness 1.0 μ] is used. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all the target hydrocarbons.

4.5 A sample trap capable of being cryogenically cooled may be used.

4.6 A computer-controlled data acquisition system is required for quantifying peak areas.

5. REAGENTS AND MATERIALS

5.1 Helium shall have a minimum purity of 99.995 percent. Higher purity helium may be required to achieve the LOD required by Section 8.7.1.

5.2 Hydrogen shall have a minimum purity of 99.995 percent.

5.3 Air shall be "Zero" grade (<1 ppmC total hydrocarbon contamination) or better.

5.4 Nitrogen shall have a minimum purity of 99.998 percent.

5.5 Calibration Standard - The quantitative calibration standard for all target hydrocarbons shall be propane at a concentration level between 0.25 and 1 ppm-mole and within the calculated linearity of the method. (See Section 8.6.) This propane standard must be a NIST-certified SRM or secondary NIST-traceable standard. A secondary standard is obtained by a comparison between a SRM and a candidate standard.

5.6 Control Standard - A quality control standard, containing at least n-hexane, n-octane, n-decane, benzene, toluene, and m- or p-xylene with concentrations between 0.2 and 1 ppmC based on a propane standard, is used for the following purposes:

1. Daily update of control charts, and
2. Daily determination of marker retention time windows.

5.7 A high concentration standard (higher than the calibration standard), containing the target hydrocarbons listed in Section 5.6, is used for linearity determinations. The high concentration standard must have concentrations verified against a NIST-traceable propane standard. (See Section 5.5 for the definition of NIST-traceable.) This verification can be performed at the laboratory performing the analysis.

5.8 A low concentration standard (one to five times the estimated LOD), containing the target hydrocarbons listed in Section 5.6, is used for LOD determinations. The low concentration standard must have concentrations verified against a NIST-traceable propane standard. (See Section 5.5 for the definition of NIST-traceable.) This verification can be performed at the laboratory performing the analysis.

5.8.1 In lieu of a low concentration standard, a higher concentration standard may be diluted.

5.9 Liquid nitrogen may be required to cool the cryogenic trap and column oven where applicable.

6. PROCEDURE

6.1 Typical operating conditions.

6.1.1 Suggested operating conditions for the manual GC are:

Helium carrier gas velocity: 30 cm/sec at 200°C
Nitrogen make-up gas flow: sufficient such that the total flow of helium plus nitrogen is 30 mL/min
Hydrogen gas flow (for FID): 30 mL/min
“Zero” air gas flow (for FID): 300 mL/min
Autozero FID at: 0.0 min
Range 11, Attenuation 8 (or another suitable value)
Sample valve temperature: 150°C
Injector temperature: 150°C
Column entrance port temperature: 95°C
Detector temperature: 250°C
Column temperature: Initial temperature 0°C; 10°C/min to 200°C

6.1.2 Suggested operating conditions for the automated GC are:

Helium carrier gas velocity: 30 cm/sec at 200°C
Nitrogen make-up gas flow: sufficient such that the total flow of helium plus nitrogen is 30 mL/min
Hydrogen gas flow (for FID): 30 mL/min
“Zero” air gas flow (for FID): 300 mL/min
Range 12, attenuation 8 (or another suitable value)
Sample valve temperature: 150°C
Detector temperature: 300°C
Injector temperature: 150°C
Column temperature: Initial temperature -50°C (5 min), 5°C/min to 50°C, 10°C/min to 200°C

6.2 Data Reduction

6.2.1 The results are calculated from the FID responses.

6.2.2 The results are examined to see that the peaks are correctly integrated.

6.2.3 After running a particularly “dirty” sample, the analyst should run a blank before proceeding to the next sample as there may be sample carryover, or flush the sampling system with air.

6.2.4 The peak identifications provided by the computer are reviewed and, if necessary, corrected using the following procedure and criteria:

1. The relative retention indices from GC/MS analyses are used to help confirm peak identifications.
2. The primary peak identification is done by the computer using the relative retention times based on reference calibration runs.
3. Confirm that the relative peak heights of the sample run (“fingerprint”) match the typical fingerprint seen in past sample runs.
4. Compare the relative retention times of the sample peaks with those of reference runs.
5. Any peak with a reasonable doubt is labeled 'Unidentified'.

6.2.5 For compounds having concentrations above the documented range of instrument linearity, a smaller aliquot must be taken (for manual systems, a smaller syringe or smaller loop; for automated systems, a smaller loop) or the sample must be diluted.

6.2.6 The concentrations of the hydrocarbons are calculated using data acquisition/ processing software which uses calibration data from a NIST-traceable propane calibration standard.

6.2.7 Target compounds that coelute are reported as the major component, as determined by the analysis of several samples by GC/MS or other methods. An exception to this is m- and p-xylene, where GC/MS data and fuel profiles are used to determine the relative contribution of each component to the peak. This method was used to determine the m- and p-xylene MIR value given in Appendix 1.

7. CALCULATIONS

7.1 The target hydrocarbon concentrations, in ppbC, are calculated by the data system using propane as an external standard.

$$\text{Concentration}_{\text{sample}}\ (\text{ppbC}) = \text{Peak Area}_{\text{sample}} * \text{Response Factor}$$

where the Response Factor (RF) is calculated during daily calibration by:

$$\text{RF} = \frac{\text{Concentration of NIST} - \text{traceable propane standard, ppbC}}{\text{Area of propane peak}}$$

8. QUALITY CONTROL

8.1 Blank Run - A blank (pure nitrogen or helium) is run each analysis day. All target hydrocarbon concentrations from the blank analysis must be below the LOD before the analysis may proceed. As an alternative to a daily blank run, a daily partial blank check in tandem with a weekly blank run may be used. A partial blank check is defined as a check of the calibration standard run for contamination over all but the propane region of the chromatograph. The calibration standard must consist of only propane and make-up gas, with the concentration of all organic compounds except methane and propane below 2 percent of the propane standard concentration. The weekly blank run will provide a check on contamination in the propane region of the chromatograph.

8.1.1 If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of the contamination must be investigated and remedied.

8.2 Calibration Run - The calibration standard is analyzed each analysis day to generate the response factor used to quantify the sample concentrations.

8.3 Control Standard Run - The quality control standard is analyzed at least once each analysis day. Measurements of all compounds specified in Section 5.6 must fall within the control limits to ensure the validity of the sample analyses that day. To meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.

8.4 Control Charts - A quality control chart is maintained for each component of the control standard listed in Section 5.6. The control charts, used on a daily basis, establish that the method is “in-control”. The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard results,
2. Calculate the control standard mean concentration and standard deviation for the target hydrocarbon, and
3. Create a control chart for the target hydrocarbon by placing the concentration on the Y-axis and the date on the X-axis. Establish upper and lower warning limits at either two standard deviations (2s) or 5 percent, whichever is greater, above and below the average concentration. Establish upper and lower control limits at either three standard deviations (3s) or 5 percent, whichever is greater, above and below the average concentration.
4. A control standard measurement is considered to be out-of-control when the analyzed value exceeds the control limit or two successive control standard measurements of the same analyte exceed the warning limit.
5. If 20 control standard measurements are not yet available to create a control chart (e.g., the control standard was expended and replaced prior

to obtaining 20 points with the new standard), measurements must be within 10% of the certified concentration. If the control standard is not a NIST standard, the cylinder should be certified by the laboratory against a NIST standard.

The measured concentrations of all target hydrocarbons contained in the control standard must be within the control limits (in-control) for the sample results to be considered acceptable.

8.5 Duplicates - A duplicate analysis of one sample is performed at least once per analysis day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\mathrm{RPD}(\%) = \frac{|\text{ Difference between duplicate and original measurements }|}{\text{Average of duplicate and original measurements}} * 100$$

For each compound specified in Section 5.6, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

Average Measurement for Duplicate Runs			Allowable RPD (%)
1 to 10	times	LOD	100
10 to 20	“	“	30
20 to 50	“	“	20
Greater than 50	“	“	15

If the results of the duplicate analyses do not meet these criteria for all compounds specified in Section 5.6, the sample may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

8.6 Linearity - A multipoint calibration to confirm instrument linearity is performed for all target hydrocarbons in the control standard for new instruments, after making instrument modifications that can affect linearity, and at least once every year unless a daily check of the instrument response indicates that the linearity has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in Section 8.4, except using calibration standard area counts rather than control standard concentrations. When the standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), each above the LOD, distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one point calibrations.

8.7 Limit of Detection - The LOD for the target hydrocarbons in the control standard must be determined for new instruments and after making instrument modifications that can affect linearity and/or sensitivity and at least once every year unless a daily check of the instrument response indicates that the LOD has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in Section 8.4, except using calibration standard area counts rather than control standard concentrations. When the calibration standard area counts are out-of-control, investigation and/or corrective action(s) must be taken. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four “low” concentration levels, each above the LOD, with at least five replicate determinations of the lowest concentration standard. A linear regression is performed and the standard deviation (in area counts) of the lowest concentration standard determined. The standard deviation is converted to concentration units using the slope of the linear regression:

$$s = s_a \div m$$

where m is the slope of the linear regression, s is the standard deviation (in concentration units) of the lowest concentration standard and s_a is the standard deviation (in area counts) of the lowest concentration standard.

The LOD must be calculated using the following equation [Ref. 12]:

$$LOD = t * s$$

where s is the standard deviation (in concentration units) of at least five replicate determinations of the lowest concentration standard and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

Degrees of Freedom	t-value
4	3.7
5	3.4
6	3.1
7	3.0

The lowest standard must be of a concentration of one to five times the estimated LOD.

8.7.1 The maximum allowable LOD for each compound is 5 ppbC. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.7.2. For the purpose of calculating the total mass of all species, the concentrations of all compounds below the LOD are considered to be zero.

8.8 Method No. 1002/Method No. 1003 Crossover Check - For each sample a compound shall be measured by both Method No. 1002 and Method No. 1003. The crossover compound shall be a compound that can reasonably be expected to be found and measured by both methods in the laboratory performing the analysis. The results of the two analyses should be compared and an acceptance criteria set for the relative percent difference.

Part F

DETERMINATION OF ALDEHYDE AND KETONE COMPOUNDS IN AUTOMOTIVE SOURCE SAMPLES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

METHOD NO. 1004

1. INTRODUCTION

1.1 This document describes a method of analyzing automotive engine exhaust for aldehyde and ketone compounds (carbonyls) using impingers, containing acidified 2,4-dinitrophenylhydrazine (DNPH)-absorbing solution, or DNPH-impregnated cartridges. Carbonyl masses ranging between 0.02 to 200 µg are measured by this method. The "target" carbonyls that shall be analyzed and reported by this method are listed in Appendix 1. All of these carbonyl compounds, when measured in concentrations above the LOD, shall be reported.

1.2 This procedure is derived from a method used by Hull [Ref. 10].

1.3 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

2.1 The samples are received by the laboratory in sample collection cartridges or impingers. (See Section 4.2.) The absorbing solution (2,4-DNPH) complexes the carbonyl compounds into their diphenylhydrazone derivatives. The cartridges are then eluted with 5 mL acetonitrile.

2.2 Separation and analysis are performed using a HPLC with an ultraviolet detector.

3. INTERFERENCES AND LIMITATIONS

3.1 An interferent is any detectable compound present in the sample with a retention time very similar to that of any target carbonyl described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method and/or instrumentation, e.g., alternative HPLC columns or mobile phase compositions.

3.2 If samples are not analyzed the same day as received, they must be refrigerated at a temperature below 40^{o}F. Impinger solutions must first be transferred to glass bottles and sealed. Refrigerated samples are stable for up to 30 days.

3.3 When using the DuPont Zorbax or Supelco's Supelcosil columns described in Section 4.1.5, methyl ethyl ketone (MEK) and butyraldehyde tend to coelute.

3.4 When using the Delta Bond column described in Section 4.1.5, formaldehyde tends to coelute with an unknown, non-carbonyl compound, and the tolualdehyde isomers tend to coelute. The guard column for the Delta Bond column must also be changed frequently in order to prevent the coelution of butyraldehyde and methacrolein and to prolong the life of the column.

4. INSTRUMENT AND APPARATUS

4.1 The HPLC analytical system consists of the following:

4.1.1 Dual high pressure pumps.
4.1.2 Automated gradient controller or pump module controller.
4.1.3 Temperature controller module for the column oven.
4.1.4 A liquid autosampler.
4.1.5 The primary system incorporates two DuPont Zorbax ODS or Supelco's Supelcosil columns in tandem and a guard column, (2 cm long packed with LC18 5 µm pellicular beads). The secondary system incorporates a Delta Bond AK (4.6 mm ID x 200 mm) packed column with a guard column 2 cm long packed with LC18 5 µm pellicular beads or equivalent). Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all target carbonyls.
4.1.6 An ultraviolet/visible (UV/VIS) detector.
4.1.7 Data system for peak integration.

4.2 Sample collection containers are glass impingers or DNPH-impregnated cartridges.

5. REAGENTS AND MATERIALS

5.1 Acetonitrile, HPLC grade, (Burdick and Jackson or equivalent).

5.2 Water, HPLC grade, (Burdick and Jackson or equivalent).

5.3 2,4-DNPH, purified, Radian Corporation or equivalent. Unpurified DNPH must be recrystallized twice from acetonitrile. The recrystallized DNPH is checked for contaminants by injecting a dilute solution of DNPH in contaminant-free acetonitrile into the HPLC.

5.4 Sulfuric acid, or perchloric acid, analytical reagent grade, (Baker Analyzed or equivalent).

5.5 The carbonyl/2,4-dinitrophenylhydrazone (DNPH) complexes [Ref. 11] listed in Table F1 may be purchased (e.g., Radian Corporation, in 1.2 mL ampules) or prepared in the laboratory. In-house standards must be recrystallized at least three times from 95 percent ethanol.

TABLE F-1
PROPERTIES OF CARBONYL/2,4-DNPH COMPLEXES

Complex	Molecular Weight (g/mole)	Melting Point °C
formaldehyde	210.15	165-166
acetaldehyde	224.18	152-153
acrolein	236.19	165[1]
acetone	238.20	125-127
propionaldehyde	238.20	144-145
butyraldehyde	252.23	119-120
hexanaldehyde	280.28	106-107
benzaldehyde	286.25	240-242
methyl ethyl ketone	252.53	117-118
methacrolein	250.21	200-201
crotonaldehyde	250.21	185-188
valeraldehyde	266.26	107-108
m-tolualdehyde	300.27	212

5.6 Stock Calibration Standard - A stock calibration standard is prepared by diluting the target carbonyl/2,4-DNPH complexes with acetonitrile. A typical stock calibration standard contains 3.0 µg/mL of each target carbonyl compound. Stock calibration standards of other concentrations may also be used.

5.7 Working Standard - A working standard is prepared when required by diluting the stock calibration solution, making sure that the highest concentration of the standard is above the expected test level. Typically, the 3.0 µg/mL stock is diluted five times with acetonitrile in a volumetric flask to yield a 0.6 µg/mL solution.

5.8 Control Standard - A quality control standard, containing all target carbonyls/2,4-DNPH complexes within the typical concentration range of real samples, is analyzed to monitor the precision of the analysis of each target carbonyl. The control standard may be purchased, prepared in the laboratory from a stock solution different from the calibration standard, or prepared by batch mixing old samples, spiking it with a stock solution of target compounds, and

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[1] This compound has been known to decompose.

stirring for a minimum of 2 hours. If necessary, the solution is filtered using filter paper to remove precipitation. All target compounds except acrolein have been found to be stable in the control standard.

5.9 Standards used for linearity and LOD determinations (Section 8) may be purchased or prepared by dilutions of an appropriate level stock solution.

6. PROCEDURE

6.1 For systems collecting the samples via impingers, an absorbing solution is prepared by dissolving 0.11 - 0.13 grams of recrystallized DNPH in 1 L of HPLC grade acetonitrile. The absorbing solution should be prepared at least every two weeks. Each batch of acetonitrile used in this procedure is checked for oxygenated impurities by adding it to a contaminant-free dilute solution of DNPH and analyzing by HPLC.

6.1.1 In the laboratory, pipette 15 mL of the DNPH absorbing solution into each of the 30 mL impingers for each emission test. Add 0.1 mL of 2.85 N sulfuric acid or 0.15 mL of 3.8 M perchloric acid to each impinger.

6.2 For systems collecting the samples via cartridges, DNPH-impregnated cartridges shall be sealed and refrigerated, at a temperature less than 40^{o}F, upon receipt from manufacturer, until ready for use.

6.2.1 At the exhaust volumes being sampled (1 L/min), a back-up cartridge may be required for CVS phase 1 but no back-up cartridge is needed for CVS phases 2 and 3.

6.3 After sampling uncap and place all impingers in preheated water at $70\text{-}80^{o}$C for 30 minutes (min) to complete derivatization. Heating is not required when using perchloric acid.

6.3.1 For cartridges, remove the caps and extract with 5 mL acetonitrile, running the extract into glass storage bottles.

6.4 Remove the impingers from the water bath and cool to room temperature. Replace any lost solvent by adding acetonitrile to the 15-mL mark.

6.4.1 Replacing lost solvent is not required when using an internal standard method (Section 7.4).

6.5 Transfer the solution from each impinger/cartridge to glass vials and seal with new septum screw caps.

6.6 Place the vials containing blank, working standard, control standard, and samples into the autosampler for subsequent injection into an HPLC. Suggested standard operating conditions for the HPLC are:

Primary System:

Columns:	4.6 mm ID x 250 mm x 1/4 inches OD Dupont Zorbax ODS or Supelco Supelcosil - two columns in series, Guard column - 2 cm long packed with C18 5 µm pellicular	
Column temperature:	40°C	
Detector:	UV/VIS at 360 nm	
Sample volume:	10 µL	
Solvent A:	acetonitrile	
Solvent B:	10 percent (volume/volume) methanol in water	
Flow:	1 mL/min	
Program:	50 percent A, 50 percent B	0 (initial time)
	65 percent A, 35 percent B	0 to 2 min
	100 percent A, 0 percent B	2 to 22 min
	50 percent A, 50 percent B	22 to 37 min

Under the above configuration, methyl ethyl ketone and butyraldehyde tend to coelute. In order to report these compounds, it is necessary to analyze the samples using a secondary system. The tolualdehyde isomers (m-, p-, and o-) are separated using this configuration. The reporting of tolualdehyde is addressed in Section 7.4.

Secondary System:

Columns:	Delta Bond AK C18 (4.6 mm ID x 200 mm x 1/4 in OD) packed column, Guard column - 2 cm long packed with C18 5 µm pellicular	
Column temperature:	40°C	
Detector:	UV/VIS at 360 nm	
Sample volume:	10 µL	
Solvent A:	acetonitrile	
Solvent B:	acetonitrile in water, 35 percent (v/v)	
Flow:	1.5 mL/min	
Program:	0 percent A, 100 percent B	0 (initial time)
	23 percent A, 77 percent B	0 - 5.5 min
	46 percent A, 54 percent B	5.5 - 13 min
	0 percent A, 100 percent B	13 to 30 min

This secondary system is not used to report all compounds because formaldehyde tends to coelute with a non-carbonyl compound. If this coelution is resolved, the secondary system may be used alone to analyze all carbonyl compounds. The tolualdehyde isomers, however, are not separated with this configuration. The reporting of tolualdehyde is addressed in Section 7.4.

Data System: The outputs from the UV/VIS detector are sent to a PC-controlled data acquisition system.

6.7 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.

6.8 Samples containing compounds having concentrations above the documented range of instrument linearity must be diluted and reanalyzed.

7. CALCULATIONS

7.1 For each target carbonyl, the carbonyl mass is calculated from its carbonyl/2,4-DNPH mass.

7.2 The mass of each carbonyl compound, per impinger or cartridge, is determined by the following calculation:

$$\text{Mass}_{\text{sample}} = \text{Peak Area}_{\text{sample}} * \text{Response Factor} * \text{Impinger}\left(\text{or Cartridge}\right) \text{volume}\left(\text{mL}\right) * \text{B}$$

where B is the ratio of the molecular weight of the carbonyl compound to its 2,4-dinitrophenylhydrazone derivative and where the response factor (RF) for each carbonyl is calculated during the calibration by:

$$\text{RF} = \frac{\text{Concentration}_{\text{standard}}\ (\mu\text{g 2,4-DNPH species/mL})}{\text{Peak Area}_{\text{standard}}}$$

7.3 For tolualdehyde, the sum of all isomers present is reported as m-tolualdehyde.

7.3.1 Under the conditions of the primary system in Section 6.6, the isomers are separated. The m-tolualdehyde response factor is applied to each peak and the sum reported as m-tolualdehyde.

7.3.2 Under the conditions of the secondary system in Section 6.6, the isomers coelute. The m-tolualdehyde response factor is applied to the single tolualdehyde peak. This concentration is reported as m-tolualdehyde.

7.4 An internal standard method may also be used.

8. QUALITY CONTROL

8.1 Blank Runs

8.1.1 Reagent Blanks - The solvents used are of the highest HPLC grade and are tested for impurities when a new lot number is used. If this lot number is found to be acceptable, (no carbonyls present at concentrations at or above the LOD), daily blank analysis is not performed.

8.1.2 Carbonyl/2,4-DNPH Purity - The carbonyl/ 2,4- DNPHs are checked for purity by their melting points and their chromatograms (See Table F-1). Analysis of the solution of carbonyl/2,4-DNPH must yield only the peak of interest. No contaminant peaks above the LOD should be observed.

8.1.3 Field Blanks – One cartridge is analyzed as a field blank for each emission test. If the field blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of the contamination must be investigated and remedied.

8.1.4 Cartridge Blanks - At least one cartridge per batch is analyzed as a batch blank. If the cartridge blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of the contamination must be investigated and remedied.

8.2 Calibration Run - The calibration standard is analyzed each analysis day to generate the response factors used to quantify the sample concentrations.

8.3 Control Standard Run - The quality control standard is analyzed at least once each analysis day. Measurements of all target compounds in the control standard, except acrolein, must fall within the control limits to ensure the validity of the sample analyses that day. To meet this requirement, it may be necessary to rerun the calibration and control standards, and inspect and repair the HPLC.

8.4 Control Charts - A quality control chart is maintained for each component of the control standard. The control charts, used on a daily basis, establish that the method is “in- control.” The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard results,
2. Calculate the control standard mean concentration, and standard deviation(s) for the target analyte, and
3. Create a control chart for the target analyte by placing the concentration on the Y-axis and the date on the X-axis. Establish an upper warning limit and a lower warning limit at two standard deviations (2s) above and below the average concentration. Establish an upper control limit and a lower

control limit at three standard deviations (3s) above and below the average concentration.

4. Due to the low variability of the carbonyl control standard measurements, a control standard measurement is considered to be out-of-control when the analyzed value exceeds either the 3s limit, or the range of ± 10% of the mean control measurement, whichever is greater, or if two successive control standard measurements of the same analyte exceed the 2s limit.
5. If 20 control standard measurements are not yet available to create a control chart (e.g., the control standard was expended and replaced prior to obtaining 20 points with the new standard), measurements must be within 10% of the assay (purchased) or theoretical (prepared in-house) concentration.

The measured concentrations of all target analytes contained in the control standard must be within the control limits (in-control) for the sample results to be considered acceptable. No control requirements have been established for acrolein, since it has been shown to degrade over time.

8.5 Duplicates - A duplicate analysis of one sample is performed at least once per analysis day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\mathrm{RPD}(\%) = \frac{|\,\text{Difference between duplicate and original measurements}\,|}{\text{Average of duplicate and original measurements}} * 100$$

For each compound, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

Average Measurement for Duplicate Runs		Allowable RPD (%)
1 to 10	times LOD	100
10 to 20	“ “	30
20 to 50	“ “	20
Greater than 50	“ “	15

If the results of the duplicate analyses do not meet these criteria for all target carbonyls, the sample may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

8.6 Linearity - A multipoint calibration to confirm instrument linearity is performed for all target analytes for new instruments, after making instrument modifications that can affect linearity, and at least once every year. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), each above the LOD, distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine regression correlation coefficient (r). The r must be greater than 0.995 to be considered linear for one point calibrations.

8.7 Limit of Detection - The LOD for the target analytes must be determined for new instruments, after making instrument modifications which can affect the LOD and at least once per year. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four “low” concentration levels, each above the LOD, with at least five replicate determinations of the lowest concentration standard. A linear regression is performed and the standard deviation (in area counts) of the lowest concentration standard determined. The standard deviation is converted to concentration units using the slope of the linear regression:

$$s = s_a \div m$$

where m is the slope of the linear regression, s is the standard deviation (in concentration units) of the lowest concentration standard and s_a is the standard deviation (in area counts) of the lowest concentration standard.

The LOD must be calculated using the following equation [Ref. 12]:

$$LOD = t * s$$

where s is the standard deviation (in concentration units) of at least five replicate determinations of the lowest concentration standard and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

Degrees of Freedom	t-value
4	3.7
5	3.4
6	3.1
7	3.0

The lowest standard must be of a concentration of one to five times the estimated LOD.

8.7.1 The maximum allowable LOD is 0.0075 µg/mL. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.7.2 For the purpose of calculating the total mass of all species, the concentrations of the compounds below the LOD are considered to be zero.

Part G
DETERMINATION OF NMOG MASS EMISSIONS

1. INTRODUCTION

1.1 NMOG mass emissions consist of non-methane hydrocarbons and oxygenated hydrocarbons.

1.2 All definitions and abbreviations are set forth in Appendix 2 of these test procedures.

2. NMOG WEIGHTED MASS EMISSIONS

2.1 NMOG weighted mass (wm) emissions shall be calculated as follows:

$$\mathrm{NMOG_{wm}} = \sum \mathrm{NMHC_{wm}} + \sum \mathrm{ROH_{wm}} + \sum \mathrm{RHO_{wm}}$$

Non-methane hydrocarbon weighted mass emissions ($\mathrm{NMHC_{wm}}$) can be determined by either FID or GC. If the FID method is used to calculate $\mathrm{NMHC_{wm}}$, refer to Part B of these test procedures entitled, "Determination of Non-Methane Hydrocarbon Mass Emissions by Flame Ionization Detection." If the GC method is used to calculate $\mathrm{NMHC_{wm}}$, refer to section 3, "Speciated Hydrocarbon Mass Emissions Calculation" contained herein. Carbonyl weighted mass emissions ($\mathrm{RHO_{wm}}$) are to be calculated according to section 5 "Carbonyl Mass Emissions Calculation" contained herein. For alcohol fueled vehicles, alcohol weighted mass emissions ($\mathrm{ROH_{wm}}$) are to be calculated according to section 4 "Alcohol Mass Emissions Calculation" contained herein.

3. SPECIATED HYDROCARBON MASS EMISSIONS CALCULATION

3.1 INTRODUCTION

Vehicular exhaust emissions are measured according to the FTP [Ref. 1]. For each of the three phases of the FTP, a tedlar bag of 0.5 $\mathrm{ft^3}$ capacity is used to collect a dilute exhaust sample. A fourth 0.5 $\mathrm{ft^3}$ tedlar bag is used to collect a composite dilution air (background) sample from all three phases of the FTP. All bag samples are analyzed according to Method No. 1002 (Part D of these test procedures) and Method No. 1003 (Part E of these test procedures) to determine the dilute exhaust and dilution air concentrations of individual hydrocarbon compounds. The measured hydrocarbon compound concentrations are used in the following equations to calculate the weighted mass emissions of each hydrocarbon compound.

3.2 HC MASS EMISSIONS CALCULATION PER TEST PHASE

3.2.1 $HC_{mass\ n} = (HC_{conc} * HC_{dens} * VMIX * 10^{-6}) / (\text{Carbon No.})$

3.2.2 $HC_{conc} = HC_e - (HC_d * (1 - (1 / DF)))$
NOTE: If HC_{conc} is calculated to be less than zero, then $HC_{conc} = 0$.

3.3. WEIGHTED HC MASS EMISSIONS CALCULATION

3.3.1 $$HC_{wm} = 0.43 * \left(\frac{HC_{mass1} + HC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{HC_{mass3} + HC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

3.4. SAMPLE CALCULATION

3.4.1 Exhaust emissions from a gasoline vehicle are collected in three dilute exhaust sample bags and one dilution air (background) sample bag during the FTP. Gas chromatography is used to determine the benzene concentration of each bag sample. Calculate the weighted benzene mass emissions based on the following data:

Test Phase	HC_e (ppbC)	HC_d (ppbC)	FID THC_e (ppmC)	CH_{4e} (ppmC)	CO_{2e} (%)	CO_{em} (ppm)	R_a (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)
1	500	25	98	6	1.20	280	28	2846	3.584
2	100	25	22	4	0.95	87	25	4854	3.842
3	120	25	29	5	1.07	101	24	2840	3.586

For Phase 1:

DF = $13.47 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$
(see section 6, DF Calc.)

$NMHC_e$ = FID $THC_e - (r_{CH_4} * CH_{4e})$
= 98 ppmC - (1.04 * 6 ppmC)
= 92 ppmC

CO = $(1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.
= (1 - (0.01925) * 1.2% - 0.000323 * 28%) * 280 ppm

= 271 ppm

DF = $13.47 / [1.2\% + (92 \text{ ppmC} + 6 \text{ ppmC} + 271 \text{ ppm}) * 10^{-4}]$

= 10.89

HC_{conc} = $HC_e - (HC_d * (1 - (1 / DF)))$

= 500 ppbC - (25 ppbC * (1 - (1 / 10.89)))

= 477 ppbC

Mol. Wt. of C_6H_6 = (6 * 12.01115) + (6 * 1.00797)

= 78.11472 g/mole

HC_{dens} = (Mol. Wt. * conversion of liter to ft^3) / (Mol. Vol.)

= (78.11472 g/mole * 28.316 liter/ft^3) / 24.055 liter/mole

= 91.952 g/ft^3

$HC_{mass\ n}$ = $(HC_{conc} * HC_{dens} * VMIX * 10^{-6}) / (\text{Carbon No.})$

$HC_{mass\ 1}$ = (477 ppbC * 91.952 g/ft^3 * 2846 ft^3 * 10^{-6}) / 6

= 20.8 mg

Similarly, for Phase 2: Hc_{mass} = 5.7 mg

and for Phase 3: Hc_{mass} = 4.2 mg

Therefore,

$$HC_{wm} = 0.43 * \left(\frac{HC_{mass1} + HC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{HC_{mass3} + HC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

$$HC_{wm} = 0.43 * \left(\frac{20.8\,\text{mg} + 5.7\,\text{mg}}{3.584 \text{ miles} + 3.842 \text{ miles}} \right) + 0.57 * \left(\frac{4.2\,\text{mg} + 5.7\,\text{mg}}{3.586 \text{ miles} + 3.842 \text{ miles}} \right)$$

HC_{wm} = 2.3 mg/mile (benzene weighted mass emissions)

4. ALCOHOL MASS EMISSIONS CALCULATION

4.1. INTRODUCTION

Vehicular emissions are measured according to the (FTP [Ref. 1]. For each of the three phases of the FTP, a set of two impingers is used to collect alcohol emissions in the dilute exhaust. A fourth set of two impingers is used to collect a composite dilution air (background) alcohol sample from all three phases of the FTP. All impingers are analyzed according to Method No. 1001 to determine the alcohol concentration in each impinger. The measured alcohol concentrations are used in the following equations to calculate the weighted mass emissions of alcohol compounds.

4.2. ALCOHOL MASS EMISSIONS CALCULATION PER TEST PHASE

4.2.1 $ROH_{mass\ n} = (ROH_{conc} * ROH_{dens} * VMIX * 10^{-6}) / (Carbon\ No.)$

4.2.2 $ROH_{conc} = ROH_e - (ROH_d * (1 - (1 / DF)))$
NOTE: If ROH_{conc} is calculated to be less than zero, then $ROH_{conc} = 0$.

4.2.3 $ROH_e = (Imass_e / Ivol_e) * (Mol.\ Vol. / Mol.\ Wt.)$

4.2.4 $Imass_e = (Iconc_{e1} + Iconc_{e2}) * Dens_{ROH} * Ivol_r$

4.2.5 $Ivol_e = Ivol_{em} * (293.16^{o}K / Itemp_e) * (P_B / 760\ mm\ Hg)$

4.2.6 $ROH_d = (Imass_d / Ivol_d) * (Mol.\ Vol. / Mol.\ Wt.)$

4.2.7 $Imass_d = (Iconc_{d1} + Iconc_{d2}) * Dens_{ROH} * Ivol_r$

4.2.8 $Ivol_d = Ivol_{dm} * (293.16^{o}K / Itemp_d) * (P_B / 760\ mm\ Hg)$

4.3. WEIGHTED ALCOHOL MASS EMISSIONS CALCULATION

$$ROH_{wm} = 0.43 * \left(\frac{ROH_{mass1} + ROH_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{ROH_{mass3} + ROH_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

4.4 SAMPLE CALCULATION

4.4.1 Alcohol emissions from an M85 fueled vehicle are collected in three sets of dilute exhaust impingers and one set of dilution air impingers during the FTP. Gas chromatography is used to determine the methanol concentration in each impinger. Calculate the weighted methanol mass emissions based on the following data:

Test Phase	$Ivol_r$ (mL)	$Iconc_{e1}$ (μg/mL)	$Iconc_{e2}$ (μg/mL)	$Ivol_{em}$ (liter)	$Iconc_{d1}$ (μg/mL)	$Iconc_{d2}$ (μg/mL)	$Ivol_{dm}$ (liter)	$Itemp_e$ (°K)	$Itemp_d$ (°K)
1	15	2.24	0.05	3.90	0.07	0.01	13.50	295	294
2	15	0.29	0.06	6.50	0.07	0.01	13.50	297	294
3	15	0.32	0.02	4.00	0.07	0.01	13.50	298	294

Test Phase	FID THC_e (ppmC)	CH_{4e} (ppmC)	CO_{2e} (%)	CO_{em} (ppm)	R_a (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)	P_B (mmHg)	$HCHO_e$ (ppm)
1	82	9	1.5	250	30	2834	3.581	760	0.81
2	19	5	0.7	20	32	4862	3.845	760	0.09
3	22	6	0.8	32	29	2835	3.583	760	0.10

For Phase 1:

$Imass_e = (Iconc_{e1} + Iconc_{e2}) * Dens_{ROH} * Ivol_r$

$= (2.24\ \mu g/mL + 0.05\ \mu g/mL) * 0.7914\ g/mL * 15\ mL * 10^6\ \mu g/g$

$= 27.2\ \mu g$

Mol. Wt. of CH_3OH $= (1 * 12.01115) + (4 * 1.00797) + (1 * 15.9994)$

$= 32.0428$ g/mole

$Ivol_e = Ivol_{em} * (293/16^o\ K / Itemp_e) * (P_B / 760\ mm\ Hg)$

$= 3.90\ liter * (293.16^oK / 295^o\ K) * (760\ mm\ Hg / 760\ mm\ Hg)$

$= 3.88$ liter

$ROH_e = (Imass_e / Ivol_e) * (Mol.\ Vol. / Mol.\ Wt.)$

$= (27.2*10^{-6}\ g / 3.88\ liter) * (24.055\ liter/mole / 32.0428\ g/mole)$

$= 5.27$ ppmC

$Imass_d = (Iconc_{d1} + Iconc_{d2}) * Dens_{ROH} * Ivol_r$

$= (0.07\ \mu g/mL + 0.01\ \mu g/mL) * 0.7914\ g/ml *$
$15\ ml * 10^{6}\ \mu g/g$
$= 0.95\ \mu g$

$Ivol_{d} = Ivol_{dm} * (293.16^{o}\ K / Itemp_{d}) * (P_{B} / 760\ mm\ Hg)$
$= 13.50\ liter * (293.16^{o}K / 294^{o}K) * (760\ mm\ Hg / 760\ mm\ Hg)$
$= 13.46\ liter$

$ROH_{d} = (Imass_{d} / Ivol_{d}) * (Mol.\ Vol. / Mol.\ Wt.)$
$= (0.95*10^{-6}\ g / 13.46\ liter) * (24.055\ liter/mole / 32.0428\ g/mole)$
$= 0.05\ ppmC$

$$DF = \frac{12.02}{CO_{2e} + \left(NMHC_{e} + CH_{4e} + CO_{e} + ROH_{e} + HCHO_{e}\right) * 10^{-4}}$$

(see section 6, DF Calc.)

$NMHC_{e} = FID\ THC_{e} - (r_{CH_4} * CH_{4e}) - (r_{CH_3OH} * ROH_{e})$
$= 82\ ppmC - (1.04 * 9\ ppmC) - (0.66 * 5.27\ ppmC)$
$= 69\ ppmC$

$CO_{e} = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_{a}) * CO_{em}$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_{e}.

$= (1 - (0.02705) * 1.5\% - 0.000323 * 30\%) * 250\ ppm$
$= 237\ ppm$

$$DF = \frac{12.02}{1.5\% + \left(69\,ppmC + 9\,ppmC + 237\,ppmC + 5.27\,ppmC + 0.81\,ppm\right) * 10^{-4}}$$

$ROH_{conc} = ROH_{e} - (ROH_{d} * (1 - (1 / DF)))$
$= 5.27\ ppmC - (0.05\ ppmC * (1 - (1 / 7.84)))$
$= 5.23\ ppmC$

$ROH_{dens} = (Mol.\ Wt. * conversion\ of\ liter\ to\ ft^{3}) / (Mol.\ Vol.)$
$= (32.0428\ g/mole * 28.316\ liter/ft) / 24.055\ liter/mole$
$= 37.719\ g/ft^{3}$

$ROH_{mass\ n} = (ROH_{conc} * ROH_{dens} * VMIX * 10^{-6}) / (Carbon\ No.)$
$ROH_{mass\ 1} = (5.23\ ppmC * 37.719\ g/ft^{3} * 2834\ ft^{3} * 10^{-6}) / 1$
$= 0.56\ g$

Similarly, for Phase 2: $ROH_{mass\ 2}$ = 0.08 g
and for Phase 3: $ROH_{mass\ 3}$ = 0.08 g

Therefore,

$$ROH_{wm} = 0.43 * \left(\frac{ROH_{mass1} + ROH_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{ROH_{mass3} + ROH_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

$$ROH_{wm} = 0.43 * \left(\frac{0.56\,mg + 0.08\,mg}{3.581\text{ miles} + 3.845\text{ miles}} \right) + 0.57 * \left(\frac{0.08\,mg + 0.08\,mg}{3.583\text{ miles} + 3.845\text{ miles}} \right)$$

ROH_{wm} = 0.05 g (methanol weighted mass emissions)

5. CARBONYL MASS EMISSIONS CALCULATIONS

5.1. INTRODUCTION

Vehicular emissions are measured according to the FTP [Ref. 1]. For each of the three phases of the FTP, a set of two impingers (or cartridges) is used to collect carbonyl emissions in the dilute exhaust. A fourth set of two impingers (or cartridges) is used to collect a composite dilution air (background) carbonyl sample from all three phases of the FTP. All impingers (or cartridges) are analyzed according to Method No. 1004 to determine the mass of individual carbonyl compounds in each impinger (or cartridge). The measured carbonyl masses are used in the following equations to calculate the weighted mass emissions of each carbonyl compound.

5.2. CARBONYL MASS EMISSIONS CALCULATION PER TEST PHASE

5.2.1 $RHO_{mass\ n}$ = $(RHO_{conc} * RHO_{dens} * VMIX * 10^{-6})$

5.2.2 RHO_{conc} = $RHO_e - (RHO_d * (1 - (1 / DF)))$
NOTE: If RHO_{conc} is calculated to be less than zero, then $RHO_{conc} = 0$.

5.2.3 RHO_e = $(Imass_e / Ivol_e) * (Mol.\ Vol. / Mol.\ Wt.)$

5.2.4 $Ivol_e$ = $Ivol_{em} * (293.16^{o}K / Itemp_e) * (P_B / 760\ mm\ Hg)$

5.2.5 RHO_d = $(Imass_d / Ivol_d) * (Mol.\ Vol. / Mol.\ Wt.)$

5.2.6 $Ivol_d$ = $Ivol_{dm} * (293.16^{o}K / Itemp_d) * (P_B / 760\ mm\ Hg)$

5.3. WEIGHTED CARBONYL MASS EMISSIONS CALCULATION

$$\mathrm{RHO}_{\mathrm{wm}} = 0.43 * \left(\frac{\mathrm{RHO}_{\mathrm{mass1}} + \mathrm{RHO}_{\mathrm{mass2}}}{\mathrm{D}_{\mathrm{phase1}} + \mathrm{D}_{\mathrm{phase2}}} \right) + 0.57 * \left(\frac{\mathrm{RHO}_{\mathrm{mass3}} + \mathrm{RHO}_{\mathrm{mass2}}}{\mathrm{D}_{\mathrm{phase3}} + \mathrm{D}_{\mathrm{phase2}}} \right)$$

5.4. SAMPLE CALCULATION

5.4.1 Carbonyl emissions from a CNG vehicle are collected in three sets of dilute exhaust impingers and one set of dilution air impingers during the FTP. HPLC is used to determine the formaldehyde mass in each impinger. Calculate the weighted formaldehyde mass emissions based on the following data:

Test Phase	Ivol_r (mL)	Imass_e (µg)	Ivol_{em} (liter)	Imass_d (µg)	Ivol_{dm} (liter)	Itemp_e (^{o}K)	Itemp_d (^{o}K)
1	15	2.45	8.49	0.17	31.57	295	292
2	15	0.76	14.55	0.17	31.57	298	292
3	15	0.64	4.00	0.17	31.57	298	292

Test Phase	FID THC_e (ppmC)	CH_{4e} (ppmC)	CO_{2e} (%)	CO_{em} (ppm)	R_a (%)	VMIX (ft^3)	$\mathrm{D}_{\mathrm{phase\ n}}$ (mile)	P_B (mmHg)
1	132	108	0.9	8	68	2866	3.581	760
2	4	3	0.1	4	67	4841	3.845	760
3	22	9	0.5	5	65	2837	3.583	760

For Phase 1:

Mol. Wt. of HCHO = (1 * 12.01115) + (2 * 1.00797) + (1 * 15.9994)
= 30.0268 g/mole

Ivol_e = Ivol_{em} * (293/16^o K / Itemp_e) * (P_B / 760 mm Hg)
= 8.49 liter * (293.16^{o}K / 295^{o}K) * (760 mm Hg / 760 mm Hg)
= 8.44 liter

RHO_e = (Imass_e / Ivol_e) * (Mol. Vol. / Mol. Wt.)
= ($2.45*10^{-6}$ g / 8.44 liter) * (24.055 liter/mole / 30.0268 g/mole)
= 233 ppb

$Ivol_d = Ivol_{dm} * (293.16^{o}K / Itemp_d) * (P_B / 760 \text{ mm Hg})$
$= 31.57 \text{ liter} * (293.16^{o}K / 292^{o}K) * (760 \text{ mm Hg} / 760 \text{ mm Hg})$
$= 31.70 \text{ liter}$

$RHO_d = (Imass_d / Ivol_d) * (\text{Mol. Vol.} / \text{Mol. Wt.})$
$= (0.17*10^{-6} g / 31.70 \text{ liter})*(24.055 \text{ liter/mole} / 30.0268 \text{ g/mole})$
$= 4 \text{ ppb}$

$DF = 9.77 / [CO_{2e} + (NMHC_e + CH_{4e} + CO^{e}) * 10^{-4}]$
(see section 6, DF Calc.)

$NMHC_e = \text{FID } THC_e - (r_{CH_4} * CH_{4e})$
$= 132 \text{ ppmC} - (1.04 * 108 \text{ ppmC})$
$= 20 \text{ ppmC}$

$CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

$= (1 - 0.02890 * 0.9\% - 0.000323 * 68\%) * 8 \text{ ppm}$
$= 7.6 \text{ ppm}$

$DF = 9.77 / [0.9\% + (20 \text{ ppmC} + 108 \text{ ppmC} + 7.6 \text{ ppm}) * 10^{-4}]$
$= 10.69$

$RHO_{conc} = RHO_e - (RHO_d * (1 - (1 / DF)))$
$= 233 \text{ ppb} - (4 \text{ ppb} * (1 - (1 / 10.69)))$
$= 229 \text{ ppb}$

$RHO_{dens} = (\text{Mol. Wt.} * \text{conversion of liter to ft}^3) / (\text{Mol. Vol.})$
$= (30.0268 \text{ g/mole} * 28.316 \text{ liter/ft}^3) / 24.055 \text{ liter/mole}$
$= 35.35 \text{ g/ft}^3$

$RHO_{mass\ n} = (RHO_{conc} * RHO_{dens} * VMIX * 10^{-6})$
$RHO_{mass\ 1} = (229 \text{ ppb} * 35.35 \text{ g/ft}^3 * 2866 \text{ ft}^3 * 10^{-6})$
$= 23.2 \text{ mg}$

Similarly, for Phase 2: $RHO_{mass\ 2} = 6.6 \text{ mg}$
and for Phase 3: $RHO_{mass\ 3} = 12.7 \text{ mg}$

Therefore,

$$\mathrm{RHO}_{\mathrm{wm}} = 0.43 * \left(\frac{\mathrm{RHO}_{\mathrm{mass1}} + \mathrm{RHO}_{\mathrm{mass2}}}{\mathrm{D}_{\mathrm{phase1}} + \mathrm{D}_{\mathrm{phase2}}} \right) + 0.57 * \left(\frac{\mathrm{RHO}_{\mathrm{mass3}} + \mathrm{RHO}_{\mathrm{mass2}}}{\mathrm{D}_{\mathrm{phase3}} + \mathrm{D}_{\mathrm{phase2}}} \right)$$

$$\mathrm{RHO}_{\mathrm{wm}} = 0.43 * \left(\frac{23.2\,\mathrm{mg} + 6.6\,\mathrm{mg}}{3.581\text{ miles} + 3.845\text{ miles}} \right) + 0.57 * \left(\frac{12.7\,\mathrm{mg} + 6.6\,\mathrm{mg}}{3.583\text{ miles} + 3.845\text{ miles}} \right)$$

$\mathrm{RHO}_{\mathrm{wm}}$ = 3.2 mg/mi (formaldehyde weighted mass emissions)

5.4.2 Carbonyl emissions from a gasoline vehicle are collected in three sets of dilute exhaust cartridges and dilution air cartridges during the FTP. HPLC is used to determine the formaldehyde mass in each cartridge. Calculate the weighted formaldehyde mass emissions based on the following data:

Test Phase	$\mathrm{Iconc}_{\mathrm{ce}}$ (µg/mL)	$\mathrm{Iconc}_{\mathrm{cd}}$ (µg/mL)	$\mathrm{Iconc}_{\mathrm{blk}}$ (µg/mL)	$\mathrm{Ivol}_{\mathrm{dm}}$ (liter)	$\mathrm{Ivol}_{\mathrm{em}}$ (liter)	$\mathrm{Itemp}_{\mathrm{e}}$ ($^{\mathrm{o}}$K)	$\mathrm{Itemp}_{\mathrm{d}}$ ($^{\mathrm{o}}$K)
1	1.212	0.028	0.0	8.61	8.57	294.26	294.26
2	0.334	0.043	0.0	14.91	13.83	294.26	294.26
3	0.172	0.026	0.0	8.68	8.74	294.26	294.26

Test Phase	FID $\mathrm{THC}_{\mathrm{e}}$ (ppmC)	$\mathrm{CH}_{4\mathrm{e}}$ (ppmC)	$\mathrm{CO}_{2\mathrm{e}}$ (%)	$\mathrm{CO}_{\mathrm{em}}$ (ppm)	R_{a} (%)	VMIX (ft^3)	$\mathrm{D}_{\mathrm{phase\ n}}$ (mile)	P_{B} (mmHg)
1	132	108	0.9	8	68	2866	3.581	760
2	4	3	0.1	4	67	4841	3.845	760
3	22	9	0.5	5	65	2837	3.583	760

For all three phases Ivolc = 4.4 mL

For Phase 1:

$\mathrm{Imass}_{\mathrm{d}} = (\mathrm{Iconc}_{\mathrm{cd}} - \mathrm{Iconc}_{\mathrm{blk}})*\mathrm{Ivol}_{\mathrm{c}}$

$\mathrm{Imass}_{\mathrm{d}} = (0.028 - 0.0)$ µg/mL * 4.4 mL = 0.1232 µg

$\mathrm{Imass}_{\mathrm{e}} = (\mathrm{Iconc}_{\mathrm{ce}} - \mathrm{Iconc}_{\mathrm{blk}})*\mathrm{Ivol}_{\mathrm{c}}$

Imass_e = (1.212 – 0.0) μg/mL * 4.4 mL = 5.33 μg

Mol. Wt. of HCHO = (1 * 12.01115) + (2 * 1.00797) + (1 * 15.9994)
= 30.0265 g/mole

Ivol_e = Ivol_{em} * ($293/16^{o}$ K / Itemp_e) * (P_B / 760 mm Hg)
= 8.57 liter * (293.16^{o}K / 294.26^{o}K) * (760 mm Hg / 760 mm Hg)
= 8.54 liter

RHO_e = (Imass_e / Ivol_e) * (Mol. Vol. / Mol. Wt.)
= (5.33×10^{-6} g / 8.54 liter) * (24.055 liter/mole / 30.0265 g/mole)
= 500 ppb

Ivol_d = Ivol_{dm} * (293.16^{o}K / Itemp_d) * (P_B / 760 mm Hg)
= 8.61 liter * (293.16^{o}K / 294.26^{o}K) * (760 mm Hg / 760 mm Hg)
= 8.58 liter

RHO_d = (Imass_d / Ivol_d) * (Mol. Vol. / Mol. Wt.)
= (0.1232×10^{-6}g / 8.58 liter)*(24.055 liter/mole / 30.0265 g/mole)
= 11.5 ppb

DF = 9.77 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]
(see section 6, DF Calc.)

NMHC_e = FID THC_e - (r_{CH_4} * CH_{4e})
= 132 ppmC - (1.04 * 108 ppmC)
= 20 ppmC

CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

= (1 - 0.02890 * 0.9% - 0.000323 * 68%) * 8 ppm
= 7.6 ppm

DF = 9.77 / [0.9% + (20 ppmC + 108 ppmC + 7.6 ppm) * 10^{-4}]
= 10.69

RHO_{conc} = RHO_e - (RHO_d * (1 - (1 / DF)))
= 500 ppb - (11.5 ppb * (1 - (1 / 10.69)))
= 489.6 ppb (formaldehyde)

RHO_{dens} = (Mol. Wt. * conversion of liter to ft^3) / (Mol. Vol.)

$= (30.0265 \text{ g/mole} * 28.316 \text{ liter/ft}^3) / 24.055 \text{ liter/mole}$
$= 35.35 \text{ g/ft}^3$

$RHO_{mass\ n} = (RHO_{conc} * RHO_{dens} * VMIX * 10^{-6})$

$RHO_{mass\ 1} = (489.6 \text{ ppb} * 35.35 \text{ g/ft}^3 * 2866 \text{ ft}^3 * 10^{-6})$
$= 49.6 \text{ mg}$ (formaldehyde)

Similarly, for Phase 2: $RHO_{mass\ 2} = 12.9 \text{ mg}$

and similarly for Phase 3: $RHO_{mass\ 3} = 5.6 \text{ mg}$

Therefore,

$$RHO_{wm} = 0.43 * \left(\frac{RHO_{mass1} + RHO_{mass2}}{D_{phase1} + D_{phase2}}\right) + 0.57 * \left(\frac{RHO_{mass3} + RHO_{mass2}}{D_{phase3} + D_{phase2}}\right)$$

$$RHO_{wm} = 0.43 * \left(\frac{49.6\text{ mg} + 12.9\text{ mg}}{3.581\text{miles} + 3.845\text{ miles}}\right) + 0.57 * \left(\frac{5.6\text{ mg} + 12.9\text{ mg}}{3.583\text{ miles} + 3.845\text{ miles}}\right)$$

$RHO_{wm} = 5.04$ mg/mi (formaldehyde weighted mass emissions)

6. DILUTION FACTOR CALCULATION

6.1. For Non-Alcohol Fueled Vehicles:

6.1.1
$$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}\right)}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

6.1.2 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

a) For gasoline, $CH_{1.85}$, where x = 1, y = 1.85, and z = 0:
$DF = 13.47 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}$
$CO_e = (1 - 0.01925 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

b) For Phase 2 gasoline, $CH_{1.94}$, where x = 1, y = 1.94 and z = 0.017,

DF = 13.29 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}
CO_e = (1 - 0.01970 * CO_{2e} - 0.000323 * R_a) * CO_{em}

c) For LPG, $CH_{2.64}$, where x = 1, y = 2.64, z = 0:
DF = 11.68 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}
CO_e = (1 - 0.02320 * CO_{2e} - 0.000323 * R_a) * CO_{em}

d) For CNG, $CH_{3.78}$, where x = 1, y = 3.78, and z = 0.016:
DF = 9.83 / [[CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}]
CO_e = (1 - 0.02890 * CO_{2e} - 0.000323 * R_a) * CO_{em}

6.2. **For Alcohol Fueled Vehicles**:

6.2.1
$$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}\right)}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

6.2.2 CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

a) For M100 (100% methanol), CH_3OH, where x = 1, y = 4, and z = 1:
DF = 11.57 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e + ROH_e + $HCHO_e$) * 10^{-4}]
CO_e = (1 - 0.03000 * CO_{2e} - 0.000323 * R_a) * CO_{em}

b) For M85 (85% methanol, 15% indolene), $CH_{3.41}O_{0.72}$, where x = 1, y = 3.41, and z = 0.72:
DF = 12.02 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e + ROH_e + $HCHO_e$) * 10^{-4}]
CO_e = (1 - 0.02705 * CO_{2e} - 0.000323 * R_a) * CO_{em}

c) For E100 (100% ethanol), C_2H_5OH, where x = 1, y = 3, and z = 0.5:
DF = 12.29 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e + ROH_e + $HCHO_e$) * 10^{-4}]
CO_e = (1 - 0.02500 * CO_{2e} - 0.000323 * R_a) * CO_{em}

APPENDIX 1

LIST OF COMPOUNDS

CAS #	COMPOUND	MIR
	Alcohols	
00067-56-1	methanol	0.71
00064-17-5	ethanol	1.69
	Light End and Mid-Range Hydrocarbons (Listed in approximate elution order)	
00074-85-1	ethene	9.08
00074-86-2	ethyne	1.25
00074-84-0	ethane	0.31
00115-07-1	propene	11.58
00074-98-6	propane	0.56
00463-49-0	1,2-propadiene	12.16
00074-99-7	1-propyne	6.45
00075-28-5	2-methylpropane	1.35
00115-11-7	2-methylpropene	6.35
00106-98-9	1-butene	10.29
00106-99-0	1,3-butadiene	13.58
00106-97-8	n-butane	1.33
00624-64-6	trans-2-butene	13.91
00463-82-1	2,2-dimethylpropane	1.68
00107-00-6	1-butyne	6.20
00590-18-1	cis-2-butene	13.22
00563-45-1	3-methyl-1-butene	6.99
00078-78-4	2-methylbutane	1.68
00503-17-3	2-butyne	16.33
00109-67-1	1-pentene	7.79
00563-46-2	2-methyl-1-butene	6.51
00109-66-0	n-pentane	1.54
00078-79-5	2-methyl-1,3-butadiene	10.69
00646-04-8	trans-2-pentene	10.23
00558-37-2	3,3-dimethyl-1-butene	6.06
00627-20-3	cis-2-pentene	10.24
00689-97-4	1-buten-3-yne	11.09
00513-35-9	2-methyl-2-butene	14.45
00542-92-7	1,3-cyclopentadiene	7.61
00075-83-2	2,2-dimethylbutane	1.33
00142-29-0	cyclopentene	7.38
00691-37-2	4-methyl-1-pentene	6.26

CAS #	COMPOUND	MIR
00760-20-3	3-methyl-1-pentene	6.22
00287-92-3	cyclopentane	2.69
00079-29-8	2,3-dimethylbutane	1.14
01634-04-4	1-methyl-tert-butyl-ether	0.78
00691-38-3	4-methyl-cis-2-pentene	8.44
00107-83-5	2-methylpentane	1.80
00674-76-0	4-methyl-trans-2-pentene	8.44
00096-14-0	3-methylpentane	2.07
00763-29-1	2-methyl-1-pentene	5.18
00592-41-6	1-hexene	6.17
00110-54-3	n-hexane	1.45
13269-52-8	trans-3-hexene	8.16
07642-09-3	cis-3-hexene	8.22
04050-45-7	trans-2-hexene	8.44
00616-12-6	3-methyl-trans-2-pentene	8.44
00625-27-4	2-methyl-2-pentene	12.28
01120-62-3	3-methylcyclopentene	8.65
07688-21-3	cis-2-hexene	8.44
00637-92-3	1-ethyl-tert-butyl-ether	2.11
00922-62-3	3-methyl-cis-2-pentene	8.44
00590-35-2	2,2-dimethylpentane	1.22
00096-37-7	methylcyclopentane	2.42
00108-08-7	2,4-dimethylpentane	1.65
00464-06-2	2,2,3-trimethylbutane	1.32
07385-78-6	3,4-dimethyl-1-pentene	4.56
00693-89-0	1-methylcyclopentene	13.95
00071-43-2	benzene	0.81
03404-61-3	3-methyl-1-hexene	4.56
00562-49-2	3,3-dimethylpentane	1.32
00110-82-7	cyclohexane	1.46
00591-76-4	2-methylhexane	1.37
00565-59-3	2,3-dimethylpentane	1.55
00110-83-8	cyclohexene	5.45
00589-34-4	3-methylhexane	1.86
01759-58-6	trans-1,3-dimethylcyclopentane	2.15
02532-58-3	cis-1,3-dimethylcyclopentane	2.15
00617-78-7	3-ethylpentane	1.63
00822-50-4	trans-1,2-dimethylcyclopentane	1.99
00592-76-7	1-heptene	4.56
00540-84-1	2,2,4-trimethylpentane	1.44
14686-14-7	trans-3-heptene	6.96
00142-82-5	n-heptane	1.28
02738-19-4	2-methyl-2-hexene	6.96
03899-36-3	3-methyl-trans-3-hexene	6.96

CAS #	COMPOUND	MIR
14686-13-6	trans-2-heptene	7.33
00816-79-5	3-ethyl-2-pentene	6.96
00107-39-1	2,4,4-trimethyl-1-pentene	3.45
10574-37-5	2,3-dimethyl-2-pentene	6.96
06443-92-1	cis-2-heptene	6.96
00108-87-2	methylcyclohexane	1.99
00590-73-8	2,2-dimethylhexane	1.13
00107-40-4	2,4,4-trimethyl-2-pentene	5.85
01640-89-7	ethylcyclopentane	2.27
00592-13-2	2,5-dimethylhexane	1.68
00589-43-5	2,4-dimethylhexane	1.80
02815-58-9	1,2,4-trimethylcyclopentane	1.75
00563-16-6	3,3-dimethylhexane	1.57
00565-75-3	2,3,4-trimethylpentane	1.23
00560-21-4	2,3,3-trimethylpentane	1.57
00108-88-3	toluene	3.97
00584-94-1	2,3-dimethylhexane	1.34
00592-27-8	2-methylheptane	1.20
00589-53-7	4-methylheptane	1.48
00589-81-1	3-methylheptane	1.35
15890-40-1	(1a,2a,3b)-1,2,3-trimethylcyclopentane	1.75
00638-04-0	cis-1,3-dimethylcyclohexane	1.72
02207-04-7	trans-1,4-dimethylcyclohexane	1.75
03522-94-9	2,2,5-trimethylhexane	1.33
02613-65-2	trans-1-methyl-3-ethylcyclopentane	1.75
16747-50-5	cis-1-methyl-3-ethylcyclopentane	1.75
00111-66-0	1-octene	3.45
14850-23-8	trans-4-octene	5.90
00111-65-9	n-octane	1.11
13389-42-9	trans-2-octene	5.90
02207-03-6	trans-1,3-dimethylcyclohexane	1.72
07642-04-8	cis-2-octene	5.90
01069-53-0	2,3,5-trimethylhexane	1.33
02213-23-2	2,4-dimethylheptane	1.48
02207-01-4	cis-1,2-dimethylcyclohexane	1.75
01072-05-5	2,6-dimethylheptane	1.25
01678-91-7	ethylcyclohexane	1.75
00926-82-9	3,5-dimethylheptane	1.63
00100-41-4	ethylbenzene	2.79
03074-71-3	2,3-dimethylheptane	1.25
00108-38-3	m-&p-xylene	8.49
02216-34-4	4-methyloctane	1.08
03221-61-2	2-methyloctane	0.96
02216-33-3	3-methyloctane	1.25

CAS #	COMPOUND	MIR
00100-42-5	styrene (ethenylbenzene)	1.95
00095-47-6	o-xylene	7.49
00124-11-8	1-nonene	2.76
00111-84-2	n-nonane	0.95
00098-82-8	(1-methylethyl)benzene	2.32
15869-87-1	2,2-dimethyloctane	1.09
04032-94-4	2,4-dimethyloctane	1.09
02051-30-1	2,6-dimethyloctane	1.27
00103-65-1	n-propylbenzene	2.20
00620-14-4	1-methyl-3-ethylbenzene	6.61
00622-96-8	1-methyl-4-ethylbenzene	6.61
00108-67-8	1,3,5-trimethylbenzene	11.22
00611-14-3	1-methyl-2-ethylbenzene	6.61
00095-63-6	1,2,4-trimethylbenzene	7.18
00124-18-5	n-decane	0.83
00538-93-2	(2-methylpropyl)benzene	1.97
00135-98-8	(1-methylpropyl)benzene	1.97
00535-77-3	1-methyl-3-(1-methylethyl)benzene	5.92
00526-73-8	1,2,3-trimethylbenzene	11.26
00099-87-6	1-methyl-4-(1-methylethyl)benzene	5.92
00496-11-7	2,3-dihydroindene (indan)	3.17
00527-84-4	1-methyl-2-(1-methylethyl)benzene	5.92
00141-93-5	1,3-diethylbenzene	5.92
00105-05-5	1,4-diethylbenzene	5.92
01074-43-7	1-methyl-3-n-propylbenzene	5.92
01074-55-1	1-methyl-4-n-propylbenzene	5.92
00135-01-3	1,2-diethylbenzene	5.92
01074-17-5	1-methyl-2-n-propylbenzene	5.92
01758-88-9	1,4-dimethyl-2-ethylbenzene	8.86
00874-41-9	1,3-dimethyl-4-ethylbenzene	8.86
00934-80-5	1,2-dimethyl-4-ethylbenzene	8.86
02870-04-4	1,3-dimethyl-2-ethylbenzene	8.86
01120-21-4	n-undecane (hendecane)	0.74
00933-98-2	1,2-dimethyl-3-ethylbenzene	8.86
00095-93-2	1,2,4,5-tetramethylbenzene	8.86
01595-11-5	1-methyl-2-n-butylbenzene	5.35
00527-53-7	1,2,3,5-tetramethylbenzene	8.86
01074-92-6	1-(1,1-dimethylethyl)-2-methylbenzene	5.35
00488-23-3	1,2,3,4-tetramethylbenzene	8.86
00538-68-1	n-pentylbenzene	1.78
00098-19-1	1-(1,1-dimethylethyl)-3,5-DMbenzene	7.33
00091-20-3	naphthalene	3.26
00112-40-3	n-dodecane	0.66

Carbonyl Compounds

CAS #	COMPOUND	MIR
00050-00-0	formaldehyde	8.97
00075-07-0	acetaldehyde	6.84
00107-02-8	acrolein	7.60
00067-64-1	acetone	0.43
00123-38-6	propionaldehyde	7.89
00123-72-8	butyraldehyde	6.74
00066-25-1	hexanaldehyde	4.98
00100-52-7	benzaldehyde	0.00
00078-93-3	methyl ethyl ketone (2-butanone)	1.49
00078-85-3	methacrolein	6.23
04170-30-3	crotonaldehyde	10.07
00110-62-3	valeraldehyde	5.76
00620-23-5	m-tolualdehyde	0.00

List of Compounds
(Listed by CAS number)

00050-00-0	formaldehyde
00064-17-5	ethanol
00066-25-1	hexanaldehyde
00067-56-1	methanol
00067-64-1	acetone
00071-43-2	benzene
00074-84-0	ethane
00074-85-1	ethene
00074-86-2	ethyne
00074-98-6	propane
00074-99-7	1-propyne
00075-07-0	acetaldehyde
00075-28-5	2-methylpropane
00075-83-2	2,2-dimethylbutane
00078-78-4	2-methylbutane
00078-79-5	2-methyl-1,3-butadiene
00078-85-3	methacrolein
00078-93-3	methyl ethyl ketone (2-butanone)
00079-29-8	2,3-dimethylbutane
00091-20-3	naphthalene
00095-47-6	o-xylene
00095-63-6	1,2,4-trimethylbenzene
00095-93-2	1,2,4,5-tetramethylbenzene
00096-14-0	3-methylpentane
00096-37-7	methylcyclopentane
00098-19-1	1-(1,1-dimethylethyl)-3,5-dimethylbenzene
00098-82-8	(1-methylethyl)benzene
00099-87-6	1-methyl-4-(1-methylethyl)benzene
00100-41-4	ethylbenzene
00100-42-5	stryrene (ethenylbenzene)
00100-52-7	benzaldehyde
00103-65-1	n-propylbenzene
00105-05-5	1,4-diethylbenzene
00106-97-8	n-butane
00106-98-9	1-butene
00106-99-0	1,3-butadiene
00107-00-6	1-butyne
00107-02-8	acrolein
00107-39-1	2,4,4-trimethyl-1-pentene
00107-40-4	2,4,4-trimethyl-2-pentene
00107-83-5	2-methylpentane
00108-08-7	2,4-dimethylpentane

00108-38-3	m- & p-xylene
00108-67-8	1,3,5-trimethylbenzene
00108-87-2	methylcyclohexane
00108-88-3	toluene
00109-66-0	n-pentane
00109-67-1	1-pentene
00110-54-3	n-hexane
00110-62-3	valeraldehyde
00110-82-7	cyclohexane
00110-83-8	cyclohexene
00111-65-9	n-octane
00111-66-0	1-octene
00111-84-2	n-nonane
00112-40-3	n-dodecane
00115-07-1	propene
00115-11-7	2-methylpropene
00123-38-6	propionaldehyde
00123-72-8	butyraldehyde
00124-11-8	1-nonene
00124-18-5	n-decane
00135-01-3	1,2-diethylbenzene
00135-98-8	(1-methylpropyl)benzene
00141-93-5	1,3-diethylbenzene
00142-29-0	cyclopentene
00142-82-5	n-heptane
00287-92-3	cyclopentane
00463-49-0	1,2-propadiene
00463-82-1	2,2-dimethylpropane
00464-06-2	2,2,3-trimethylbutane
00488-23-3	1,2,3,4-tetramethylbenzene
00496-11-7	2,3-dihydroindene (indan)
00503-17-3	2-butyne
00513-35-9	2-methyl-2-butene
00526-73-8	1,2,3-trimethylbenzene
00527-53-7	1,2,3,5-tetramethylbenzene
00527-84-4	1-methyl-2-(1-methylethyl)benzene
00535-77-3	1-methyl-3-(1-methylethyl)benzene
00538-68-1	n-pentylbenzene
00538-93-2	(2-methylpropyl)benzene
00540-84-1	2,2,4-trimethylpentane
00542-92-7	1,3-cyclopentadiene
00558-37-2	3,3-dimethyl-1-butene
00560-21-4	2,3,3-trimethylpentane
00562-49-2	3,3-dimethylpentane
00563-16-6	3,3-dimethylhexane
00563-45-1	3-methyl-1-butene

00563-46-2	2-methyl-1-butene
00565-59-3	2,3-dimethylpentane
00565-75-3	2,3,4-trimethylpentane
00584-94-1	2,3-dimethylhexane
00589-34-4	3-methylhexane
00589-43-5	2,4-dimethylhexane
00589-53-7	4-methylheptane
00589-81-1	3-methylheptane
00590-18-1	cis-2-butene
00590-35-2	2,2-dimethylpentane
00590-73-8	2,2-dimethylhexane
00591-76-4	2-methylhexane
00592-13-2	2,5-dimethylhexane
00592-27-8	2-methylheptane
00592-41-6	1-hexene
00592-76-7	1-heptene
00611-14-3	1-methyl-2-ethylbenzene
00616-12-6	3-methyl-trans-2-pentene
00617-78-7	3-ethylpentane
00620-14-4	1-methyl-3-ethylbenzene
00620-23-5	m-tolualdehyde
00622-96-8	1-methyl-4-ethylbenzene
00624-64-6	trans-2-butene
00625-27-4	2-methyl-2-pentene
00627-20-3	cis-2-pentene
00637-92-3	1-ethyl-tert-butyl-ether
00638-04-0	cis-1,3-dimethylcyclohexane
00646-04-8	trans-2-pentene
00674-76-0	4-methyl-trans-2-pentene
00689-97-4	1-buten-3-yne
00691-37-2	4-methyl-1-pentene
00691-38-3	4-methyl-cis-2-pentene
00693-89-0	1-methylcyclopentene
00760-20-3	3-methyl-1-pentene
00763-29-1	2-methyl-1-pentene
00816-79-5	3-ethyl-2-pentene
00822-50-4	trans-1,2-dimethylcyclopentane
00874-41-9	1,3-dimethyl-4-ethylbenzene
00922-62-3	3-methyl-cis-2-pentene
00926-82-9	3,5-dimethylheptane
00933-98-2	1,2-dimethyl-3-ethylbenzene
00934-80-5	1,2-dimethyl-4-ethylbenzene
01069-53-0	2,3,5-trimethylhexane
01072-05-5	2,6-dimethylheptane
01074-17-5	1-methyl-2-n-propylbenzene
01074-43-7	1-methyl-3-n-propylbenzene

01074-55-1	1-methyl-4-n-propylbenzene
01074-92-6	1-(1,1-dimethylethyl)-2-methylbenzene
01120-21-4	n-undecane (hendecane)
01120-62-3	3-methylcyclopentene
01595-11-5	1-methyl-2-n-butylbenzene
01634-04-4	1-methyl-tert-butyl-ether
01640-89-7	ethylcyclopentane
01678-91-7	ethylcyclohexane
01758-88-9	1,4-dimethyl-2-ethylbenzene
01759-58-6	trans-1,3-dimethylcyclopentane
02051-30-1	2,6-dimethyloctane
02207-01-4	cis-1,2-dimethylcyclohexane
02207-03-6	trans-1,3-dimethylcyclohexane
02207-04-7	trans-1,4-dimethylcyclohexane
02213-23-2	2,4-dimethylheptane
02216-33-3	3-methyloctane
02216-34-4	4-methyloctane
02532-58-3	cis-1,3-dimethylcyclopentane
02613-65-2	trans-1-methyl-3-ethylcyclopentane
02738-19-4	2-methyl-2-hexene
02815-58-9	1,2,4-trimethylcyclopentane
02870-04-4	1,3-dimethyl-2-ethylbenzene
03074-71-3	2,3-dimethylheptane
03221-61-2	2-methyloctane
03404-61-3	3-methyl-1-hexene
03522-94-9	2,2,5-trimethylhexane
03899-36-3	3-methyl-trans-3-hexene
04032-94-4	2,4-dimethyloctane
04050-45-7	trans-2-hexene
04170-30-3	crotonaldehyde
06443-92-1	cis-2-heptene
07385-78-6	3,4-dimethyl-1-pentene
07642-04-8	cis-2-octene
07642-09-3	cis-3-hexene
07688-21-3	cis-2-hexene
10574-37-5	2,3-dimethyl-2-pentene
13269-52-8	trans-3-hexene
13389-42-9	trans-2-octene
14686-13-6	trans-2-heptene
14686-14-7	trans-3-heptene
14850-23-8	trans-4-octene
15869-87-1	2,2-dimethyloctane
15890-40-1	(1a,2a,3b)-1,2,3-trimethylcyclopentane
16747-50-5	cis-1-methyl-3-ethylcyclopentane

APPENDIX 2

DEFINITIONS AND COMMONLY USED ABBREVIATIONS

I. The abbreviations and definitions set forth in this section apply to Parts A through G of these test procedures:

ASTM = American Society for Testing and Materials

Carbon No. = number of carbon atoms in the hydrocarbon or organic compound being measured.

CCR = California Code of Regulations

CH_3OH_d = the methanol concentration in the dilution air as determined from the dilution air methanol sample using the procedure specified in Method No. 1001, ppmC.

CH_3OH_e = the methanol concentration in the dilute exhaust as determined from the dilute exhaust methanol sample using the procedure specified in Method No. 1001, ppmC.

CH_{4d} = the methane concentration in the dilution air, ppmC.

CH_{4e} = the methane concentration in the dilute exhaust, ppmC.

$C_2H_5OH_d$ = the ethanol concentration in the dilution air as determined from the dilution air ethanol sample using the procedure specified in Method No. 1001, ppmC.

$C_2H_5OH_e$ = the ethanol concentration in the dilute exhaust as determined from the dilute exhaust ethanol sample using the procedure specified in Method No. 1001, ppmC.

CNG = compressed natural gas

CO_e = the carbon monoxide concentration in the dilute exhaust corrected for carbon dioxide and water removal, ppm.

CO_{em} = the carbon monoxide concentration in the dilute exhaust uncorrected for carbon dioxide and water removal, ppm.

CO_{2e} = the carbon dioxide concentration in the dilute exhaust, %.

CVS = constant volume sampler

$D_{\text{phase n}}$ = the distance driven by the test vehicle on a chassis dynamometer during test phase n (where n is either 1, 2, or 3), mile.

Dens_{ROH} = density of alcohol, g/mL.

DF = dilution factor (see Dilution Factor Calculation).

FID = flame ionization detector

FID THC_d = the total hydrocarbon concentration including methane and methanol (for methanol-fueled engines) or ethanol (for ethanol-fueled engines) in the dilution air as measured by the FID, ppmC.

FID THC_e = the total hydrocarbon concentration including methane and methanol (for methanol-dueled engines) or ethanol (for ethanol-fueled engines) in the dilution exhaust as measured by the FID, ppmC.

FTP = Federal Test Procedure

GC = gas chromatograph

GC/MS = gas chromatography/mass spectrometry

HC_{conc} = net concentration of an HC compound in the dilute exhaust corrected for background per test phase, ppbC.

HC_d = composite concentration of an HC compound in the dilution air (background) for all three test phases as determined from the composite dilution air sample using the procedure specified in Method No. 1002 and Method No. 1003, ppbC.

HC_{dens} = mass per unit volume of an HC compound corrected to standard conditions (293.16 K and 760 mm Hg) g/ft^3.

HC_e = concentration of an HC compound in the dilute exhaust per test phase as determined from the dilute exhaust sample using the procedure specific in Method No. 1002 and Method No. 1003, ppbC.

$\text{HC}_{\text{mass n}}$ = mass emissions of an HC compound per test phase n (where n is either 1, 2, or 3), mg.

HC_{wm} = total weighted mass of an HC compound per mile, g/mile.

HCHO_{e} = formaldehyde concentration in the dilute exhaust as determined from the dilute exhaust carbonyl sample using the procedure specified in Method No 1004, ppm.

HCR = the hydrogen-to-carbon ratio for the fuel used.

HPLC = high performance liquid chromatography

$\text{Iconc}_{\text{blk}}$ = concentration of the blank cartridge, µg/mL

Iconc_{cd} = total concentration of carbonyl compound extracted from both cartridges for the dilution air, µg/mL

Iconc_{ce} = total concentration of carbonyl compound extracted from both cartridges for the diluted exhaust, µg/mL

Iconc_{d1} = dilution air (background) alcohol concentration in the primary impinger for all three test phases as determined by the procedure specified in Method No. 1001, µg/mL.

Iconc_{d2} = dilution air (background) alcohol concentration in the secondary impinger for all three test phases as determined by the procedure specified in Method No. 1001, µg/mL.

Iconc_{e1} = dilute exhaust alcohol concentration in the primary impinger per test phase as determined by the procedure specified in Method No. 1001, µg/mL.

Iconc_{e2} = dilute exhaust alcohol concentration in the secondary impinger per test phase as determined by the procedure specified in Method No. 1001, µg/mL.

Imass_{d} = total mass of an alcohol or carbonyl compound collected from the dilution air (background) in both primary and secondary impingers/cartridges for all three test phases as determined by the procedure specified in Method No. 1001 (alcohol) or Method No. 1004 (carbonyl), µg.

Imass_{e} = total mass of an alcohol or carbonyl compound collected from the dilute exhaust in both primary and secondary impingers/cartridges per test phase as determined by the procedure specified in Method No. 1001 (alcohol) or Method No. 1004 (carbonyl), µg.

$Itemp_d$ = dilution air temperature at the flowmeter inlet for impinger/cartridge sampling, ^{o}K.

$Itemp_e$ = dilute exhaust temperature at the flowmeter inlet for impinger/cartridge sampling, ^{o}K.

$Ivol_c$ = elution volume of the cartridge, mL
(The cartridge is extracted with 5 mL acetonitrile, but 0.6 mL is retained in the cartridge, so the elution volume is 4.4 mL.)

$Ivol_d$ = total volume of dilution air (background) drawn through the impingers/cartridges for all three test phases corrected to standard conditions (293.16^{o}K and 760 mm Hg), liter.

$Ivol_{dm}$ = total volume of dilution air (background) drawn through the impingers/cartridges for all three test phases as measured during testing, liter.

$Ivol_e$ = total volume of dilute exhaust drawn through the impingers/cartridges per test phase corrected to standard conditions (293.16^{o}K and 760 mm Hg), liter.

$Ivol_{em}$ = total volume of dilute exhaust drawn through the impingers/cartridges per test phase as measured during testing, liter.

$Ivol_r$ = volume of the reagent used in an impinger, mL.

LOD = limit of detection

LPG = liquified petroleum gas

Mol. Vol. = molecular volume which is 24.055 liter/mole at standard conditions (293.16^{o}K and 760 mm Hg).

Mol. Wt. = molecular weight of the compound being measured, g/mole.

NIST = National Institute of Standards and Technology

NMHC = non-methane hydrocarbons

$NMHC_{conc}$ = the non-methane hydrocarbon concentration in the dilute exhaust corrected for background, ppmC.

$NMHC_d$ = the non-methane hydrocarbon concentration in the dilution air corrected for methane and alcohol removal, ppmC.

$NMHC_{dens}$ = the mass per unit volume of non-methane hydrocarbon corrected to standard conditions (16.33 g/ft^3 at 293.16^{o}K and 760 mm Hg assuming a C:H ratio of 1:1.85 for gasoline; 16.78 g/ft^3 at 293.16^{o}K and 760 mm HG assuming a C:H ratio of 1:1.94 for Phase 2 reformulated gasoline; 19.52 g/ft^3 at 293.16^{o}K and 760 mm HG assuming a C:H ratio of 1:3.78 for natural gas; and 17.26 g/ft^3 for LPG at 293.16^{o}K and 760 mm Hg assuming a C:H ratio of 1:2.64), g/ft^3 .

$NMHC_e$ = non-methane hydrocarbon concentration in the dilute exhaust corrected for methane and alcohol removal, ppmC.

$NMHC_{mass\ n}$ = the mass emission of non-methane hydrocarbon per test phase n (where n is either 1, 2, or 3), g.

$NMHC_{wm}$ = the total weighted mass of non-methane hydrocarbon per mile for all three phases of the FTP, g/mile.

NMOG = non-methane organic gases

P_B = barometric pressure during testing, mm Hg.

PID = photoionization detector

PLOT = porous layer open tubular

R_a = the relative humidity of the ambient air, %.

r_{CH_3OH} = the FID response factor to methanol (see CFR 40, 86.121-90(c)).

r_{CH_4} = the FID response factor to methane (see Part B, “Determination of NMHC by FID”).

$r_{C_2H_5OH}$ = the FID response factor to ethanol (same procedure for methanol response factor, see CFR 40, 86.121-90(c)).

RHO = generic symbol representing a carbonyl compound such as formaldehyde, acetaldehyde, acetone, etc.

RHO_{conc} = net concentration of a carbonyl compound in the dilute exhaust corrected for background per test phase, ppm.

RHO_{d} = composite concentration of a carbonyl compound in the dilution air (background) for all three test phases, ppm.

RHO_{dens} = mass per unit volume of a carbonyl compound corrected to standard conditions (293.16^{o}K and 760 mm Hg), g/ft^{3}.

RHO_{e} = concentration of a carbonyl compound in the dilute exhaust per test phase, ppm.

$RHO_{mass\ n}$ = mass emissions of a carbonyl compound per test phase n (where n is either 1, 2, or 3), g.

RHO_{wm} = total weighted mass emissions of a carbonyl compound per mile, g/mile.

ROH = generic symbol representing an alcohol compound such as methanol or ethanol.

ROH_{conc} = net concentration of an alcohol compound in the dilute exhaust corrected for background per test phase, ppm.

ROH_{d} = composite concentration of an alcohol compound in the dilution air (background) for all three test phases, ppm.

ROH_{dens} = mass per unit volume of an alcohol compound corrected to standard conditions (293.16^{o}K and 760 mm Hg), g/ft^{3}.

ROH_{e} = concentration of an alcohol compound in the dilute exhaust per test phase, ppmC.

$ROH_{mass\ n}$ = mass emissions of an alcohol compound per test phase n (where n is either 1, 2, or 3), g.

ROH_{wm} = total weighted mass emissions of an alcohol compound per mile, g/mile.

SAE = Society of Automotive Engineers

SRM = Standard Reference Material

VMIX = the total dilute exhaust volume measured per test phase and corrected to standard conditions (293.16^{o}K and 760 mm Hg), ft^{3}.

II. The following list is commonly used measurement abbreviations:

g = gram
µg = microgram
m = meter
cm = centimeter
µm = micrometer
µ = micron
L = liter
mL = milliliter
µL = microliter
ppb = parts per billion.
ppbC = parts per billion carbon equivalent.
ppm = parts per million.
ppmC = parts per million carbon equivalent.

APPENDIX 3

REFERENCES

[1] Code of Federal Regulations, Title 40, Part 86, Subpart B

[2] SAE J254, "Instrumentation and Techniques for Exhaust Gas Emissions Measurement"

[3] SAE J1094a, "Constant Volume Sampler System for Exhaust Emissions Measurement"

[4] SAE 770141, "Optimization of a Flame Ionization Detector for Determination of Hydrocarbons in Diluted Automotive Exhausts". G.D. Reschke, Vehicle Emissions Laboratory, General Motors Proving Ground

[5] SAE J1154, "Methane Measurement Using Gas Chromatography," (revised December 1991)

[6] U.S. Environmental Protection Agency, Characterization of Exhaust Emissions from Methanol and Gasoline Fueled Automobiles, EPA 460/3-82-004.

[7] U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, (Method T03-15) EPA-600/4-89-017 Research Triangle Park, North Carolina, June, 1989.

[8] Standard Test Method for C_1 through C_6 Hydrocarbons in the Atmosphere by Gas Chromatography, American Standards for Testing Materials (ASTM) Standards on Chromatography (1981).

[9] U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, (Method T03-15) EPA-600/4-84-041 Research Triangle Park, North Carolina, April, 1989.

[10] Hull, L.A., Procedures for 2,4-Dinitrophenylhydrazone Aldehyde-Ketone Air Analysis, Internal Report at U.S. EPA.

[11] Shriner, R.L. and Fuson, R.C., Identification of Organic Compounds, 2nd. Ed., John Wiley and Sons, Inc., 1940, p. 143.

[12] Keith, L. H., Taylor, J.K., et al, "Principles of Environmental Analysis", Analytical Chemistry, Vol. 55, No. 14, December 1983.

AMEND: 340-257-0050

RULE TITLE: Incorporation by Reference

NOTICE FILED DATE: 08/30/2018

RULE SUMMARY: Updating dates of CCRs referenced.

RULE TEXT:

(1) For purposes of applying the incorporated sections of the California Code of Regulations, unless otherwise specified in this division or the application is clearly inappropriate, "California" means "Oregon," "Air Resources Board (ARB)" or "California Air Resources Board (CARB)" means Department of Environmental Quality or Environmental Quality Commission depending on context, and “Executive Officer” means director or director’s designee.

(2) Emission standards, warranty, recall and other California provisions adopted by reference. Each manufacturer of new 2009 and subsequent model year passenger cars, light-duty trucks, and medium-duty vehicles must comply with each applicable standard specified in the following sections of the California Code of Regulations (CCR), Title 13, which are incorporated by reference herein. References to provisions of CCR, Title 13 in this division are to such provisions effective on the California effective dates listed in this section:

(a) Section 1900: Definitions. California effective date 7/25/16.

(b) Section 1956.8(g) and (h): Exhaust Emission Standards and Test Procedures — 1985 and Subsequent Model Heavy Duty Engines and Vehicles. California effective date 12/5/14.

(c) Section 1960.1: Exhaust Emission Standards and Test Procedures — 1981 and through 2006 Model Passenger Cars, Light-Duty and Medium-Duty Vehicles. California effective date 12/31/12.

(d) Section 1961: Exhaust Emission Standards and Test Procedures — 2004 and Subsequent Model Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles. California effective date 12/31/12.

(e) Section 1961.1: Greenhouse Gas Exhaust Emission Standards and Test Procedures - 2009 and Subsequent Model Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles. California effective date 8/7/12.

(f) Section 1961.2: Exhaust Emission Standards and Test Procedures — 2015 and Subsequent Model Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles. California effective date 9/28/18.

(g) Section 1961.3: Greenhouse Gas Emission Standards and Test Procedures — 2017 and Subsequent Model Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles. California effective date 9/28/18.

(h) Section 1962: Zero-Emission Vehicle Standards for 2005 through 2008 Model Year Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles. California effective date 2/13/2010.

(i) Section 1962.1: Zero-Emission Vehicle Standards for 2009 through 2017 Model Year Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles. California effective date 1/1/16.

(j) Section 1962.2: Zero-Emission Vehicle Standards for 2018 and Subsequent Model Year Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles. California effective date 1/1/16.

(k) Section 1962.3: Electric Vehicle Charging Requirements. California effective date 8/7/12.

(l) Section 1965: Emission Control and Smog Index Labels - 1979 and Subsequent Model Year Vehicles. California effective date 10/8/15.

(m) Section 1968.2: Malfunction and Diagnostic System Requirements — 2004 and Subsequent Model Year Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles. California effective date 7/25/16.

(n) Section 1968.5: Enforcement of Malfunction and Diagnostic System Requirements for 2004 and Subsequent Model Year Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles and Engines. California effective date 7/25/16.

(o) Section 1976: Standards and Test Procedures for Motor Vehicle Fuel Evaporative Emissions. California effective date 10/8/15.

(p) Section 1978: Standards and Test Procedures for Vehicle Refueling Emissions. California effective date 10/8/15.

(q) Section 2035: Purpose, Applicability and Definitions. California effective date 11/9/07.

(r) Section 2037: Defects Warranty Requirements for 1990 and Subsequent Model Year Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles and Motor Vehicle Engines Used in Such Vehicles. California effective date 12/5/14.

(s) Section 2038: Performance Warranty Requirements for 1990 and Subsequent Model Year Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles and Motor Vehicle Engines Used in Such. California effective date 8/7/12.
(t) Section 2039: Emission Control System Warranty Statement. California effective date 12/26/90.
(u) Section 2040: Vehicle Owner Obligations. California effective date 12/26/90.
(v) Section 2046: Defective Catalyst. California effective date 2/15/79.
(w) Section 2109: New Vehicle Recall Provisions. California effective date 12/30/83.
(x) Section 2111: Applicability. California effective date 12/8/10.
(y) Section 2112: Definitions. California effective date 12/5/14.
(z) Appendix A to Article 2.1. California effective date 8/16/2009.
(aa) Section 2113: Initiation and Approval of Voluntary and Influenced Recalls. California effective date 1/26/95.
(bb) Section 2114: Voluntary and Influenced Recall Plans. California effective date 11/27/99.
(cc) Section 2115: Eligibility for Repair. California effective date 1/26/95.
(dd) Section 2116: Repair Label. California effective date 1/26/95.
(ee) Section 2117: Proof of Correction Certificate. California effective date 1/26/95.
(ff) Section 2118: Notification. California effective date 1/26/95.
(gg) Section 2119: Record keeping and Reporting Requirements. California effective date 11/27/99.
(hh) Section 2120: Other Requirements Not Waived. California effective date 1/26/95.
(ii) Section 2122: General Provisions. California effective date 12/8/2010.
(jj) Section 2123: Initiation and Notification of Ordered Emission-Related Recalls. California effective date 1/26/95.
(kk) Section 2124: Availability of Public Hearing. California effective date 1/26/95.
(ll) Section 2125: Ordered Recall Plan. California effective date 1/26/95.
(mm) Section 2126: Approval and Implementation of Recall Plan. California effective date 1/26/95.
(nn) Section 2127: Notification of Owners. California effective date 1/26/95.
(oo) Section 2128: Repair Label. California effective date 1/26/95.
(pp) Section 2129: Proof of Correction Certificate. California effective date 1/26/95.
(qq) Section 2130: Capture Rates and Alternative Measures. California effective date 11/27/99.
(rr) Section 2131: Preliminary Tests. California effective date 1/26/95.
(ss) Section 2132: Communication with Repair Personnel. California effective date 1/26/95.
(tt) Section 2133: Record keeping and Reporting Requirements. California effective date 1/26/95.
(uu) Section 2135: Extension of Time. California effective date 1/26/95.
(vv) Section 2141: General Provisions. California effective date 12/8/10.
(ww) Section 2142: Alternative Procedures. California effective date 2/23/90.
(xx) Section 2143: Failure Levels Triggering Recall. California effective date 11/27/99.
(yy) Section 2144: Emission Warranty Information Report. California effective date 11/27/99.
(zz) Section 2145: Field Information Report. California effective date 8/7/12.
(aaa) Section 2146: Emissions Information Report. California effective date 11/27/99.
(bbb) Section 2147: Demonstration of Compliance with Emission Standards. California effective date 12/5/14.
(ccc) Section 2148: Evaluation of Need for Recall. California effective date 11/27/99.
(ddd) Section 2149: Notification of Subsequent Action. California effective date 2/23/90.
(eee) Section 2235: Requirements. California effective date 8/8/12.

STATUTORY/OTHER AUTHORITY: ORS 468.020, 468A.025, 468A.360

STATUTES/OTHER IMPLEMENTED: ORS 468.010, 468A.015, 468A.025, 468A.360

AMEND: 340-257-0090

RULE TITLE: ZEV Credit Bank and Reporting

NOTICE FILED DATE: 08/30/2018

RULE SUMMARY: Added TZEV requirements for credit banking and reporting.

RULE TEXT:

(1) Beginning model year 2009, each intermediate volume and large volume manufacturer of ZEVs, ATPZEVs, PZEVs, and TZEVs may open an account in the ZEV Credit Bank operated by DEQ.

(2) In order to generate and deposit credits for vehicles delivered for sale in Oregon during the 1999 through 2005 model years, a manufacturer must open an account with the ZEV Credit Bank and submit an appropriate Notice of Generation to DEQ on or before September 1, 2006.

(3) Manufacturers wishing to claim ZEV credits must use the format and process contained in CARB's Manufacturer's Advisory Correspondence (MAC) 2011-02 for reporting and tracking ZEV deliveries and placements, unless this division specifies different requirements. DEQ will follow CARB's procedures contained in that MAC for tracking and recording ZEV sales and credits.

(4) Except as provided in section (2) of this rule, annually each manufacturer must submit to DEQ a Notice of Credit Generation or Notice of Credit Transfer to or from another manufacturer. Credits generated or acquired must be reported to DEQ on or before September 1 following the close of the model year in which the qualifying vehicle was produced and delivered for sale in Oregon.

(5) To deposit credits into the ZEV Credit Bank, a manufacturer must submit a Notice of Credit Generation to DEQ. The Notice of Generation must include the following:

(a) For ZEVs delivered for sale in Oregon:

(A) Manufacturer's ZEV Credit Bank account identifier;

(B) Model year of vehicle qualifying for credit;

(C) CARB Executive Order number;

(D) ZEV Tier type (NEV, 0, I, II, III for California, III for Section 177 states);

(E) Vehicle identification number (only through model year 2017); and

(F) Date the vehicle was delivered for sale in Oregon.

(b) For model years through 2017, ZEVs placed in service in Oregon, all information listed under subsection (6)(a) of this rule, plus the following:

(A) Date the vehicle was placed in service, and

(B) Whether the vehicle was placed in service with an option to purchase or lease the vehicle.

(c) For ATPZEVs and PZEVs delivered for sale in Oregon:

(A) Vehicle certification class (ATPZEV or PZEV);

(B) Manufacturer's ZEV Credit Bank account identification;

(C) Model year of vehicle(s);

(D) For ATPZEVs, the Federal test group;

(E) The CARB Executive Order number;

(F) Number of vehicles delivered;

(d) For TZEVs delivered for sale in Oregon:

(A) Manufacturer's ZEV Credit Bank account identifier;

(B) Model year of vehicle qualifying for credit;

(C) CARB Executive Order number;

(D) Date the vehicle was delivered for sale in Oregon, and

(6) The number of the credits generated and deposited for each qualifying vehicle must be the number of qualifying vehicles multiplied by the applicable multiplier specified in CCR, Title 13, sections 1962, 1962.1 or 1962.2 as appropriate, except the multiplier applied to vehicles produced and delivered for sale in Oregon from January 1, 1999

to January 13, 2004 will be the highest applicable multiplier used by the CARB for the period January 1, 1999 to January 13, 2004.

(7) A vehicle equivalent credit does not constitute or convey a property right.

(8) A manufacturer with an account in the ZEV Credit Bank may acquire credits from another manufacturer with an account in the ZEV Credit Bank. However, if the credits are to be used for future compliance with the ZEV sales requirement at CCR Title 13, section 1962.1, the transaction must be recorded in the ZEV Credit Bank and certified by both parties to the transaction.

(9) A manufacturer may deposit into its account in the ZEV Credit Bank a number of credits equal to its California credit balance at the beginning of the 2009 model year. The transferred credit balance will be multiplied by the number of new motor vehicles registered in Oregon, and divided by the number of new motor vehicles registered in California. The proportion of new motor vehicles in Oregon and California will be determined by the average number of vehicles registered in model years 2003 through 2005, or by the average number of vehicles registered in model year 2009. The deposit may be made only after all credit obligations for model years 2008 and earlier have been satisfied in California.

(10) Each manufacturer with a ZEV Credit Bank account under this rule must report to DEQ the following information:

(a) By May 1, 2009, the total number of PC and LDT1 vehicles produced and delivered for sale in Oregon and California for 2003 through 2005 model years; or

(b) By May 1, 2009, the total projected number of PC and LDT1 vehicles to be produced and delivered for sale in Oregon and California during model year 2009 and, by March 1, 2010, the actual number of 2009 model year PC and LDT1 vehicles produced and delivered for sale in Oregon and California; and

(c) By May 1, 2009, provide DEQ with the total number of banked California credits after all 2008 model year and earlier obligations have been met.

(11) A manufacturer electing to deposit credits under section (9) of this rule must offer for sale in Oregon in model years 2009 through 2011 any PZEV, ATPZEV or ZEV, except Type III ZEVs, that it offers for sale in California during the same period.

Note: A copy of CARB's Manufacturer's Advisory Correspondence (MAC) 2011-02 is available through the link below.

STATUTORY/OTHER AUTHORITY: ORS 468.020, 468A.025, 468A.360

STATUTES/OTHER IMPLEMENTED: ORS 468.020

Air Resources Board

Mary D. Nichols, Chairman
9480 Telstar Avenue, Suite 4
El Monte, California 91731 • www.arb.ca.gov

Linda S. Adams
Acting Secretary for
Environmental Protection

Edmund G. Brown Jr.
Governor

March 23, 2011

REVISED MANUFACTURERS ADVISORY CORRESPONDENCE (MAC) 2011-02

TO:
ALL PASSENGER CAR MANUFACTURERS
ALL LIGHT-DUTY TRUCK MANUFACTURERS
ALL MEDIUM-DUTY VEHICLE MANUFACTURERS
ALL OTHER INTERESTED PARTIES

SUBJECT: Zero Emission Vehicle (ZEV) Credit Reporting and Tracking System

This letter transmits a Revised Manufacturers Advisory Correspondence (MAC) that provides vehicle manufacturers and other interested parties with the Air Resources Board's mechanism and format to be used for reporting and tracking ZEV deliveries and placements to determine ZEV credit compliance. This revised MAC corrects the applicable model year to 2010 and subsequent. This revised MAC supersedes MAC 2011-01 and MAC 2006-03. The primary purpose of modifying this MAC is to incorporate the amendments to the ZEV Regulation in 2008.

If you have any questions regarding this matter, please contact Ms. Krista Eley, Air Pollution Specialist, at (916) 322-2333, or via email at keley@arb.ca.gov .

Sincerely,

Robert H. Cross, Chief
Mobile Source Control Division

Attachments

cc:
Ms. Krista Eley
Air Pollution Specialist
Sustainable Transportation Technology Branch

State of California
Air Resources Board

Revised Manufacturers' Advisory Correspondence (MAC) #2011-02

Subject: Format and policies for manufacturer Zero Emission Vehicle (ZEV) Reporting for 2010 and subsequent model-year ZEVs, Enhanced Advanced Technology Partial ZEVs (Enhanced AT PZEVs), AT PZEVs and Partial ZEVs (PZEVs). This MAC supersedes MAC 2011-01 and MAC 2006-03.

Applicability: Manufacturers of 2010 and subsequent model-year ZEVs, Enhanced AT PZEVs, AT PZEVs, and PZEVs certified for sale in California and any person or entity that transacts credits for these vehicles including, but not limited to, credit brokers and transportation project managers.

References: Section 1962.1, Title 13, California Code of Regulations (CCR), and the incorporated "California Exhaust Emission Standards and Test Procedures for 2009 and Subsequent Model Zero Emission Vehicles, and 2001 and Subsequent Model Hybrid Electric Vehicles, in the Passenger Car, Light-Duty Truck and Medium-Duty Vehicle Classes," adopted by the state board on December 17, 2008.

Background: The California ZEV regulations were originally adopted by the Air Resources Board (ARB or Board) in 1990, as part of the first generation California low-emission vehicle regulations. The ZEV program is an integral part of California's mobile source control efforts, and is intended to encourage the development of advanced technologies that will secure increasing air quality benefits and greenhouse gas reduction goals. The ZEV regulations nominally require that a certain percent of the passenger cars and light-duty trucks produced and delivered for sale in California by all but small volume manufacturers be ZEVs – vehicles with no emissions. However, there are mechanisms under which a manufacturer may satisfy part – or in some cases all – of its ZEV obligation with PZEV allowances generated from vehicles with extremely low emissions.

Discussion: This MAC provides a consistent format for reporting delivery and placement of ZEV program vehicles in California for demonstration of compliance with the regulation. Additionally, the process and format for submitting data related to other ZEV credit activities is provided.

ARB requests that manufacturers, and other interested parties provide both a hard copy and an electronic version of the appropriate forms and ZEV reports be submitted with an attached cover letter for all ZEVs, Enhanced AT PZEVs, AT PZEVs and PZEVs. Vehicle manufacturers will continue to report production data as previously required.

ARB forms and specified electronic format for reporting credits and debits for ZEV reporting include: 1) an application form for opening a "ZEV account" with the ARB/Change of Company Representative or address, 2) a form for selecting the calculation method and Non-Methane Organic Gases (NMOG) production numbers, 3) credit and debit electronic format, 4) example data files, and 5) a form for transferring credits. These electronic forms are presented in the following Attachments:

Application for California Zero Emission Vehicle (ZEV) Account /Change of Company Representative or Address	Attachment A
Calculation Method for Zero Emission Vehicle (ZEV) Credit Requirement	Attachment B
Credits	Attachment C
Debits	Attachment D
Example Data files – Credits and Debits	Attachment E
Zero Emission Vehicle (ZEV) Credit Transfer Form	Attachment F

Guidance: Credit Bank

ARB will utilize the ZEV Bank to track ZEVs and the credits earned by vehicle manufacturers and transacted by credit traders. The system will also generate ZEV credit balance and summary statements.

Manufacturers of 2010 and subsequent model-year ZEVs, Enhanced AT PZEVs, AT PZEVs, and PZEVs certified for sale in California and any person or entity that holds ZEV credits for any length of time including, but not limited to, credit brokers and transportation project managers need to apply for a ZEV account with ARB. See Attachment A Application for Zero Emission Vehicle (ZEV) Account with the ZEV Bank.

ARB will record ZEVs in the ZEV Bank. The recording of vehicles is then subject to verification of the information substantiating delivery and placement of ZEVs. If ARB determines that discrepancies exist in any ZEV information submitted, staff will notify the appropriate party and will accordingly adjust the ZEV Account. ARB may perform audits at any time.

Recorded ZEV credits will be multiplied by NMOG fleet average requirement for the appropriate model year. ZEV credits will be stored in the ZEV Bank in units of grams per mile (g/mi) NMOG. Please note that the g/mi NMOG units are only used as an index and do not represent actual values of g/mi NMOG.

Frequency of Reporting

ZEV account holders are to report ZEV data as indicated in Attachments B, C and D, annually by May 1st of the calendar year following the close of a model year. Attachment A must be resubmitted if there are any changes to the Company Representatives or the Company address, email or phone. Annual Reports may be updated by September 1 of the same year. ZEV account holders may choose to report more frequently, however, please contact the ZEV Bank Program Manager prior to transmittal. The schedule is as follows:

Annual

Report Date	Data Represents
May 1 of a given calendar year	preceding model year

Supplement to Annual

Report Date	Data Represents
September 1 of a given calendar year	preceding model year April 1 to June 30

Credit Statements

The ZEV Bank Program Manager will issue credit statements to ZEV account holders annually. Additional credit statements are available upon request.

Credit Types and Conditions

ZEVs

ZEVs may generate ZEV credits at several points in time including "Delivered for sale," "Placed in service" and "Extended service." Vehicles receive a base credit when "delivered for sale in California" and remaining ZEV credits based on applicable multipliers when "Placed in Service." ((§1962.1(d)(5)(C))

Placed in service – As defined in the ZEV regulation "means having been sold or leased to an end-user and not to a dealer or other distribution chain entity, and having been individually registered for on-road use by the California Department of Motor Vehicles (DMV)." (§1962.1(i)(7))

Vehicles sold en masse to another state by one person, entity or company shortly after registering at the California DMV do not meet the definition of "Placed in service" in the ZEV regulation. Specifically they do not meet the criteria of being sold or leased to an end-user and not to a dealer or other distribution chain entity. The person, entity or company in this situation would be a dealer or other distribution chain entity. Therefore vehicles in this circumstance do not qualify for ZEV credits.

All "Placed in service" vehicles will be verified with the California DMV with the exception of vehicles leased or sold to the government (see below). If any vehicles within a reported batch cannot be verified with the DMV, the ZEV Program Manager will contact the Account Holder and request that those records be corrected and resubmitted.

Vehicles Leased Or Sold To the Government - Vehicles sold to the federal government may or may not be registered at the California DMV. Indicate government agency name, agency contact and agency email when reporting credits.

Multiplier for Certain ZEVs – ZEVs produced in model years 2009 to 2011, excluding Neighborhood Electric Vehicles and Type 0 ZEVs, may receive a one time multiplier of 1.25 if it is either sold to a motorist or is leased for 3 or more years to a motorist who is given the option to purchase or re-lease the vehicle for 2 years or more at the end of the first term. (§1962.1(d)(5)(D))

Neighborhood Electric Vehicles (NEVs) and non-NEVs – For reporting and tracking purposes, a distinction is made between NEVs and ZEVs that are not NEVs regarding the limited use of banked NEV credits.

Enhanced AT PZEVs, AT PZEVs and PZEVs

Enhanced AT PZEVs, AT PZEVs and PZEVs may earn credits for having been "Delivered for sale" as described for ZEVs. No additional credits or multipliers are applied when the vehicles are placed. Thus, the ZEV Bank does not track placement for Enhanced AT PZEVs, AT PZEVs and PZEVs.

Phase-In Multiplier for Enhanced AT PZEVs

A PZEVs produced in model years 2009 through 2011 model year that earn zero-emission vehicle miles traveled allowance under §1962.1(c)(3) may receive a one time multiplier of 1.25 if it is either sold to a motorist or is leased for 3 or more years to a motorist who is given the option to purchase or re-lease the vehicle for 2 years or more at the end of the first term. (§1962.1(c)(7)(B))

Extended Service Multiplier

ZEVs and some AT PZEVs in model years 1997-2003 may earn ZEV credits for having been re-leased after an initial 3 years in accordance with the ZEV regulation. NEVs are not eligible to earn the credit for the Extended Service Multiplier. (§1962.1(f))

Advanced Technology Demonstration Programs

ZEVs and Enhanced AT PZEVs, excluding NEVs, placed in a California advanced technology demonstration program may earn ZEV credits even if it is not "delivered for sale" in accordance with the ZEV regulation. (§1962.1(g)(4)) Approval by the ARB's Executive Officer is required for Advance Technology Demonstration Program credits.

Transportation Systems

In model years 2009 and subsequent, a ZEV and Enhanced AT PZEV placed as part of a transportation system may earn ZEV credits in accordance with the ZEV regulation. In model years 2009 to 2011 AT PZEVs and PZEVs placed as part of a transportation system may also earn ZEV credits in accordance with the ZEV regulation. (§1962.1(g)(5)) Approval by the Executive Officer is required for transportation system credits. NEVs are not eligible to earn credit for transportation systems.

Transferring Credits

Credits may be transferred between parties and entities. Any party or entity that holds ZEV credits for any length of time including, but not limited to, credit brokers and transportation project managers, needs to have an account with the ARB ZEV Bank. Credit transfers can take place outside of the ZEV Bank at anytime. However, if credits are to be acknowledged for ZEV compliance, each transfer needs to be recorded in the ZEV Bank and all parties need to have an account with the ZEV Bank as indicated above. The ZEV Bank Program Manager will contact the Primary Account Holders and confirm the transfer request. See Attachment F for the Transferring ZEV Credit Form.

If a transferor double sells credits (sells the same credits to two or more parties or manufacturers), only the transferee to first record with the ZEV Bank will receive credit. The transferee that records with the ZEV Bank after the transferor's credits have been exhausted will not receive credit and will be notified of the shortfall. The ZEV Bank Program Manager will notify the appropriate parties of the discrepancy.

Confidentiality

Public Disclosure

Please see section 1962.1, Title 13, CCR for provisions of how records in the Board's possession for the vehicles subject to the requirements of section 1962.1 are subject to public disclosure.

Trade Secret

In accordance with Title 17, CCR, sections 91000 to 91022, and the California Public Records Act (Government Code Section 6250 et seq.), the information that a company provides to the ARB may be released (1) to the public upon request, except trade secrets which are not emissions data or other information which is exempt from disclosure or the disclosure of which is prohibited by law; and (2) to the Federal Environmental Protection Agency, which protects trade secrets as provided in Section 114(c) of the Clean Air Act and amendments thereto (42 USC 7401 et seq.) and in federal regulation; and (3) to other public agencies provided that those agencies preserve the protections afforded information which is identified as a trade secret, or otherwise exempt from disclosure by law (Government Code Section 6254.5 (e)).

Trade secrets as defined in Government Code Section 6254.7 are not public records and therefore will not be released to the public. However, the California Public Records Act provides that air pollution emission data are always public records, even if data come within the definition of trade secrets. On the other hand, the information used to calculate emission data can be trade secret.

If any company believes that any of the information it may provide is trade secret or otherwise exempt from disclosure under any other provision of law, it must identify the confidential information as such at the time of submission to ARB and must provide the name, address, and telephone number of the individual to be consulted if ARB receives a request for disclosure or seeks to disclose the data. ARB may ask the company to provide documentation of its claim of trade secret or exemption at a later date. Data identified as confidential will not be disclosed unless ARB determines, in accordance with the above referenced regulations that the data do not qualify for a legal exemption from disclosure. In such a case the party claiming confidentiality will be notified at least 21 days before disclosure.

Guidance for Electronic Submittal of Data Files

Manufacturers and other persons or entities transacting ZEV credits need to submit ZEV data reports electronically using all applicable fields with the domains as defined in Attachment C and Attachment D. Note that all fields are required. The preferred electronic format is Microsoft Office Excel.

If an electronic submittal has incomplete or incorrectly formatted data, the data will take longer to process. In addition, the ZEV Bank Program Manager will contact the Account Holder and request that the records be corrected and a complete new data batch submitted. Only if the entire data batch is complete and correctly formatted will the data be recorded in the ZEV bank.

Each file should be named using the format, MMMM_MM_DD_YYYY.XXX, as defined below:

MMMM = Manufacturer code
MM_DD_YYYY = Date report sent for example March 25, 2011 = 03252011
XXX = file extension

The electronic file formats provided in Attachments C and D describe each field in detail. The columns are:

Sequence	Order of the data in the record
Data Name	Name of the data field
Type	Identifies type of the field C = Characters (i.e. Alpha-Numeric) N = Numeric D = Date - date format should be used
Length	Specifies the number of characters in each field. For numeric, specifies the number of digits including the decimal, if any.
Range or Domain	Lists the possible inputs or format for the field
Description	Describes the field