

APPENDIX C

California Environmental Protection Agency
AIR RESOURCES BOARD

PROPOSED

CALIFORNIA NON-METHANE ORGANIC GAS TEST PROCEDURES FOR 1993 THROUGH 2016 MODEL YEAR VEHICLES

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Amended: September 22, 1993
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Amended: [INSERT DATE OF AMENDMENT]

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NOTE: Mention of any trade name or commercial product does not constitute endorsement or recommendation of this product by the Air Resources Board. The proposed amendments to this document are shown in underline to indicate additions and ~~strikeout~~ to indicate deletions compared to the test procedures as amended December 6, 2012. Existing intervening text that is not amended in this rulemaking is indicated by “* * * *”.

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 or NMOG plus oxides of nitrogen (NOx) emission standards. These test procedures shall apply to all LEV630, LEV395, LEV160, ULEV, ULEV570, ULEV400, ULEV340, ULEV270, ULEV250, ULEV200, ULEV125, ULEV70, ULEV50, SULEV, SULEV230, SULEV200, SULEV170, SULEV150, SULEV30, and SULEV20 vehicles certifying to NMOG plus NOx emission standards.

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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 [Ref. 5] is a reference on generally accepted GC principles and analytical techniques for this application. A density of 18.89 g/ft³ shall be used to determine the methane mass emissions. Prior to the 2015 model year, 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 2001 through 2014 Model Criteria Pollutant Exhaust Emission Standards and Test Procedures and 2009 through 2016 Model Greenhouse Gas Exhaust Emission Standards and Test Procedures for 2001 and Subsequent Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles," incorporated by reference in section 1961, title 13, California Code of Regulations (CCR). For the 2015 and subsequent model years, methane mass emissions shall be multiplied by the appropriate methane reactivity adjustment factor and then added to the NMOG emissions as specified in the "California 2015 and Subsequent Model Criteria Pollutant Exhaust Emission Standards and Test Procedures and 2017 and Subsequent Model Greenhouse Gas Exhaust Emission Standards and Test Procedures Passenger Cars, Light Duty Trucks, and Medium Duty Vehicles," incorporated by reference in section 1961.2, title 13, CCR.

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Part C

DETERMINATION OF ALCOHOLS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1001

1. INTRODUCTION

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- 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.

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8. QUALITY CONTROL

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8.7 Limit of Detection –

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The LOD must be calculated using the following equation [Ref. ~~11~~42]:

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Part D

DETERMINATION OF C₂ TO C₅ HYDROCARBONS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1002

1. INTRODUCTION

- 1.1 This document describes a gas chromatographic method of measuring C₂ to C₅ hydrocarbons (light-end hydrocarbons) in the ppbC range from automotive source samples. This method, based on an ASTM method [Ref. 8], does not include sample collection procedures ~~[Ref. 8]~~.

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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:

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

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

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8. QUALITY CONTROL

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8.7 Limit of Detection –

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The LOD must be calculated using the following equation [Ref. 1142]:

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Part E

DETERMINATION OF C₆ TO C₁₂ HYDROCARBONS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1003

1. INTRODUCTION

- 1.1 This document describes a gas chromatographic method of measuring C₆ to C₁₂ hydrocarbons (mid-range hydrocarbons) in the ppbC range from automotive source samples. This method, based on a U.S. EPA method [Ref. 7], does not include sample collection procedures ~~[Ref. 7]~~.

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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:

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

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

8. QUALITY CONTROL

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8.7 Limit of Detection -

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The LOD must be calculated using the following equation [Ref. 1112]:

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Part F

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

METHOD NO. 1004

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1. INTRODUCTION

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1.2 This procedure is derived from a method used by Hull [Ref. 910].

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3. INTERFERENCES AND LIMITATIONS

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3.3 The presence of NO_x in exhaust samples depletes DNPH in the cartridges. Laboratories should develop criteria to validate test results by ensuring that enough DNPH is left to trap the carbonyl compounds, particularly in samples with high NO_x levels.

3.3.1 The area counts of the DNPH peak show the amount of excess DNPH left in the cartridge.

3.3.2 Comparison of DNPH area counts in the sample to those in the blank show the approximate percentage of DNPH remaining in the sample cartridge:

$$\% \text{ of excess DNPH in sample cartridge} = \frac{\text{DNPH area counts, sample}}{\text{DNPH area counts, blank}}$$

3.3.3 Laboratories should set an acceptable percentage of excess DNPH remaining in the cartridge for results to be considered valid.

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5. **REAGENTS AND MATERIALS**

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- 5.7 The carbonyl/DNPH complexes [Ref. 1044] 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.

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6. **PROCEDURE**

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- 6.3 After sampling uncap and place all impingers in preheated water at 70-80°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.

6.3.1.1 Some acetonitrile is retained in the cartridge. The amount of acetonitrile collected after extraction is the elution volume. This volume may be measured for each extraction or an average elution volume for a given cartridge type may be experimentally determined by measuring a random sampling of blank cartridges. This volume will be used in Part G of these procedures to convert the measurements to mass units.

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7. **CALCULATIONS**

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

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

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:

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

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

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8. QUALITY CONTROL

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8.7 Limit of Detection –

* * *

The LOD must be calculated using the following equation [Ref. 1112]:

* * *

Part G

DETERMINATION OF NMOG MASS EMISSIONS

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55. ALCOHOL MASS EMISSIONS CALCULATION

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5.2. ALCOHOL MASS EMISSIONS CALCULATION PER TEST PHASE

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$$5.2.5 \quad I_{vol_e} = I_{vol_{em}} * (293.15^{\circ}K / I_{temp_e}) * (P_B / 760 \text{ mm Hg})$$

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$$5.2.8 \quad I_{vol_d} = I_{vol_{dm}} * (293.15^{\circ}K / I_{temp_d}) * (P_B / 760 \text{ mm Hg})$$

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5.4 SAMPLE CALCULATION

5.4.1 Alcohol emissions from an E85 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 alcohol concentration in each impinger. This is the same vehicle test as the

example in section 3.3. Calculate the weighted ethanol mass emissions based on the following data, along with the data presented in section 3.3:

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	4.984	0.106	8.18	0	0	31.16	294.26	294.26
2	15	0	0	14.65	0	0	31.16	294.26	294.26
3	15	0	0	8.67	0	0	31.16	294.26	294.26

* * * *

$$\begin{aligned}
 \text{Ivol}_e &= \text{Ivol}_{em} * (293.15 / \text{Itemp}_e) * (P_B / 760 \text{ mm Hg}) \\
 &= 8.18 \text{ liter} * (293.15 / 294.26) * (760 \text{ mm Hg} / 760 \text{ mm Hg}) \\
 &= 8.15 \text{ liters}
 \end{aligned}$$

* * * *

$$\begin{aligned}
 \text{Ivol}_d &= \text{Ivol}_{dm} * (293.15 / \text{Itemp}_d) * (P_B / 760 \text{ mm Hg}) \\
 &= 31.16 \text{ liter} * (293.15 / 294.26) * (760 \text{ mm Hg} / 760 \text{ mm Hg}) \\
 &= 31.04 \text{ liters}
 \end{aligned}$$

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6.6. CARBONYL MASS EMISSIONS CALCULATIONS

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6.2. CARBONYL MASS EMISSIONS CALCULATION PER TEST PHASE

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$$6.2.5 \quad \text{Ivol}_e = \text{Ivol}_{em} * (293.15 / \text{Itemp}_e) * (P_B / 760 \text{ mm Hg})$$

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$$6.2.8 \quad \text{Ivol}_d = \text{Ivol}_{dm} * (293.15 / \text{Itemp}_d) * (P_B / 760 \text{ mm Hg})$$

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6.4. SAMPLE CALCULATION

6.4.1 Carbonyl emissions from an E85 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 carbonyl mass in each impinger. This is the same vehicle test as the example in section 3.3. Calculate the weighted formaldehyde and acetaldehyde mass emissions based on the following data, along with the data presented in section 3.3:

Test Phase	Ivol _c (mL)	Formaldehyde		Ivol _{em} (liter)	Acetaldehyde		Ivol _{dm} (liter)	Itemp _e (°K)	Itemp _d (°K)
		Iconc _{ce} (µg/mL)	Iconc _{cd} (µg/mL)		Iconc _{ce} (µg/mL)	Iconc _{cd} (µg/mL)			
1	4.4	0.387	0.006	8.47	4.114	0.006	8.23	294.26	294.26
2	4.4	0.048	0.016	15.35	0.013	0.009	13.88	294.26	294.26
3	4.4	0.016	0.006	9.01	0.012	0.005	8.16	294.26	294.26

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$$\begin{aligned}
 \text{Ivol}_e &= \text{Ivol}_{em} * (293/156^\circ \text{ K} / \text{Itemp}_e) * (P_B / 760 \text{ mm Hg}) \\
 &= 8.47 \text{ liter} * (293.156^\circ \text{ K} / 294.26^\circ \text{ K}) * (760 \text{ mm Hg} / 760 \text{ mm Hg}) \\
 &= 8.44 \text{ liter}
 \end{aligned}$$

* * * *

$$\begin{aligned}
 \text{Ivol}_d &= \text{Ivol}_{dm} * (293.156^\circ \text{ K} / \text{Itemp}_d) * (P_B / 760 \text{ mm Hg}) \\
 &= 8.23 \text{ liter} * (293.156^\circ \text{ K} / 294.26^\circ \text{ K}) * (760 \text{ mm Hg} / 760 \text{ mm Hg}) \\
 &= 8.20 \text{ liter}
 \end{aligned}$$

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APPENDIX 1

LIST OF COMPOUNDS

* * * *

Light End and Mid-Range Hydrocarbons (Listed in approximate elution order)

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CAS #	COMPOUND	MIR
<u>02613-66-3</u>	<u>16747-50-5</u> cis-1-methyl-3-ethylcyclopentane	1.64

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List of Compounds (Listed by CAS number)

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<u>02613-66-3</u>	<u>cis-1-methyl-3-ethylcyclopentane</u>
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16747-50-5	cis-1-methyl-3-ethylcyclopentane
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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:

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CFR = Code of Federal Regulations

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C₂H₅OH = ethanol

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HC_{dens} = mass per unit volume of an HC compound corrected to standard conditions (293.15 K and 760 mm Hg) g/ft³.

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HCHO = formaldehyde

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Itemp_d = dilution air temperature at the flowmeter inlet for impinger/cartridge sampling, °K.

Itemp_e = dilute exhaust temperature at the flowmeter inlet for impinger/cartridge sampling, °K.

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Ivol_d = total volume of dilution air (background) drawn through the impingers/cartridges for all three test phases corrected to standard conditions (293.15 K and 760 mm Hg), liter.

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Ivol_e = total volume of dilute exhaust drawn through the impingers/cartridges per test phase corrected to standard conditions (293.15 K and 760 mm Hg), liter.

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MIR = Maximum Incremental Reactivity

Mol. Vol.	=	molecular volume which is 24.055 liter/mole at standard conditions (293.15°K and 760 mm Hg).
		* * * *
NMHC _{dens}	=	the mass per unit volume of non-methane hydrocarbon corrected to standard conditions (16.33 g/ft ³ at 293.15°K and 760 mm Hg assuming a C:H ratio of 1:1.85 for gasoline; 16.78 g/ft ³ at 293.15°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 293.15°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 293.15°K and 760 mm Hg assuming a C:H ratio of 1:2.64), g/ft ³ .
		* * * *
<u>NONMHC</u>	=	<u>non-oxygenated non-methane hydrocarbon</u>
		* * * *
RHO _{dens}	=	mass per unit volume of a carbonyl compound corrected to standard conditions (293.15°K and 760 mm Hg), g/ft ³ .
		* * * *
ROH _{dens}	=	mass per unit volume of an alcohol compound corrected to standard conditions (293.15°K and 760 mm Hg), g/ft ³ .
		* * * *
VMIX	=	the total dilute exhaust volume measured per test phase and corrected to standard conditions (293.15°K and 760 mm Hg), ft ³ .
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APPENDIX 3

REFERENCES

		* * * *
[5]	SAE J11514, "Methane Measurement Using Gas Chromatography," (revised December 1991)	
		* * * *
[9]	<u>U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,</u>	

(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 Procedures for 2,4-Dinitrophenylhydrazone Aldehyde-Ketone Air Analysis, Internal Report at U.S. EPA.
- [1011] Shriner, R.L. and Fuson, R.C., Identification of Organic Compounds, Identification of Organic Compounds, 2nd. Ed., John Wiley and Sons, Inc., 1940, p. 143.
- [1112] Keith, L. H., Taylor, J.K., et al, "Principles of Environmental Analysis", Analytical Chemistry Analytical Chemistry, Vol. 55, No. 14, December 1983.