Proposed

State of California
AIR RESOURCES BOARD

CALIFORNIA EXHAUST EMISSION STANDARDS AND TEST PROCEDURES FOR 1987 AND SUBSEQUENT MODEL HEAVY-DUTY OTTO-CYCLE ENGINES AND VEHICLES

Adopted:	April 25, 1986
Amended:	June 2, 1988
Amended:	January 22, 1990
Amended:	May 15, 1990
Amended:	December 26, 1990
Amended:	July 12, 1991
Amended:	October 23, 1992
Amended:	May 28, 1993
Amended:	________________
Amended:	________________

Date of Release: 2/13/96; second 15-day changes
Board Hearing: 9/28/95

NOTE: This document is printed in a style to indicate amendments to the existing standards and test procedures. The amendments being proposed in the present rulemaking are shown in underline to indicate additions to the text and ~~strikeout~~ to indicate deletions. On June 28, 1995, the Board approved new emission standards. For modifications proposed in that rulemaking, additions to the text are identified in *italics* and deletions are shown in ~~*strikeout*~~. Modifications to the originally noticed text (August 1995) are designated by ***bold italics*** and ~~***bold strikeout***~~ to represent additions and deletions, respectively. Modifications to the modified text (October 1995) are designated by ***underlined bold italics*** and ~~***underlined bold strikeout***~~ to indicate additions and deletions, respectively.

This document incorporates by reference various sections of the Code of Federal Regulations, some with modifications. California provisions which replace specific federal provisions are denoted by the words "DELETE" for the federal language and "REPLACE WITH" for the new California language. The symbols "*****" and "..." mean that the remainder of the federal text for a specific section, which is not shown in these procedures, has been included by reference, with only the printed text changed. For those portions of federal provisions incorporated in this document with modifications, the modifications to the federal text are displayed in *italicized double underline* and ~~*italicized strikeout*~~ to indicate additions to and deletions from the federal language. Federal regulations which are not listed are not part of the procedures.

CALIFORNIA EXHAUST EMISSION STANDARDS AND TEST PROCEDURES FOR 1987 AND SUBSEQUENT MODEL HEAVY-DUTY OTTO-CYCLE ENGINES AND VEHICLES

The following provisions of Subparts A, L, N, and P, Part 86, Title 40, Code of Federal Regulations, as adopted or amended by the U.S. Environmental Protection Agency on the date listed, and only to the extent they pertain to the testing and compliance of exhaust emissions from heavy-duty Otto-cycle gasoline engines and vehicles, are adopted and incorporated herein by this reference as the California Exhaust Emission Standards and Test Procedures for 1987 and Subsequent Model Heavy-Duty Otto-Cycle Engines and Vehicles, except as altered or replaced by the provisions set forth below.

The federal regulations contained in the subparts identified above which pertain to evaporative emissions and oxides of nitrogen emission averaging shall not be applicable to these procedures. Regulations pertaining to evaporative emissions are contained in "California Evaporative Emission Standards and Test Procedures for 1978 and Subsequent Model ~~Liquefied Petroleum Gas or Gasoline or Methanol Fueled~~ Motor Vehicles," as incorporated in Title 13, California Code of Regulations, Section 1976.

The federal regulations contained in the subparts identified above which pertain to nonconformance penalty shall be applicable for the 1988 model year. The Executive Officer shall not implement a nonconformance fee schedule until it is established that payment of nonconformance fees in California may substitute, on the basis of each heavy-duty engine or vehicle certified for sale in California, for payment of nonconformance fees to the federal government.

Starting with the 1990 model year, these regulations shall be applicable to all heavy-duty Otto-cycle natural-gas-fueled and liquefied-petroleum-gas-fueled engines (and vehicles) except those engines derived from existing Diesel engines. For any engine which is not a distinctly Otto-cycle engine nor derived from such, the Executive Officer shall determine whether the engine shall be subject to these regulations or alternatively to the heavy-duty Diesel engine regulations, in consideration of the relative similarity of the engine's torque-speed characteristics and vehicle applications with those of Otto-cycle and Diesel engines.

The regulations concerning the certification of methanol-fueled vehicles and engines including dedicated methanol and fuel-flexible vehicles and engines are not applicable in California until the 1993 and subsequent model years. Regulations concerning the certification of incomplete medium-duty Otto-cycle low-emission vehicles and engines and ultra-low-emission vehicles and engines operating on any fuel are applicable for the 1992 and subsequent model years.

Subpart A, General Provisions for Emission Regulations for 1977 and Later Model Year New Light-Duty Vehicles, Light-Duty Trucks, and Heavy-Duty Engines, and for 1985 and Later Model Year Gasoline-Fueled and Methanol-Fueled Heavy-Duty Vehicles.

86.085-1 General Applicability. March 15, 1985.

* * * * *

(b) ...GVWR or less to the medium-duty vehicle...

* * * * *

(e) ...projected combined California sales of passenger cars, light-duty trucks, medium-duty vehicles and heavy-duty engines in its product line are fewer than 3,000 units for the model...

* * * * *

86.090-1 General Applicability. April 11, 1989.

(a) ... heavy-duty engines. Starting with the 1990 model year, the provisions of this subpart are also applicable to all Otto-cycle dedicated gaseous-fuel, dual-fuel and multi-fuel engines (or vehicles) except those engines derived from existing Diesel engines. Any reference to Otto-cycle heavy-duty engines and vehicles shall also apply to gaseous-fuel engines and vehicles, except where specifically noted. Starting with the 1992 model year, the provisions of this subpart are also applicable to all Otto-cycle low-emission vehicles and engines and ultra-low-emission vehicles and engines operating on any fuel.

* * * * *

(b) ...may request to certify any pre-1996 model-year heavy-duty vehicle of 10,000 pounds Gross Vehicle Weight Rating or less to the medium-duty vehicle...

* * * * *

(e) ...projected combined California sales of passenger cars, light-duty trucks, medium-duty vehicles and heavy-duty engines in its product line are fewer than 3,000 units for the model...

* * * * *

86.085-2 Definitions. November 16, 1983.

"Administrator" DELETE
REPLACE WITH:
"Administrator" means the Executive Officer of the Air Resources Board.

* * * * *

"Certificate of Conformity" DELETE
REPLACE WITH:
"Certificate of Conformity" means "Executive Order" certifying vehicles for sale in California.

"Certification" DELETE
REPLACE WITH:
"Certification" means certification as defined in Section 39018 of the Health and Safety Code.

* * * * *

"EPA Enforcement Officer" DELETE
REPLACE WITH:
"EPA Enforcement Officer" means the Executive Officer or his delegate.

* * * * *

"Heavy-Duty Engine" DELETE
REPLACE WITH:
"Heavy-duty engine" means an engine which is used to propel a heavy-duty vehicle.
"Heavy-Duty Vehicle" DELETE
REPLACE WITH:
"Heavy-duty vehicle" means any motor vehicle having a manufacturer's gross vehicle weight rating greater than 6,000 pounds, except passenger cars.

* * * * *

"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 and subsequent model-year heavy-duty low-emission vehicle or ultra-low-emission vehicle having a manufacturer's gross vehicle weight rating of 14,000 pounds or less, or any

1995 or subsequent model year heavy-duty vehicle having a manufacturer's gross vehicle weight rating of 14,000 pounds or less.

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86.088-2 Definitions. March 15, 1985.

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86.090-2 Definitions. April 11, 1989.

* * * * *

"Dedicated Methanol Vehicle" means any methanol-fueled motor vehicle that is engineered and designed to be operated solely on methanol.

"Dedicated Methanol Engine" means any methanol-fueled heavy-duty engine that is engineered and designed to be operated solely on methanol.

"Flexible-Fuel Vehicle (or Engine)" or "Fuel-Flexible Vehicle (or Engine)" means ...

86.091-2 Definitions. March 15, 1985.

* * * * *

"Gaseous Fuels" means compressed natural gas or liquefied petroleum gas fuel for use in motor vehicles and engines.

"Dedicated Gaseous-Fuel Engine" means any gaseous-fuel engine that is engineered and designed to be operated solely on a gaseous fuel.

"Dual-Fuel Engine" means any gaseous-fuel engine that is engineered and designed to be operated on either a gaseous fuel or petroleum fuel.

"Multi-Fuel Engine" means any gaseous-fuel engine that is engineered and designed to be operated with a gaseous fuel simultaneously with a petroleum fuel.

# # # # #

86.098-2 Definitions. April 6, 1994

~~The definitions of § 86.096-2 continue to apply to 1996 and later model year vehicles.~~
The definitions listed in this section apply beginning with the 1998 model year.

"Dispensed fuel temperature" DELETE
"Evaporative/refueling emission control system" DELETE
"Evaporative/refueling emission family" DELETE
"Integrated refueling emission control system" DELETE
"Non-integrated refueling emission control system" DELETE
"Refueling emissions" DELETE.
"Refueling emission canister(s)" DELETE
"Resting losses" DELETE
Useful life means:

- *(1) DELETE*
- *(2) DELETE*
- *(3) For an Otto-cycle heavy-duty engine family:*
  - *(I) DELETE*
  - *(ii) For the oxides of nitrogen standard, a period of use of 10 years or 110,000 miles whichever first occurs.*
  - *(iii) DELETE*
- *(4) DELETE*

86.078-3 Abbreviations. January 21, 1980.
86.090-3 Abbreviations. April 11, 1989.
86.084-4 Section numbering; construction. September 25, 1980.
86.084-5 General Standards; increase in emissions; unsafe conditions. November 2, 1982.
86.090-5 General Standards; increase in emissions; unsafe conditions. April 11, 1989.
86.078-7 Maintenance of records; submittal of information; right of entry. November 2, 1982.
86.087-10 Emission standards for 1987 and later model year gasoline-fueled heavy-duty engines and vehicles. November 16, 1983.
86.088-10 Emission standards for 1988 and 1989 model year gasoline-fueled heavy-duty engines and vehicles. March 15, 1985.
86.090-10 Emission standards for 1990 and later model year Otto-cycle heavy-duty engines and vehicles. April 11, 1989.
86.091-10 Emission standards for 1991 and later model year Otto-cycle heavy-duty engines and vehicles. April 11, 1989.

* * * * *

(a)(2) Manufacturers may choose to certify incomplete medium-duty vehicles from 8501-14,000 pounds, gross vehicle weight to the emission standards and test procedures specified below as an alternative to the primary standards and test procedures specified in Section 1960.1, Title 13, California Code of Regulations. Manufacturers certifying medium-duty vehicles to these optional heavy-duty standards and test procedures shall specify, in the application for certification, an in-use compliance test procedure, as provided in Section 2139(c), Title 13, California Code of Regulations. Exhaust emissions from new 1995 and later model year incomplete medium-duty vehicles certifying to the optional heavy-duty engine test procedures shall not exceed the following:

(I) Carbon Monoxide. 14.4 grams per brake horsepower-hour, as measured under transient operating conditions.

(ii) Non-methane Hydrocarbon and Oxides of Nitrogen. 3.9 grams per brake horsepower-hour total, as measured under transient operating conditions.

(a)(3) Manufacturers may choose to certify incomplete medium-duty low-emission and ultra-low-emission vehicles from 8501-14,000 pounds, gross vehicle weight to the emission standards and test procedures specified below as an alternative to the primary standards and test procedures specified in Section 1960.1, Title 13, California Code of Regulations. Manufacturers certifying medium-duty low-emission and ultra-low-emission vehicles to these optional heavy-duty standards and test procedures shall specify, in the application for certification, an in-use compliance test procedure, as provided in Section 2139(c), Title 13, California Code of Regulations. Exhaust emissions from new 1992 and later model year incomplete medium-duty low-emission (LEV)and ultra-low-emission (ULEV) vehicles certifying to the optional heavy-duty engine test procedures shall not exceed the following:

(I) Carbon Monoxide. 14.4 grams per brake horsepower-hour for LEVs and ~~7.2 grams per brake horsepower-hour for~~ ULEVs, as measured under transient operating conditions.

(ii) Non-methane Hydrocarbon and Oxides of Nitrogen. 3.5 grams per brake horsepower-hour total for LEVs <u>through the 2001 model year; 3.0 grams per brake horsepower-hour for LEVs through the 2003 model year;</u> and 2.5 grams per brake horsepower-hour total for ULEVs <u>through the 2003 model year</u>, as measured under transient operating conditions.

(iii) Formaldehyde Emissions. 0.050 grams per brake horsepower-hour for LEVs and ~~0.025 grams per brake horsepower-hour for~~ ULEVs, as measured under transient operating conditions.

~~*(a)(4) Manufacturers may choose to certify incomplete medium-duty ULEVs from 8501-14,000 pounds, gross vehicle weight to the emission standards and test procedures specified below as an alternative to the primary standards and test procedures specified in Section 1960.1, Title 13, California Code of Regulations. Manufacturers certifying medium-duty ultra-low-emission vehicles to these optional*~~

~~*heavy-duty standards and test procedures shall specify, in the application for certification, an in-use compliance test procedure, as provided in Section 2139(c), Title 13, California Code of Regulations. Exhaust emissions from new 2004 and later model year incomplete medium-duty ULEVs certifying to the optional heavy-duty engine test procedures shall not exceed the following:*~~

~~*(I) Carbon Monoxide. 14.4 grams per brake horsepower-hour for ULEVs, as measured under transient operating conditions.*~~

~~*(ii) Oxides of Nitrogen. 2.0 grams per brake horsepower-hour total for ULEVs, as measured under transient operating conditions.*~~

~~*(iii) Non-Methane Organic Gases. 0.5 grams per brake horsepower-hour for ULEVs, as measured under transient operating conditions.*~~

~~*(iv) Formaldehyde Emissions. 0.050 grams per brake horsepower-hour for ULEVs, as measured under transient operating conditions.*~~

(4) The standards set forth in paragraphs (a)(1), (a)(2), and (a)(3)...

(5) A manufacturer...

* * * * *

86.098-10 Emission Standards for 1998 and Later Model Year Otto-Cycle Heavy-Duty Engines and Vehicles and Optional Standards for 1995 Through 1997 Model Year Otto-Cycle Heavy-Duty Engines. September 21, 1994.

~~*Section 86.098 10 includes text that specifies requirements that differ from §86.096 10. Where a paragraph in §86.096 10 is identical and applicable to §86.096 10, this may be indicated by specifying the corresponding paragraph and the statement "[Reserved]. For guidance see §86.096 10."*~~

(a)(1) Exhaust emissions from new 1998 and later model year Otto-cycle heavy-duty engines shall not exceed.

- *(I) DELETE*
- *(ii) For Otto-cycle heavy-duty engines fueled with either gasoline or liquefied petroleum gas and intended for use only in vehicles with a Gross Vehicle Weight Rating of greater than 14,000 pounds.*
  - *(A) DELETE*
  - *(B) DELETE*

(C) *Oxides of nitrogen (1) (4.0) grams per brake horsepower-hour (1.49 grams per megajoule), as measured under transient operating conditions.*

(2) *DELETE*
(3) *DELETE*
(4) *A manufacturer may elect to certify to an optional oxides of nitrogen standard between 0.5 grams per brake horsepower-hour and 1.5 grams per brake horsepower-hour, inclusive, at 0.5 grams per brake horsepower-hour increments, as measured under transient operating conditions.*

(iii) *DELETE*
(iv) *For methanol-fueled Otto-cycle heavy-duty engines intended for use only in vehicles with a Gross Vehicle Weight Rating of greater than 14,000 lbs.*

(A) *DELETE*
(B) *DELETE*
(C) *Oxides of nitrogen. (1) 4.0 grams per brake horsepower-hour (1.49 grams per megajoule), as measured under transient operating conditions.*

(2) DELETE; REPLACE WITH:
(2) *A manufacturer may elect to certify to an optional oxides of nitrogen standard between 0.5 grams per brake horsepower-hour and 1.5 grams per brake horsepower-hour, inclusive, at 0.5 grams per brake horsepower-hour increments, as measured under transient operating conditions.*

(v) *DELETE*
(vi) *For natural gas-fueled Otto-cycle engines intended for use only in vehicles with a Gross Vehicle Weight Rating of greater than 14,000 pounds.*

(A) *DELETE*
(B) *DELETE*
(C) *Oxides of nitrogen. (1) ~~5.0~~ 4.0 grams per brake horsepower-hour (~~1.9~~) 1.49 grams per megajoule, as measured under transient operating conditions.*

(2) *DELETE*
(3) *A manufacturer may elect to certify to an optional oxides of nitrogen standard between 0.5 grams per brake horsepower-hour and 1.5 grams per brake horsepower-hour, inclusive, at 0.5 grams per brake horsepower-hour increments, as measured under transient operating conditions.*

(2) *The standards set forth in paragraph (a)(1) of this section refer to the exhaust emitted over the operating schedule set forth in paragraph (f)(1) of Appendix I to this part, and measured and calculated in accordance with the procedures set forth in subpart N or P of this part.*

(3) *DELETE*

* * * * * *

(c) *DELETE*
(d) *DELETE*
(e) *A manufacturer may elect to certify 1995 through 1997 model year Otto-cycle engines for use in vehicles with a Gross Vehicle Weight Rating of greater than 14,000 pounds, to an optional oxides of nitrogen standard between 0.5 grams per brake horsepower-hour and 2.5 grams per brake horsepower-hour, inclusive, at 0.5 grams per brake horsepower-hour increments, as measured under transient operating conditions.*

ADD SUBPARAGRAPH (f) WHICH READS:

(f)(1) Exhaust emissions from new 2004 and later model year Otto-cycle heavy-duty engines shall not exceed:

(I) For Otto-cycle heavy-duty engines fueled with either gasoline or liquefied petroleum gas and intended for use only in vehicles with a Gross Vehicle Weight Rating ~~*between 8,500 and*~~ ***greater than*** 14,000 pounds.

~~*(A) Total Hydrocarbons or OMHCE[1]. 0.7 grams per brake horsepower-hour, as measured under transient operating conditions.*~~

~~*(B) Optional Non-Methane Hydrocarbons[1]. 0.4 grams per brake horsepower-hour, as measured under transient operating conditions.*~~

— ~~*The total or optional non-methane hydrocarbon standards apply to petroleum-fueled, natural gas-fueled and liquefied petroleum gas-fueled engines. The Organic Material Hydrocarbon Equivalent, or OMHCE, standards apply to methanol fueled engines.*~~ —

~~(C)~~ *(A)* Carbon Monoxide. ~~14.4~~ *37.1* grams per brake horsepower-hour, as measured under transient operating conditions.

~~*(D) Oxides of Nitrogen. 2.0 grams per brake horsepower-hour, as measured under transient operating conditions.*~~

(B) Non-Methane Hydrocarbons + Oxides of Nitrogen.

(a) 2.5 grams per brake horsepower-hour total for ULEVs, as measured under transient operating conditions, including a cap of 0.5 grams per brake horsepower-hour for Non-Methane Hydrocarbons; or

(b) 2.4 grams per brake horsepower-hour total for ULEVs as measured under transient operating conditions.

(f)(2) Manufacturers may choose to certify incomplete medium-duty vehicles from 8501-14,000 pounds, gross vehicle weight, to the emission standards and test procedures specified above in section (f)(1) as an alternative to the primary standards and test procedures specified in Section 1960.1, Title 13, California Code of Regulations. Manufacturers certifying medium-duty vehicles to these optional heavy-duty standards and test procedures shall specify, in the application for certification, an in-use compliance test procedure, as provided in Section 2139(c), Title 13, California Code of Regulations. Exhaust emission from new 2004 and later model year incomplete medium-duty vehicles certifying to the optional heavy-duty engine test procedures shall not exceed the standards set forth in 86.098-10 subparagraph (f)(1).

# # # # #

86.080-12 Alternative certification procedures. April 17, 1980.
86.084-14 Small-volume manufacturers certification procedures. January 31, 1985.

* * * * *

(b)(1) ... produced by manufacturers with California sales (for the model year in which certification is sought) of fewer than 3,000 units (PC, LDT, MDV, and HDE combined).

* * * * *

(c)(4) DELETE
REPLACE WITH:
(c)(4) The manufacturer shall include in its records all of the information that EPA requires in 86.084-21 of this subpart. This information will be considered part of the manufacturer's application for certification.

* * * * *

(c)(7)(I)(C) ... determines and prescribes based on design specifications or sufficient control over design specifications, development data, in-house testing procedures, and in-use experience. However, ...

* * * * *

(c)(11)(ii)(D)(1)...We project the total California sales of vehicles (engines) subject to this subpart to be fewer than 3,000 units.

* * * * *

(c)(13)(ii)...affect vehicle emissions. All running changes which do not adversely affect emissions or the emissions control system durability are deemed approved unless disapproved by the Executive Officer within 30 days of the implementation of the running change. This ...

* * * * *

86.090-14 Small-volume manufacturers certification procedures. April 11, 1989.

* * * * *

(b)(1)...produced by manufacturers with California sales (for the model year in which certification is sought) of fewer than 3,000 units (PC, LDT, MDV, and HDE combined).

* * * * *

(c)(4) DELETE
REPLACE WITH:
(c)(4) The manufacturer shall include in its records all of the information that EPA requires in 86.088-21 of this subpart. This information will be considered part of the manufacturer's application for certification.

* * * * *

(c)(7)(I)(C)...determines and prescribes based on design specifications or sufficient control over design specifications, development data, in-house testing procedures, and in-use experience. However,...

* * * * *

(c)(11)(ii)(D)(1)...We project the total California sales of vehicles (engines) subject to this subpart to be fewer than 3,000 units.

* * * * *

(c)(13)(ii)...affect vehicle emissions. All running changes which do not adversely affect emissions or the emissions control system durability are deemed approved unless disapproved by the Executive Officer within 30 days of the implementation of the running change. This...

86.085-20 Incomplete vehicles, classification. January 12, 1983.
86.087-21 Application for certification. November 16, 1983.
86.088-21 Application for certification. March 15, 1985.
86.090-21 Application for certification. April 11, 1989.
86.091-21 Application for certification. April 11, 1989.

* * * * *

(b)(2) For 1992 and subsequent model-year low-emission and ultra-low-emission vehicles and engines not powered exclusively by gasoline, projected California sales data and fuel economy estimates two years prior to certification, and projected California sales data for all vehicles and engines, regardless of operating fuel or vehicle emission category, sufficient to enable the Executive Officer to select a test fleet representative of the vehicles (or engines) for which certification is requested at the time of certification.

* * * * *

86.085-22 Approval of application for certification; test fleet selections; determinations of parameters subject to adjustment for certification and Selective Enforcement Audit, adequacy of limits, and physically adjustable ranges. August 30, 1985.

DELETE any reference to Selective Enforcement Audit.

86.090-22 Approval of application for certification; test fleet selections; determinations of parameters subject to adjustment for certification and Selective Enforcement Audit, adequacy of limits, and physically adjustable ranges. April 11, 1989.

DELETE any references to Selective Enforcement Audit.

86.087-23 Required data. March 15, 1985.

* * * * *

(b)(1)(ii) ... useful life of the engine. Such data shall be submitted to the Executive Officer for review. If the durability test method is accepted by EPA, it shall also be accepted by ARB, subject to the following condition. If, after certification for the first model year in which the method is used, the Executive Officer determines that a manufacturer's durability test procedures do not conform with good engineering practices, the Executive Officer may require changes to that manufacturer's durability test procedures for subsequent model years. The manufacturer's revised durability test procedures shall be submitted to the Executive Officer for review and approval.

* * * * *

86.088-23 Required data. July 19, 1985.

* * * * *

(b)(1)(ii) ... useful life of the engine. Such data shall be submitted to the Executive Officer for review. If the durability test method is accepted by EPA, it shall also be accepted by ARB; subject to the following condition. If, after certification for the first model year in which the method is used, the Executive Officer determines that a manufacturer's durability test procedures do not conform with good engineering practices, the Executive Officer may require changes to that manufacturer's durability test procedures for subsequent model years. The manufacturer's revised durability test procedures shall be submitted to the Executive Officer for review and approval.

* * * * *

86.090-23 Required data. April 11, 1989.

* * * * *

(b)(1)(ii) ... useful life of the engine. Such data shall be submitted to the Executive Officer for review. If the durability test method is accepted by EPA, it shall also be accepted by ARB, subject to the following condition. If, after certification for the first model year in which the method is used, the Executive Officer determines that a manufacturer's durability test procedures do not conform with good engineering practices, the Executive Officer may require changes to that manufacturer's durability test procedures for subsequent model years. The manufacturer's revised durability test procedures shall be submitted to the Executive Officer for review and approval.

* * * * *

86.091-23 Required data. April 11, 1989.

* * * * *

(b)(1)(ii) ... useful life of the engine. Such data shall be submitted to the Executive Officer for review. If the durability test method is accepted by EPA, it shall also be accepted by ARB, subject to the following condition. If, after certification for the first model year in which the method is used, the Executive Officer determines that a manufacturer's durability test procedures do not conform with good engineering practices, the Executive Officer may require changes to that manufacturer's durability test procedures for subsequent model years. The manufacturer's revised durability test procedures shall be submitted to the Executive Officer for review and approval.

* * * * *

86.085-24 Test vehicles and engines. December 10, 1984.

* * * * *

(e)(1)(I) DELETE
REPLACE WITH:
(e)(1)(I) a combined total of 3000 California passenger cars, light-duty trucks, medium-duty vehicles, and heavy-duty engines,

(e)(1)(ii) DELETE
(e)(1)(iii) DELETE
(e)(1)(iv) DELETE
(e)(1)(v) DELETE
(e)(1)(vi) may request a reduction in the number of test vehicles (or engines) . . .

(e)(2)...total sales of fewer than 3,000...

* * * * *

(f) ...submitted. Durability data submitted may be from engines previously certified by the EPA or the Air Resources Board.

* * * * *

86.090-24 Test vehicles and engines. April 11, 1989.

* * * * *

(e)(1)(I) DELETE
REPLACE WITH:
(e)(1)(I) A combined total of 3,000 California passenger cars, light-duty trucks, medium-duty vehicles, and heavy-duty engines,

(e)(1)(ii); (e)(1)(iii); (e)(1)(iv); (e)(1)(v); DELETE

(e)(1)(vi) may request a reduction in the number of test vehicles (or engines)...

(e)(2)...total sales of fewer than 3,000...

* * * * *

(f)...submitted. Durability data submitted may be from engines previously certified by the EPA or the Air Resources Board.

* * * * *

86.087-25	Maintenance. March 15, 1985.
86.088-25	Maintenance. March 15, 1985.
86.090-25	Maintenance. April 11, 1989.
86.084-26	Mileage and service accumulation; emission measurements. October 19, 1983.
86.090-26	Mileage and service accumulation; emission measurements. April 11, 1989.
86.085-27	Special test procedures. January 12, 1983.
86.090-27	Special test procedures. April 11, 1989.
86.087-28	Compliance with emission standards. March 15, 1985.
86.088-28	Compliance with emission standards. March 15, 1985.
86.090-28	Compliance with emission standards. April 11, 1989.

* * * * *

(c)(4)(iii)(A)(1) . . . For transient HC (OMHCE), formaldehyde (methanol-fueled engines and vehicles, low-emission vehicles and engines, and ultra-low-emission vehicles and engines), CO, and NOx, the official exhaust emission . . .

(c)(4)(iii)(A)(2) . . . For transient HC (OMHCE), formaldehyde (methanol-fueled engines and vehicles, low-emission vehicles and engines, and ultra-low-emission vehicles and engines), CO, and NOx, the official exhaust emission . . .

* * * * *

86.091-28 Compliance with emission standards. April 11, 1989.

* * * * *

(c)(4)(iii)(A)(1) . . . For transient HC (OMHCE), formaldehyde (methanol-fueled engines and vehicles, low-emission vehicles and engines, and ultra-low-emission vehicles and engines), CO, and NOx, the official exhaust emission . . .

(c)(4)(iii)(A)(2) . . . For transient HC (OMHCE), formaldehyde (methanol-fueled engines and vehicles, low-emission vehicles and engines, and ultra-low-emission vehicles and engines), CO, and NOx, the official exhaust emission . . .

* * * * *

86.087-29 Testing by the Administrator. January 24, 1984.
86.088-29 Testing by the Administrator. March 15, 1985.
86.090-29 Testing by the Administrator. April 11, 1989.
86.091-29 Testing by the Administrator. April 11, 1989.
86.087-30 Certification. August 30, 1985.
86.088-30 Certification. March 15, 1985.
86.090-30 Certification. April 11, 1989.
86.091-30 Certification. April 11, 1989.
86.079-31 Separate certification. September 8, 1977.
86.079-32 Addition of a vehicle or engine after certification. September 8, 1977.
86.079-33 Changes to a vehicle or engine covered by certification. September 8, 1977.
86.082-34 Alternative procedure for notification of additions and changes. November 2, 1982.
86.087-35 Labeling. Labels shall comply with the requirements set forth in the "California Motor Vehicle Emission Control Label Specifications", as last amended ~~March 24, 1994~~ ______________.
86.085-37 Production vehicles and engines. January 12, 1983.
86.087-38 Maintenance instructions. March 15, 1985.
86.084-40 Automatic expiration of reporting and recordkeeping requirements. September 25, 1980.

Subpart L - Nonconformance Penalties for Gasoline-Fueled and Diesel Heavy-Duty Engines and Heavy-Duty Vehicles, Including Light-Duty Trucks

86.1101-87 Applicability. August 30, 1985.

* * * * *

...applicable for 1988 model...

* * * * *

86.1102-87 Definitions. August 30, 1985.
86.1103-87 Criteria for availability of nonconformance penalties. August 30, 1985.
86.1104-87 Determination of upper limits. August 30, 1985.
86.1105-87 Emission standards for which nonconformance penalties are available. December 31, 1985.
86.1106-87 Production compliance auditing. August 30, 1985.

* * * * *

(b) A 50-state engine or vehicle configuration with engines available for sale in California fails a Selective Enforcement...

* * * * *

(c) A 50-state engine or vehicle configuration with engines available for sale in California, for which an NCP has been previously...

* * * * *

86.1107-87 Testing by the Administrator. August 30, 1985.
86.1108-87 Maintenance of records. August 30, 1985.
86.1109-87 Entry and access. August 30, 1985.
86.1110-87 Sample selection. August 30, 1985.
86.1111-87 Test procedures for PCA testing. August 30, 1985.
86.1112-87 Determining the compliance level and reporting of test results. August 30, 1985.
86.1113-87 Calculation and payment of penalty. December 31, 1985.

* * * * *

(a)(3)(iv)...not affect the previous year's penalty. In calculating AAFi for the California heavy-duty engines, it shall be equal to the value of n as is used federally.

* * * * *

(g)(1)(ii)...payable to: Air Pollution Control Fund, c/o Executive Officer, Air Resources Board, P.O. Box 2815, Sacramento, CA 95812.

* * * * *

(g)(3)...date to: Chief, Mobile Source Division, Air Resources Board, 9528 Telstar Avenue, El Monte, CA 91731 and Director, Manufacturers Operations...

* * * * *

(h)...PCA take place. The refund to manufacturers shall be made from the Air Pollution Control Fund. The amount refunded will be as follows...

* * * * *

86.1114-87 Suspension and voiding of certificates of conformity. August 30, 1985.

Subpart N, Emission Regulations for New Otto-cycle and Diesel Heavy-Duty Engines; Gaseous and Particulate Exhaust Test Procedures

86.1301-84 Scope; applicability. November 16, 1983.
86.1301-88 Scope; applicability. March 15, 1985.
86.1301-90 Scope; applicability. April 11, 1989.
86.1302-84 Definitions. November 16, 1983.
86.1303-84 Abbreviations. November 16, 1983.
86.1304-84 Section numbering; construction. November 16, 1983.
86.1304-90 Section numbering; construction. April 11, 1989.
86.1305-84 Introduction; structure of subpart. November 16, 1983.
86.1305-90 Introduction; structure of subpart. April 11, 1989.
86.1306-84 Equipment required and specification; overview. November 16, 1983.
86.1306-88 Equipment required and specification; overview. March 15, 1985.
86.1306-90 Equipment required and specification; overview. April 11, 1989.
86.1308-84 Dynamometer and engine equipment specifications. December 10, 1984.
86.1309-84 Exhaust gas sampling system; gasoline-fueled engines. November 16, 1983.
86.1309-90 Exhaust gas sampling system; gasoline-fueled and methanol-fueled Otto-cycle engines. April 11, 1989.

* * * * *

(a)(3)...For methanol-fueled engines, the sample lines for the methanol and formaldehyde samples are heated to 235° ± 15° F (113° ± 8° C).

* * * * *

86.1311-84 Exhaust gas analytical system; CVS bag sample. November 16, 1983.
86.1311-88 Exhaust gas analytical system; CVS bag sample. August 29, 1986.
86.1313-84 Fuel specifications. December 10, 1984.

86.1313-90 Fuel specifications. April 11, 1989.

* * * * *

ADD SUBPARAGRAPH (A)(1) WHICH READS:

(a)(1)(I) For 1993-1994 model-year Otto-cycle LEVs and ULEVs, and for all 1995 and subsequent model-year heavy-duty and medium-duty Otto-cycle vehicles and engines, gasoline having the specifications listed below may be used in exhaust and evaporative emission testing as an option to the specifications referred to in paragraph (a).

Fuel Property a/	Limit	Test Method b/
Octane, (R+M)/2 (min)	91	D2699-88, D 2700-88
Sensitivity (min)	7.5	D 2699-88, D 2700-88
Lead, g/gal (max) (No lead added)	0-0.01	Title 13 CCR §2253.4(c)
Distillation Range, degrees F c/		Title 13 CCR §2263
10 pct. point,	130-150	
50 pct. point,	200-210 d/	
90 pct. point,	290-300 e/	
EP, maximum	390	
Residue, vol% (max)	2.0	
Sulfur, ppm by wt.	30-40	Title 13 CCR §2263
Phosphorous, g/gal (max)	0.005	Title 13 CCR §2253.4(c)
RVP, psi	6.7-7.0	Title 13 CCR §2263
Olefins, vol %	4.0-6.0	Title 13 CCR §2263
Total Aromatic Hydrocarbons (vol%)	22-25	Title 13 CCR §2263
Benzene, vol %	0.8-1.0 f/	Title 13 CCR §2263
Multi-Substituted Alkyl Aromatic Hydrocarbons, vol %	12-14	g/
MTBE, vol %	10.8-11.2	Title 13 CCR §2263
Additives :	Sufficient to meet requirements of Title 13, CCR §2257	
Copper Corrosion	No. 1	D 130-88
Gum, Washed, mg/100 ml (max)	3.0	D 381-86
Oxidation Stability, minutes (min)	1000	D 525-88
Specific Gravity	Report h/	
Heat of Combustion	Report h/	
Carbon, wt%	Report h/	
Hydrogen, wt%	Report h/	

a/ The gasoline must be blended from typical refinery feedstocks.

b/ ASTM specification unless otherwise noted. A test method other than that specified may be used following a determination by the Executive Officer that the other method produces results equivalent to the results with the specified method.

c/ Although Title 13 CCR § 2263 refers to the temperatures of the 50 and 90 percent points, this procedure can be extended to the 10 percent and end point temperatures, and to the determination of the residue content.

d/ The range for interlaboratory testing is 195-215° F.

e/ The range for interlaboratory testing is 285-305° F.

f/ The range for interlaboratory testing is 0.7-1.1 percent by volume.

g/ "Detailed Hydrocarbon Analysis of Petroleum Hydrocarbon Distillates, Reformates, and Gasoline by Single Column High Efficiency (Capillary) Column Gas Chromatography," by Neil Johansen, 1992, Boulder, CO.

h/ The fuel producer should report this fuel property to the fuel purchaser. Any generally accepted test method may be used and shall be identified in the report.

* * * * *

(a)(3)(I) Methanol-Gasoline Fuel Specifications for 1993 Model-Year Engines. Methanol fuel used in service accumulation of methanol-fueled Otto-cycle engines shall be representative of commercially available methanol fuel. Methanol used in fuel for exhaust emission testing shall be chemical grade methanol. For fuel-flexible vehicles and engines, the gasoline used for blending fuel for use in service accumulation shall be representative of commercial regular unleaded gasoline which will be generally available through retail outlets. Gasoline used for blending fuel for use in emission testing shall conform with the unleaded gasoline specification noted in paragraph (a) above. The requirements set forth in subparagraph (a)(3)(ii) may be used as an option for 1993 model-year vehicles.

(a)(3)(ii) Methanol-Gasoline Fuel Specifications for 1994 and Subsequent Model-Year Engines.

(a)(3)(ii)(A) Otto-cycle methanol-fuel vehicles

Mileage-accumulation fuel: For methanol-fueled Otto-cycle methanol engines, fuel which meets the specifications listed in Title 13, CCR, Section 2292.1 or 2292.2 as applicable.

Emission-testing fuel: For methanol-fueled Otto-cycle methanol engines, fuel which meets the specifications listed in Title 13, CCR, Section 2292.1 or 2292.2 as modified by the following:

The fuel specification for 2292.1 shall be modified to: a) require methanol content at 98.0 ± 0.5 volume percent; b) require ethanol content at 1.0 ± 0.1

volume percent; c) require certification gasoline as noted in paragraph 9(a) of the California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles, at 1.0 ± 0.1 volume percent.

The fuel specification for 2292.2 shall be modified to require certification gasoline as noted in paragraph 9(a) of the California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles, as the hydrocarbon fraction. The vapor pressure specification for the emission-testing fuel shall be adjusted to 8.0 - 8.5 psi, using common blending components from the gasoline stream.

(a)(3)(ii)(B) Fuel-flexible vehicles

Mileage-accumulation fuel: For both durability-data vehicles and emission-data vehicles, mileage accumulation shall be conducted with one fuel. For vehicles designed to operate on methanol, a fuel that meets the specifications listed in Title 13, CCR, Section 2292.2 shall be used.

Emission-test fuel: For emission testing, fuel that meets the specifications listed in Title 13, CCR, Section 2292.2 with the following exception. The fuel specification for 2292.2 shall be modified to require certification gasoline as noted in paragraph 9(a) of the California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles, as the hydrocarbon fraction. The vapor pressure specification for the emission-testing fuel shall be adjusted to 8.0 - 8.5 psi, using common blending components from the gasoline stream.

(a)(3)(iii) Fuel additives and ignition improvers intended for use in methanol test fuels shall be subject to the approval of the Executive Officer. In order for such approval to be granted, a manufacturer must demonstrate that emissions will not be adversely affected by the use of the fuel additive or ignition improver.

* * * * *

ADD SUBPARAGRAPH (e) TO READ:

(e) **Natural Gas and Liquefied Petroleum Gas Test Fuel.**

(e)(1)(I) **Natural Gas Test Fuel.** Natural gas used in service accumulation for 1990 through 1993 model-year engines shall be representative of commercial natural gas which is generally available. Natural gas meeting the specifications below, or substantially equivalent specifications approved by the Executive

Officer, shall be used in exhaust emission testing for 1990 through 1993 model-year engines. The specifications set forth in subparagraph (e)(1)(ii) may be used as an option for 1993 model-year vehicles..

Natural Gas Emission Test Fuel Specification

Specification	Value	Tolerance	Calculation Method
Wobbe Number	1350	± 0.5%	ASTM D 1945 Using AGA Bulletin No. 36
Hydrocarbons (expressed as percent of total organic carbon present)			
Methane	88%	± 0.5%	ASTM D 1945
Ethane	8%	± 0.3%	ASTM D 1945
C_3 and higher HC	4%	± 0.2%	ASTM D 1945
C_6 and higher HC	0.5%	maximum	ASTM D 1945
Total unsaturated HC	0.5%	maximum	ASTM D 2650
Other Species (expressed as mole percent)			
Hydrogen	0.1%	maximum	ASTM D 2650
Carbon Monoxide	0.1%	maximum	ASTM D 2650

Other Requirements:

1. Free from liquids over the entire range of temperatures and pressures encountered in the engine and fuel system.
2. Free from solid particulate matter.

(e)(1)(ii) Natural gas used in service accumulation and in exhaust emission testing for 1994 and subsequent model-year engines shall meet the specification as follows:

Mileage accumulation fuel: Natural gas meeting the specifications listed in Title 13, CCR, Section 2292.5 shall be used in service accumulation.

Emission-test fuel: Natural gas meeting the following specifications listed in Title 13, CCR, Section 2292.5 as modified by the following: a) methane content at 90.0 ± 1.0 mole percent; b) ethane content at 4.0 ± 0.5 mole percent; c) C_3 and higher hydrocarbon content at 2.0 ± 0.3 mole percent; d) oxygen content at 0.5 mole percent maximum; e) inert gas (sum of CO_2 and N_2) content at 3.5 ± 0.5 mole percent.

(e)(2)(I) **Liquefied Petroleum Gas Test Fuel.** Liquefied petroleum gas used in service accumulation for 1990 through 1993 model-year engines shall be representative of commercial liquefied petroleum gas which is generally available through retail outlets. Liquefied petroleum gas used in exhaust and evaporative emission testing for 1990 through 1993 model-year engines shall conform to NGPA HD-5 specification. The specifications set forth in subparagraph (e)(2)(ii) may be used as an option for 1993 model-year vehicles.

(e)(2)(ii) Liquefied petroleum gas fuel that will be used in service accumulation and in exhaust and evaporative emission testing for 1994 and subsequent model-year engines shall meet the specifications as follows.

Mileage accumulation fuel: Liquefied petroleum gas meeting the specifications listed in Title 13, CCR, Section 2292.6 shall be used in service accumulation.

Emission-test fuel: Liquefied petroleum gas meeting the specifications listed in Title 13, CCR, Section 2292.6 shall be used for exhaust and evaporative emission testing with the following exceptions: a) propane content limited to 93.5 ± 1.0 volume percent; b) propene content limited to 3.8 ± 0.5 volume percent; and c) butane and heavier components limited to 1.9 ± 0.3 volume percent.

(e)(3) The specification range of the fuels to be used under paragraphs (e)(1) and (e)(2) of this section shall be reported in accordance with 86.090-21(b)(3).

86.1314-84 Analytical gases. December 10, 1984.
86.1316-84 Calibration; frequency and overview. December 10, 1984.
86.1316-90 Calibration; frequency and overview. April 11, 1989.
86.1318-84 Engine dynamometer system calibrations. November 16, 1983.
86.1319-84 CVS calibration. December 10, 1984.
86.1319-90 CVS calibration. April 11, 1989.
86.1320-88 Gas meter or flow instrumentation calibration; particulate measurement. December 16, 1987.
86.1320-90 Gas meter or flow instrumentation calibration; particulate, methanol, and formaldehyde measurement. April 11, 1989.
86.1321-84 Hydrocarbon analyzer calibration. December 10, 1984.
86.1321-90 Hydrocarbon analyzer calibration. April 11, 1989.
86.1322-84 Carbon monoxide analyzer calibration. November 16, 1983.
86.1323-84 Oxides of nitrogen analyzer calibration. December 10, 1984.
86.1324-84 Carbon dioxide analyzer calibration. November 16, 1983.
86.1326-84 Calibration of other equipment. November 16, 1983.

86.1326-90 Calibration of other equipment. April 11, 1989.
86.1327-84 Engine dynamometer test procedures; overview. December 10, 1984.
86.1327-88 Engine dynamometer test procedures; overview. March 15, 1985.
86.1327-90 Engine dynamometer test procedure; overview. April 11, 1989.

* * * * *

(a)...sample collection impingers (or capsules) for formaldehyde (HCHO). A bag or continuous sample of the dilution air...

* * * * *

86.1330-84 Test sequence, general requirements. November 16, 1983.
86.1330-90 Test sequence, general requirements. April 11, 1989.
86.1332-84 Engine mapping procedures. December 10, 1984.
86.1332-90 Engine mapping procedures. April 11, 1989.
86.1333-84 Transient test cycle generation. November 16, 1983.
86.1333-90 Transient test cycle generation. April 11, 1989.
86.1334-84 Pre-test engine and dynamometer preparation. December 10, 1984.
86.1335-84 Optional forced cool-down procedure. December 10, 1984.
86.1335-90 Optional forced cool-down procedure. April 11, 1989.
86.1336-84 Engine starting and restarting. March 15, 1985.
86.1337-84 Engine dynamometer test run. November 16, 1983.
86.1337-88 Engine dynamometer test run. March 15, 1985.
86.1337-90 Engine dynamometer test run. April 11, 1989.
86.1338-84 Emission measurement accuracy. November 16, 1983.
86.1340-84 Exhaust sample analysis. December 10, 1984.
86.1340-90 Exhaust sample analysis. April 11, 1989.
86.1341-84 Test cycle validation criteria. March 15, 1985.
86.1341-90 Test cycle validation criteria. April 11, 1989.
86.1342-84 Calculations; exhaust emissions. March 15, 1985.
86.1342-90 Calculations; exhaust emissions. April 11, 1989.

* * * * *

(d) Meaning of symbols:

* * * * *

(1)(ii) . . . (101.3 kPa) pressure; or, if gaseous fuels are being used, 18.64 g/ft^3 for natural gas and 17.28 g/ft^3 for liquefied petroleum gas, assuming an average carbon to hydrogen ratio of 1:3.803 for natural gas and 1:2.656 for liquefied petroleum gas, at 68° F and 760 mm Hg pressure. The Executive Officer may approve other density values deemed appropriate by a manufacturer when gaseous fuels are being used.

* * * * *

(3)(v)(A) $CO_e = (1-0.01925CO_{2e} - 0.000323R)CO_{em}$ for gasoline and petroleum diesel fuel, with hydrogen to carbon ratio of 1.85:1.

(3)(v)(B) $CO_e = [1-(0.01 + 0.005HCR)CO_{2e} - 0.00323R]CO_{em}$ for methanol fuel, where HCR is hydrogen to carbon ratio as measured for the fuel used. For natural gas and liquefied petroleum gas, HCR is assumed to be 2.656 and 3.802 respectively.

* * * * *

(8)(I) K_H = Humidity correction factor.
(ii) For gasoline-fueled, gaseous-fuel, and methanol-fueled diesel engines: $K_H = 1/[1-0.0047(H-75)]$ (or for SI units, ...

* * * * *

<u>86.1342-94 Calculations; Exhaust Emissions. September 21, 1994.</u>
86.1344-84 Required information. December 10, 1984.
86.1344-88 Required information. March 15, 1985.
86.1344-90 Required information. April 11, 1989.

Subpart P - Emission Regulations for New Gasoline-Fueled and Methanol-Fueled Otto-Cycle Heavy-Duty Engines and New Gasoline-Fueled and Methanol-Fueled Otto-Cycle Light-Duty Trucks; Idle Test Procedures

86.1501-84 Scope, applicability. December 10, 1984.
86.1501-90 Scope, applicability. April 11, 1989.
86.1502-84 Definitions. November 16, 1983.
86.1503-84 Abbreviations. November 16, 1983.
86.1504-84 Section numbering; construction. November 16, 1983.
86.1504-90 Section numbering; construction. April 11, 1989.
86.1505-84 Introduction; structure of subpart. November 16, 1983.
86.1505-90 Introduction; structure of subpart. April 11, 1989.
86.1506-84 Equipment required and specifications; overview. November 16, 1983.
86.1506-90 Equipment required and specifications; overview. April 11, 1989.
86.1509-84 Exhaust gas sampling system. November 16, 1983.
86.1511-84 Exhaust gas analysis system. November 16, 1983.
86.1513-84 Fuel specifications. November 16, 1983.
86.1513-87 Fuel specifications. July 7, 1986.
86.1513-90 Fuel specifications. January 8, 1988.
86.1514-84 Analytical gases. November 16, 1983.

86.1516-84 Calibration; frequency and overview. November 16, 1983.
86.1519-84 CVS calibration. November 16, 1983.
86.1522-84 Carbon monoxide analyzer calibration. November 16, 1983.
86.1524-84 Carbon dioxide analyzer calibration. November 16, 1983.
86.1526-84 Calibration of other equipment. November 16, 1983.
86.1527-84 Idle test procedure; overview. November 16, 1983.
86.1530-84 Test sequence; general requirements. November 16, 1983.
86.1537-84 Idle test run. November 16, 1983.
86.1540-84 Idle exhaust sample analysis. November 16, 1983.
86.1542-84 Information required. December 10, 1984.
86.1544-84 Calculation; idle exhaust emissions. March 15, 1985.

Appendix I- Urban Dynamometer Schedules.

(f)(1) EPA Engine Dynamometer Schedule for Heavy-Duty Gasoline-Fueled Engines. December 10, 1984.

Appendix XII - Tables for Production Compliance Auditing of Heavy-Duty Engines and Heavy-Duty Vehicles.

Additional Requirements

1. Any reference to vehicle or engine sales throughout the United States shall mean vehicle or engine sales in California.

2. Regulations concerning EPA hearings, EPA inspections, and specific language on the Certificate of Conformity, shall not be applicable to these procedures.

3. Any reference made to Selective Enforcement Auditing (SEA) shall not be applicable to these procedures except as explicitly stated in regards to nonconformance penalties.

4. In addition to the standards and provisions specified in CFR Section 86.091-10 (emission standards for 1991 and later model year Otto-cycle heavy-duty engines and vehicles), the following formaldehyde emission levels as measured under transient operating conditions shall not be exceeded for dedicated methanol and fuel-flexible vehicles and engines:

	(g/bhp-hr)
1993-1995	0.10
1996 and Subsequent	0.05

The following formaldehyde emission levels as measured under transient operating conditions shall not be exceeded for 1992 and subsequent low-emission vehicles and ultra-low-emission vehicles operating on any fuel.

	(g/bhp-hr)
1992 and Subsequent Low-Emission Vehicles	0.050
1992 and Subsequent Ultra-Low-Emission Vehicles	0.025

5. All dedicated methanol-fueled and fuel-flexible vehicles and engines shall comply with the requirements which are applicable to heavy-duty gasoline-fueled Otto-cycle vehicles and engines, except where otherwise noted. In particular, for fuel-flexible vehicles and engines, a manufacturer's proposed

durability demonstration program, as required in sections 86.091-21(b)(4)(iii)(A) and 86.091-23(b)(1)(ii), shall provide for the assessment of the durability of the engine in operation with methanol and gasoline, as well as intermediate mixtures of both fuels. A manufacturer's proposed mileage and service accumulation, as required in section 86.090-24(c), shall be conducted on methanol.

The provisions of section 86.091-28(c), "Compliance with emissions standards," shall be used to determine the compliance requirements with the emission standards. For fuel-flexible vehicles and engines, the noted deterioration factors shall be determined from testing conducted with gasoline fuel. However, as an assurance that fuel-flexible vehicles and engines will comply with applicable exhaust emission standards throughout their useful lives when operated on methanol fuel, the manufacturer shall demonstrate that exhaust emissions tests conducted with methanol fuel at the beginning, middle, and end of the durability service accumulation schedule do not exceed the applicable exhaust emission standards. For certification to be granted, the vehicle or engine may not exceed applicable certification exhaust emission standards.

6. All dedicated gaseous-fuel, dual-fuel, and multi-fuel Otto-cycle engines (and vehicles), except engines derived from existing Diesel engines, shall comply with the requirements which are applicable to heavy-duty Otto-cycle engines, except where otherwise noted.

7. Non-methane hydrocarbon emissions shall be measured in accordance with the "California Non-methane Hydrocarbon Test Procedures" as last amended July 12, 1991, which is incorporated herein by reference.

8. For dual-fuel or multi-fuel gaseous engines and vehicles, the noted deterioration factors shall be determined separately for operation on each type of fuel or combination of fuels that the engine is designed to use. For certification to be granted, the provisions of 86.091-28(c) must be met separately for emissions using each type and combination of fuels.

California Environmental Protection Agency
AIR RESOURCES BOARD

PROPOSED

CALIFORNIA NON-METHANE ORGANIC GAS TEST PROCEDURES

Adopted: July 12, 1991
Amended: September 22, 1993
Amended: ______________

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.

The regulatory amendments proposed in this rulemaking are shown in underline to indicate additions and ~~strikeout~~ to indicate deletions from the version of the test procedures adopted on September 22, 1993. Modifications to the originally noticed text are designated by ***bold italics*** and ***~~bold strikeout~~*** to represent additions and deletions, respectively. Modifications to the modified text are designated by ***underlined bold italics*** and ***underlined bold strikeout*** to represent additions and deletions, respectively.

Date of Release: 2/13/96; second 15-day changes
Board Hearing: 9/28/95

TABLE OF CONTENTS

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), and ultra low-emission vehicles (ULEV) 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

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

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

~~where "LPG" means "liquified petroleum gas", "CNG" means "compressed natural gas", "NMHC" means "non-methane hydrocarbon", "FID" means "flame ionization detector", and "GC" means "gas chromatograph."~~ 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 which 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 which 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 "California Exhaust Emission Standards and Test Procedures for 1988 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 ~~non-methane hydrocarbon (~~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 ~~flame ionization detector (~~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~~,~~ ~~"Optimization of Flame Ionization Detector for Determination of Hydrocarbons in Diluted Automobile Exhaust;" author, Glenn D. Reschke~~[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 ~~gas chromatograph (~~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 ~~National~~

~~Institute of Standards and Technology (~~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:

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

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:
$CO_e = (1 - 0.01970 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

~~b~~c) For LPG, $CH_{\cancel{2.66}\ 2.64}$, where HCR = ~~2.66~~ 2.64:
$CO_e = (1 - \cancel{0.02330}\ 0.02320 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

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 =

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

(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, $CH_{\cancel{2.66}\ 2.64}$, where x = 1, y = ~~2.66~~ 2.64, and z = 0:
DF = ~~11.64~~ 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 $NMHC_e = \text{FID } THC_e - (r_{CH_4} * CH_{4e}) - (r_{CH_3OH} * CH_3OH_e)$
NOTE: If $NMHC_e$ is calculated to be less than zero, then $NMHC_e = 0$.

5.3.2 $NMHC_d = \text{FID } THC_d - (r_{CH_4} * CH_{4d}) - (r_{CH_3OH} * CH_3OH_d)$
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 =

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

(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

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

(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 $$NMHC_{wm} = 0.43 * \frac{NMHC_{mass\,1} + NMHC_{mass\,2}}{D_{phase\,1} + D_{phase\,2}} + 0.57 * \frac{NMHC_{mass\,3} + NMHC_{mass\,2}}{D_{phase\,3} + D_{phase\,2}}$$

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.

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

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

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

$$= 11.15$$

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

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

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

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

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

Therefore,

$$NMHC_{wm} = 0.43 * \frac{NMHC_{mass\ 1} + NMHC_{mass\ 2}}{D_{phase\ 1} + D_{phase\ 2}} + 0.57 * \frac{NMHC_{mass\ 3} + NMHC_{mass\ 2}}{D_{phase\ 3} + D_{phase\ 2}}$$

$$= 0.43 * \frac{1.45 \text{ g} + 0.33 \text{ g}}{3.583 \text{ mile} + 3.848 \text{ mile}} + 0.57 * \frac{0.27 \text{ g} + 0.33 \text{ g}}{3.586 \text{ mile} + 3.848 \text{ mile}}$$

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

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:

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

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

$= 2.57 \text{ ppmC}$

$CO_e = (1 - 0.02705 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

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.

$= (1 - 0.02705 * 1.28\% - 0.000323 * 32\%) * 303.2 \text{ ppm}$

$= 289.6 \text{ ppm}$

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

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

$= 9.10$

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

$= 21.92 \text{ ppmC} - 2.57 \text{ ppmC} * [1 - (1 / 9.10)]$

$= 19.63 \text{ ppmC}$

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

$NMHC_{mass\ 1} = 0.91 \text{ g}$

Similarly, Phase 2: $NMHC_{mass\ 2} = 0.0 \text{ g}$

and for Phase 3: $NMHC_{mass\ 3} = 0.10 \text{ g}$

Therefore,

$$NMHC_{wm} = 0.43 * \frac{NMHC_{mass\ 1} + NMHC_{mass\ 2}}{D_{phase\ 1} + D_{phase\ 2}} + 0.57 * \frac{NMHC_{mass\ 3} + NMHC_{mass\ 2}}{D_{phase\ 3} + D_{phase\ 2}}$$

$$= 0.43 * \frac{0.91 \text{ g} + 0.00 \text{ g}}{3.570 \text{ mile} + 3.850 \text{ mile}} + 0.57 * \frac{0.10 \text{ g} + 0.0 \text{ g}}{3.586 \text{ mile} + 3.850 \text{ mile}}$$

$NMHC_{wm} = 0.06 \text{ g/mile}$

~~8. DEFINITIONS~~

~~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.~~

~~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, %.~~

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

~~DF =~~ ~~dilution factor.~~

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

~~$HCHO_e$ =~~ ~~the 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.~~

~~$NMHC_{conc}$ =~~ ~~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° K and 760 mm Hg assuming a C:H ratio of 1:1.85 and 17.28 g/ft^3 for LPG at 293.16° K and 760 mm Hg), g/ft^3.~~

~~$NMHC_e$ =~~ ~~the 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.~~

~~R_a =~~ ~~the relative humidity of the ambient air, percent.~~

~~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 section 4).~~

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

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

~~9. 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 Hydrocarbon 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)~~

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 8 to 1200 ~~micrograms~~ µg per 15 ~~milliliters (~~mL~~)~~ of solution. The "target" alcohols which shall be analyzed and reported by this method are methanol and ethanol. These alcohols, when present 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 ~~9.1~~ 6] which involves flowing diluted engine exhaust through deionized or purified water contained in glass impingers and analyzing this solution by gas chromatography ~~(GC)~~.

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 ~~constituents~~ is performed by ~~using~~ a temperature-programmed capillary column ~~operated with a temperature gradient~~. A ~~flame ionization detector (~~FID~~)~~ is used for alcohol detection and quantification.

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

3. INTERFERENCES AND LIMITATIONS

3.1 An ~~interference~~ interferent is any component present in the sample with a retention time similar to that of any ~~the~~ target alcohols described in this method. To reduce interference error, proof of chemical identity may require ~~performance of~~ periodic confirmations using an alternate method and/or instrumentation, e.g., ~~gas chromatograph/mass spectrometer (~~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 ~~meter (~~m~~)~~, 0.53 ~~millimeter (~~mm~~)~~ ID, 1.0 ~~micron (~~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 ~~quantitation~~ quantifying ~~of~~ 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 ~~American Standards for Testing Materials~~ ASTM Type I purified or Type II deionized water shall be used.

5.4 A stock solution is prepared gravimetrically ***or volumetrically*** by diluting methanol and ethanol with deionized or purified water, e.g., for this method the stock solution contains ~~is~~ approximately ~~*1 µg/mL*~~ *10 mg/mL* ~~percent by volume~~ of each target alcohol.

5.4.1 A **calibration standard** within ~~at~~ the expected concentration range of the samples is prepared by successive dilutions of the stock solution with deionized or purified water, e.g., 50 ~~parts per million (ppm)~~ µg/mL ~~volume to volume (v/v)~~ is typical.

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 ~~update control charts for~~ each target alcohol.

5.4.3 All standards should be refrigerated at ~~less than~~ a temperature below 40° F during storage.

5.5 Gas requirements.

- 5.5.1 Air shall be "Zero" grade. "Ultra-zero" grade may be required to achieve the LOD required by Section 8.8.
- 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 ~~fritted~~ 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 impingers are allowed to warm to room temperature and~~ the solution contained in each impinger is transferred to a vial and sealed.

- 6.3.1 Samples ~~should~~ shall be refrigerated ~~(~~at a temperature below 40° F ~~or lower)~~ 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:, ~~configured as follows:~~

Column:	DB-~~w~~Wax, 30 m, 0.53 mm ID, 1.0μ film thickness
Carrier gas flow:	Helium at 5 ~~milliliters per minute (~~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 t~~T~~emperature:	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

- 6.4.1 One calibration standard, one control standard, and one deionized or purified water blank are analyzed daily at the beginning of each set of samples.
- 6.4.2 A replicate analysis is performed at least once per 24 hour period.
- 6.4.3 The control standard is analyzed ~~performed~~ at least once per 24 hour period.
- 6.4.4 ~~For~~ Samples containing compounds having concentrations above the documented range of instrument linearity~~, the sample~~ must be diluted and reanalyzed.
- 6.4.5 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.
- 6.4.6 The peak identifications provided by the computer are checked and corrected if necessary.
- 6.4.7 The target alcohol peaks at or above the ~~maximum allowable limit of detection~~ ~~(~~LOD~~)~~ are reported (Section 8.8). ~~At the laboratory's discretion, peaks at or~~

~~above the LOD calculated in section 8.8 may be reported. The calculated LOD must be lower than the maximum allowable LOD~~.

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:

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

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 Calibration and control standards are prepared at least every six months and analyzed daily.

8.2 Blank Run. A deionized or purified water blank run is performed before running the calibration standard. All target alcohol concentrations from the blank analysis must be below the LOD before the analysis may proceed.

8.3 Calibration Run. One run of the calibration standard is performed daily to generate the response ~~calibration~~ factor needed for ~~quantitating~~ quantifying sample analyses.

8.4 Control Standard Run. One run of the quality control standard is performed after the calibration run. Measurements of all target alcohols in the control standard must fall within the control limits before sample analysis may proceed. To meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.

8.5 Control Charts. A qQuality control chart~~(s)~~ is ~~are~~ maintained for each analyte in ~~of~~ the control standard ~~sample~~. The control charts, used on a daily basis, establishes that the method is "in ~~"statistical~~ control". The following describes how to construct a typical control chart:

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

~~The control sample must be "in-control" for~~ 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. A control standard ~~sample~~ measurement is considered to be "out-of-control" when the analyzed value exceeds the 3s limit, or two successive control standard ~~sample~~ measurements of the same analyte exceed the 2s limit.

8.6 Duplicates. A duplicate analysis of one sample is performed at least once a 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, 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 must be reanalyzed. If the criteria are still not met, all sample results for the day from this instrument must be deleted and the samples reanalyzed.

8.7 Linearity. A multipoint calibration to confirm ~~check for~~ instrument linearity is performed for all target alcohols for new instruments, after making instrument modifications which can affect linearity, and at least once every year ~~six months~~. The multipoint calibration consists of at least five concentration or mass loading levels, each above the LOD, ~~evenly~~ distributed over the range of expected sample concentration ~~linearity of the instrument~~. 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.

8.8 Limit of Detection. The LOD ~~limit of detection~~ for the target alcohols must be determined for new instruments, after making instrument modifications which can affect the LOD and at least once every year. ~~every six months.~~ 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. A linear regression is performed on the data. The LOD must be calculated using the following equation [Ref. 7] ~~(Ref 9.2)~~:

$$\text{LOD} = \frac{|b| + (t \times s)}{m}$$

~~LOD = |A| + 3.3(S)~~

where ~~each term in the equation is expressed in concentration units, and |A| is the absolute value of the least-squares X intercept calculated from the multipoint data. S~~ |b| is the absolute value of the y-intercept, m is the slope of the linear regression, s is the standard deviation 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

~~At least three replicates are required.~~ The lowest standard must be of a concentration of ~~at~~ one to five times the estimated LOD ~~detection limit.~~ ~~If data is not available in the concentration range near the detection limit, S may be estimated by:~~

~~S = RSD x |A|~~

~~RSD is the relative standard deviation of the lowest standard analyzed.~~

~~An example of typical LODs is given in the table below:~~

~~CAS Nos.~~	~~COMPOUND~~	~~LOD (ug/ml)~~
~~00067-56-1~~	~~methanol~~	~~0.24~~
~~00064-17-5~~	~~ethanol~~	~~0.17~~

8.8.1 The maximum allowable LOD for each alcohol is 0.50 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 either the maximum allowable LOD or the calculated laboratory LOD.

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

~~9. REFERENCES~~

~~9.1 U.S. Environmental Protection Agency, Characterization of Exhaust Emissions from Methanol and Gasoline Fueled Automobiles, EPA 460/3-82-004.~~

~~9.2 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.~~

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 method of analyzing, by gas chromatography, C_2 to C_5 hydrocarbons (light-end hydrocarbons) in the range of ~~parts per billion carbon (~~ppbC~~)~~ from automotive source samples. This method does not include sample collection procedures [Ref. 8] ~~(Ref 9.1)~~. The "target" hydrocarbons which shall be analyzed and reported by this method and M~~m~~ethod 1003 are listed in ~~Attachment~~ Appendix 1. All compounds on this list, when present 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 which best suits the laboratory instrumentation. All compounds on the list not targeted by M~~m~~ethod 1002 must be targeted by M~~m~~ethod 1003. ~~More compounds may be measured than those on the target list.~~

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

2. METHOD SUMMARY

2.1 This is a ~~rapid~~ method intended for routine analysis.

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

2.3 The gas chromatographic analysis is performed on a packed column operated isothermally at 35°C, or an Alumina (Al_2O_3) ~~Porous Layer Open Tubular (~~PLOT~~)~~ column temperature programmed from 0°C to 200°C. An ~~flame ionization detector (~~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 ~~constituents~~ 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 ~~of the~~ peaks. The hydrocarbon concentrations are determined by integrating the peak areas and using response ~~calibration~~ factors determined from ~~with~~ NIST-traceable standards.

3. INTERFERENCES AND LIMITATIONS

3.1 An ~~interference~~ interferent is any component present in the sample with a retention time very similar to that of any ~~the~~ target hydrocarbons described in this method. To reduce interference error, proof of chemical identity may require ~~performance of~~ periodic confirmations using an alternate method and/or instrumentation, e.g., ~~gas chromatograph/mass spectrometer (~~GC/MS~~)~~, ~~photoionization detector (~~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 reactions occurring due to reactive hydrocarbons. The compound 1,3-butadiene, most of which is in CVS bag no. 1, is unstable. Therefore all CVS bag no. 1 samples must be analyzed within 8 4 hours; CVS bag no. 2, CVS bag no. 3, and background 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 A stainless steel column [6 ~~feet (~~ft~~)~~ x 1/8 ~~inch (~~in~~)~~] packed with phenylisocyanate Durapak 80/100 mesh is used. An ~~Al~~ Alumina PLOT column (50 ~~-60~~ m x 0.32 mm) may also be used. ~~has been shown to be equivalent~~ 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.~~5~~6 An electronic integrator for quantitation of peak areas is required. If the data acquisition system cannot record the chromatogram, an analog recorder is also required.

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. "Ultra-zero" grade may be required to achieve the LOD required by Section 8.7.1.

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 traceable to a NIST-certified SRM ~~to a Standard Reference Material (SRM) certified for propane by the National Institute of Standards and Technology (NIST). NIST traceable means that the standard has been compared~~ with not more than one intermediate standard ~~to a NIST certified SRM~~. A comparison between a SRM and a candidate standard will yield a secondary NIST traceable standard, while a comparison between a secondary NIST traceable standard and a candidate standard will yield a tertiary NIST traceable standard. A NIST SRM propane standard, secondary NIST traceable propane standard, or tertiary NIST traceable propane standard is required for calibration of M~~m~~ethod 1002 or 1003.

~~The minimum requirements for the manufacture and use of a secondary or tertiary NIST traceable propane standard shall be the following: 1) the standard must be packaged in aluminum cylinders which have been precleaned and passivated, 2) a gas chromatograph shall be used to compare the candidate cylinders with the NIST traceable standard using either direct or interpolation comparison. (In the direct comparison, the analyte concentration for the candidate standard may not differ more than 10 percent from the analyte concentration of the NIST traceable standard; while in the interpolation comparison, the analyte concentration of a candidate standard is bracketed between the analyte concentrations of the NIST SRM standards.), 3) analytes and balance gases in secondary candidate cylinders must be the same composition as the NIST SRM propane standards used in an interpolation comparison procedure, 4) hydrocarbon analytes (except propane) and balance gases may differ in secondary candidate cylinders from the NIST SRM propane standard used in a direct comparison procedure if there are no interferences with the propane measurement or stability, 5) comparison between a secondary and tertiary standard must be direct, 6) all candidate cylinders must be analyzed a minimum of 4 times and stated uncertainties must be determined for all secondary and tertiary standard analytes, and 7) gas in the cylinder cannot be used when the pressure of the cylinder falls below 300 pounds per square inch.~~

~~It is recommended that either the laboratory or standard supplier(s) for the laboratory certify the secondary standards through the NIST Traceable Reference Material program or obtain Research Gas Material/Mixtures of propane standards from NIST for use as secondary standards.~~

5.6 **Control Standard** - A quality control standard, containing at least ethene, propane, n-butane, and 2-methylpropene with a concentration between 0.2 and 1 ~~parts per million carbon (~~ppmC~~)~~ based on a propane standard, is used for the following quality control purposes:

1. Daily update of control charts, and

2. Daily determination of marker retention time windows.

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

~~6.4 For automated systems, connect the samples to the GC and begin the analytical process.~~

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

6.6 Concentrations of hydrocarbons are calculated by an electronic integrator device, which has been calibrated using a 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).

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 All ~~The~~ peaks ~~areas of~~ identified as target compounds (Appendix 1) at or above the ~~maximum allowable~~ LOD are reported (Section 8.7). ~~At the laboratory's discretion, peaks at or above the LOD calculated in section 8.7 may be reported. The calculated LOD must be lower than the maximum allowable LOD.~~

6.11 Target compounds which 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 maximum retention time in this analysis is typically about 15 30 mins.~~

6.12 After each run, the packed column is back-flushed with helium while the oven temperature is raised and maintained at 60°C for 15 mins, or as required to flush the column.

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

6.1~~3~~4 Before the next run, sufficient time ~~(typically 15 mins)~~ is allowed after back-flush of the packed column to re-establish the required temperature of the column.

~~6.14 The total run time is typically about 45 60 mins.~~

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 once daily before running the calibration standard, control standard, and samples. 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 where the calibration standard, consisting of only propane and make-up gas (all organic compounds except methane and propane are below 2 percent of the propane standard concentration), is run daily and is checked for contamination except in the propane region of the chromatograph. The weekly blank run will provide a check on contamination in the propane region of the chromatograph.

8.2 Calibration Run. One run of the calibration standard is performed per day to generate the response ~~calibration~~ factor needed for ~~quantitating~~ quantifying sample analyses.

8.3 Control Standard Run. One run of the quality control standard is performed daily. Measurements of all compounds in the control standard must fall within the control limits before sample analysis may proceed. 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 ~~Q~~quality control chart~~(s) are~~ is maintained for each component of the control standard ~~sample~~. The control charts, used on a daily basis, establishe~~s~~ that the method is "in- ~~"statistical~~ control." The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard ~~sample~~ results;
2. Calculate the ~~average~~ control standard ~~sample~~ mean concentration and standard deviation~~(s)~~ for the ~~each~~ target hydrocarbon; and
3. Create a control chart for the ~~each~~ target hydrocarbon 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.

~~The control sample must be "in control" for~~ The measured concentrations of all target hydrocarbons contained ~~listed~~ in the control standard ~~sample~~ must be within the control limits ("in-control") for the sample results to be considered acceptable. A control standard ~~sample~~ measurement is considered to be "out-of-control" when the analyzed value ~~of the sample measurement~~ exceeds the 3s limit, or two successive control standard ~~sample~~ measurements of the same analyte exceed the 2s limit.

8.5 Duplicates. A duplicate analysis of one sample is performed at least once a 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 in the control standard, 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 target hydrocarbons in the control standard, the sample must be reanalyzed. If the criteria are still not met, all sample results for the day from this instrument must be deleted and the samples reanalyzed.

8.6 Linearity. A multipoint calibration to confirm ~~check for~~ instrument linearity is performed for the target hydrocarbons in the control standard for new instruments, after making instrument modifications which can affect linearity, and at least once every year ~~six months~~ 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, ~~evenly~~ distributed over the range of expected sample concentration ~~linearity of the instrument~~. 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 ~~limit of detection~~ LOD for the target hydrocarbons in the control standard must be determined must be determined at least once every year ~~six months~~. 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 standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. To make the ~~necessary~~ calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the LOD. The LOD must be calculated using the following equation [Ref. 9] ~~(Ref 9.2)~~:

$$\text{LOD} = \frac{|b| + (t \times s)}{m}$$

~~LOD = |A| + 3.3(S)~~

where ~~each term in the equation is expressed in concentration units, and |A| is the absolute value of the least-squares X intercept calculated from the multipoint data. S~~ |b| is the absolute value of the y-intercept, m is the slope of the linear regression, s is the standard deviation 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

~~At least three replicates are required.~~ The lowest standard must be of a concentration of ~~at~~ one to five times the estimated LOD ~~detection limit~~. ~~If data is not available in the concentration range near the detection limit, S may be estimated by:~~

~~S = RSD x |A|~~

~~RSD is the relative standard deviation of the lowest standard analyzed.~~

8.7.1. The maximum allowable LOD for each compound is 20 ppbC ~~propane~~. 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 either the maximum allowable LOD or the calculated laboratory LOD.

8.7.2. For the purposes of calculating the total mass ~~(ppbC)~~ 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

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 method of analyzing, by gas chromatography, C_6 to C_{12} hydrocarbons (mid-range hydrocarbons) in the range of parts per billion carbon (ppbC) from automotive source samples. This method does not include sample collection procedures [Ref. 7] ~~(Ref 9.1)~~. The target hydrocarbons which shall be analyzed and reported by this method and M~~m~~ethod 1002 are listed in ~~attachment~~ Appendix 1. All compounds on this list, when present 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 which best suits the laboratory instrumentation. All compounds on the list not targeted by M~~m~~ethod 1003 must be targeted by M~~m~~ethod 1002. ~~More compounds may be measured than those on the target list~~.

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

2. METHOD SUMMARY

2.1 This is a ~~rapid~~ method intended for routine analysis.

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

2.3 The gas chromatographic analysis is performed through a temperature-programmed capillary column. ~~operated using gradient temperature~~. A ~~flame ionization detector (~~FID~~)~~ is used for detection. ~~A photoionization detector (PID) may be used to help with compound identification~~.

2.4 The sample is injected into the GC by means of gas sampling valves. Separation of the sample hydrocarbon mixture into its components ~~constituents~~ 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 ~~of the~~ peaks. The hydrocarbon concentrations are determined by integrating the peak areas and using a response ~~calibration~~ factor determined from ~~with~~ NIST-traceable standards.

3. INTERFERENCES AND LIMITATIONS

3.1 An ~~interference~~ interferent is any component present in the sample with a retention time similar to that of any ~~the~~ target hydrocarbons described in this method. To reduce interference error, proof of chemical identity may require ~~performance of~~ periodic confirmations using an alternate method and/or instrumentation, e.g., ~~gas chromatograph/mass spectrometer (~~GC/MS~~)~~, ~~photoionization detector (~~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 losses from reaction of the 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, ~~a PID~~, 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 ~~micron~~ 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.~~5~~6 A computer-controlled data acquisition system is required for ~~the~~ quantifying ~~quantitation of~~ 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. "Ultra-zero" grade may be required to achieve the LOD required by Section 8.7.1.

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 traceable to a NIST-certified SRM ~~to a Standard Reference Material (SRM) certified for propane by the National Institute of Standards and Technology (NIST). NIST traceable means that the standard has been compared~~ with not more than one intermediate standard~~, to a NIST certified SRM~~. A comparison between a SRM and a candidate standard will yield a secondary NIST traceable standard, while a comparison between a secondary NIST traceable standard and a candidate standard will yield a tertiary NIST traceable standard. A NIST SRM propane standard, a secondary NIST traceable propane standard, or a tertiary NIST traceable propane standard is required for calibration of M~~m~~ethod 1002 or 1003.

~~The minimum requirements for the manufacture and use of a secondary or tertiary NIST traceable propane standard shall be the following: 1) the standard must be packaged in aluminum cylinders which have been precleaned and passivated 2) a gas chromatograph shall be used to compare the candidate cylinders with the NIST traceable standard using either direct or interpolation comparison (In the direct comparison the analyte concentration for the candidate standard may not differ more than 10 percent from the analyte concentration of the NIST traceable standard, while in the interpolation comparison the analyte concentration of a candidate standard is bracketed between the analyte concentrations of the NIST SRM standards.), 3) analytes and balance gases in secondary candidate cylinders must be the same composition as the NIST SRM propane standards used in an interpolation comparison procedure, 4) hydrocarbon analytes (except propane) and balance gases may differ in secondary candidate cylinders from the NIST SRM propane standard used in a direct comparison procedure if there are no interferences with the propane measurement or stability, 5) comparison between a secondary and tertiary standard must be direct, and 6) all candidate cylinders must be analyzed a minimum of 4 times and stated uncertainties must be determined for all secondary and tertiary standard analytes, and 7) gas in the cylinder cannot be used when the pressure of the cylinder falls below 300 pounds per square inch.~~

~~It is recommended that either the laboratory or standard supplier(s) for the laboratory certify the secondary standards through the NIST Traceable Reference Material program or obtain Research Gas Material/Mixtures of propane standards from NIST for use as secondary standards.~~

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 ~~parts per million carbon (~~ppmC~~)~~ based on a propane standard, is used for the following quality control purposes:

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

~~The control standard(s) must have concentrations verified against a NIST-traceable propane standard (See Section 5.5 for definition of NIST-traceable) when used for either LOD determinations or linearity checks. This verification can be performed at the laboratory conducting the sample analysis.~~

5.7 A high concentration standard (higher than the calibration standard), containing the target hydrocarbons listed in section 5.6 is used ~~semi-annually~~ for linearity determinations. The high concentration ~~calibration~~ 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 Liquid nitrogen may be required ~~is used~~ 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 ~~average linear~~ velocity: 30 cm/sec ~~centimeters/second~~ 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 ~~and PID~~ 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 ~~average linear~~ velocity: ~~20~~ 30 cm/sec~~ond~~ 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 and PID at 0.0 min~~
Range 11, attenuation 8 (or another suitable value)
Sample valve temperature: 150°C
Detector temperature: ~~250~~ 300 °C
Column Temperature: Initial temperature ~~0~~ -50°C (5 min), 5°C/min to 50°C, 10°C/min to 200°C

6.2 Data Reduction

6.2.1 All peaks identified as target compounds (Appendix 1) at or above the ~~maximum allowable limit of detection (~~LOD~~)~~ are reported (Section 8.7). ~~At the laboratory's discretion, peaks at or above the LOD calculated in section 8.7 may be reported. The calculated LOD must be lower than the maximum allowable LOD.~~

6.2.2 The results are calculated from the FID responses. ~~The PID responses are used to help with peak identifications as the PID responds more strongly to aromatics and olefins.~~

6.2.3 The results are examined to see that the peaks are correctly ~~identified and~~ integrated.

6.2.4 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.

6.2.5 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 ~~largest peaks~~ of the sample run ("fingerprint") match the typical fingerprint seen in past sample runs.

(4) Compare the relative retention time of the sample peaks with those of reference runs.

(5) Any peak with a reasonable doubt is labeled 'Unidentified'.

6.2.6 The concentrations of the hydrocarbons are calculated by an electronic integrator device.

6.2.7 Target compounds which 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.

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

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 once daily before running the calibration standard, control standard, and samples. 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 where the calibration standard, consisting of only propane and make-up gas (all organic compounds except methane and propane are below 2 percent of the propane standard concentration), is run daily and is checked for contamination except in the propane region of the chromatograph. The weekly blank run will provide a check on contamination in the propane region of the chromatograph.

8.2 Calibration Run. One run of the calibration standard is performed per day to generate the response ~~calibration~~ factor needed for ~~quantitating~~ quantifying sample analyses.

8.3 Control Standard Run. One run of the quality control standard is performed daily. Measurements of all compounds in the control standard must fall within the control limits before sample analysis may proceed. 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 ~~Q~~quality control chart~~(s)~~ is ~~are~~ maintained for each component of the control standard ~~sample~~. The control charts, used on a daily basis, establish~~es~~ that the method is "in- ~~"statistical~~ control". The following describes how to construct a typical control chart:

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

~~The control sample must be "in control" for~~ The measured concentrations of all target hydrocarbons contained in the control standard ~~sample~~ must be within the control limits ("in-control") for the sample results to be considered acceptable. A control standard ~~sample~~ measurement is considered to be "out-of-control" when the analyzed value ~~of the sample measurement~~ exceeds the 3s limit, or two successive control standard ~~sample~~ measurements of the same analyte exceed the 2s limit.

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

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

For each compound in the control standard, 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 in the control standard, the sample must be reanalyzed. If the criteria are still not met, all sample results for the day from this instrument must be deleted and the samples reanalyzed.

8.6 Linearity. A multipoint calibration to confirm ~~check for~~ instrument linearity is performed for all target hydrocarbons in the control standard for new instruments, after making instrument modifications which can affect linearity, and at least once every year ~~six months.~~ 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, ~~evenly~~ distributed over the range of expected sample concentration ~~linearity of the instrument~~. 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 ~~limit of detection~~ for the target hydrocarbons in the control standard must be determined for new instruments and after making instrument modifications which can affect linearity and/or sensitivity and at least once every year ~~six months.~~ 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 standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. To make the ~~necessary~~ calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the LOD. The LOD must be calculated using the following equation [Ref. 7[~~(Ref 9.1~~):

$$LOD = \frac{|b| + (t \times s)}{m}$$

~~LOD = |A| + 3.3(S)~~

where ~~each term in the equation is expressed in concentration units, and |A| is the absolute value of the least-squares X-intercept calculated from the multipoint data. S~~ |b| is the absolute value of the y-intercept, m is the slope of the linear regression, s is the standard deviation 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

~~At least three replicates are required~~. The lowest standard must be of a concentration of ~~at~~ one to five times the estimated LOD ~~detection limit~~. ~~If data is not available in the concentration range near the detection limit, S may be estimated by:~~

~~S = RSD x |A|~~

~~RSD is the relative standard deviation of the lowest standard analyzed.~~

8.7.1 The maximum allowable LOD for each ~~any~~ compound is 20 ppbC ~~propane~~. 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 either the maximum allowable LOD or the calculated laboratory LOD.

8.7.2 For the purposes of calculating the total mass ~~(ppbC)~~ of all species, the concentrations of the 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.

~~9. REFERENCE~~

~~9.1 U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Method T93 15), EPA 600/4-89-017, Research Triangle Park, North Carolina, June 1989~~

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 which shall be analyzed and reported by this method are listed in Appendix 1. ~~are formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, butyraldehyde, hexanal, benzaldehyde, methyl ethyl ketone, methacrolein, crotonaldehyde, valeraldehyde, and m- or p-tolualdehyde~~ All of these carbonyl compounds, when present in concentrations above the LOD, shall be reported.

1.2 This procedure is derived from a method used by Hull [Ref. 10] ~~(Ref. 9.1)~~.

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 ~~is~~ performed using a ~~High Performance Liquid Chromatograph~~ HPLC with an ultraviolet detector.

3. INTERFERENCES AND LIMITATIONS

3.1 An interferent ~~interference~~ is any detectable compound present in the sample with a retention time very similar to that of any ~~the~~ target carbonyl~~s~~ described in this method. To reduce interference error, proof of chemical identity may require ~~performance of~~ 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 ~~transferred to glass bottles, sealed, and~~ refrigerated at a temperature below 40°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 column 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.

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 columns in tandem and a guard column, (2 ~~centimeters~~ cm long packed with LC18 5 ~~micrometers (~~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 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 ~~may also be used~~.

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-~~Dinitrophenylhydrazine (~~DNPH~~)~~, purified, Radian Corporation ~~Eastman~~ 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 ~~Synthesized 2,4 dinitrophenylhydrazones (ref. 9.2)~~ The carbonyl/2,4-dinitrophenylhydrazone (DNPH) complexes [Ref. 11] listed in Table F-1 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. ~~are:~~

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

Complex	Molecular Weight (g/mole)	Melting Point ºC
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

~~5.5.1 Formaldehyde/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 168° C.~~
~~5.5.2 Acetaldehyde/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 166 168° C.~~
~~5.5.3 Acrolein/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol and acetonitrile, melting point (m.p.) 158 159°C.~~
~~5.5.4 Acetone/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 126 128°C.~~
~~5.5.5 Propionaldehyde/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 138 140°C.~~

___ This compound has been known to decompose.

~~5.5.6 Butyraldehyde/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 109-111°C.~~
~~5.5.7 Hexanal/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 105-106°C.~~
~~5.5.8 Benzaldehyde/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 235-237°C.~~
~~5.5.9 Methyl ethyl ketone/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 115-116°C.~~
~~5.5.10 Methacrolein/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 206°C.~~
~~5.5.11 Crotonaldehyde/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 185-188°C.~~
~~5.5.12 Valeraldehyde/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 103-106°C.~~
~~5.5.13 m- or p-Tolualdehyde/2,4 dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 239°C.~~

5.6 Stock Calibration Standard - A stock calibration standard is prepared by diluting the target carbonyl/2,4-DNPH complexes ~~s~~ with acetonitrile. ~~, e.g., a~~ A typical ~~100 ml acetonitrile standard~~ stock calibration standard ~~solution~~ contains ~~:~~ approximately 5 to 15 mg/mL of each target carbonyl/DNPH complex.

~~14.8 milligrams (mg) formaldehyde/2,4 dinitrophenylhydrazone~~
~~8.4 mg acetaldehyde/2,4 dinitrophenylhydrazone~~
~~6.0 mg acrolein/2,4 dinitrophenylhydrazone~~
~~5.7 mg acetone/2,4 dinitrophenylhydrazone~~
~~4.7 mg propionaldehyde/2,4 dinitrophenylhydrazone~~
~~5.0 mg butyraldehyde/2,4 dinitrophenylhydrazone~~
~~5.0 mg benzaldehyde/2,4 dinitrophenylhydrazone~~
~~5.0 mg hexanal/2,4 dinitrophenylhydrazone~~
~~5.0 mg methyl ethyl ketone/2,4 dinitrophenylhydrazone~~
~~5.0 mg methacrolein/2,4 dinitrophenylhydrazone~~
~~5.0 mg crotonaldehyde/2,4 dinitrophenylhydrazone~~
~~5.0 mg valeraldehyde/2,4 dinitrophenylhydrazone~~
~~5.0 mg m or p tolualdehyde/2,4 dinitrophenylhydrazone~~
~~Commercial standards are also available for these compounds.~~

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; e.g., ~~1~~ 5 mL of the stock calibration solution is diluted to ~~100~~ 20 mL.

5.8 Control Standard - A quality control standard, containing all target carbonyls/2,4-DNPH~~dinitrophenylhydrazone~~ complexes within the typical concentration range of real samples, is analyzed to monitor the precision of the analysis of each target carbonyl. ~~update daily control charts.~~ The control standard may be prepared by batch mixing old samples and stirring for 24 hours. All target compounds except acrolein have been found to be stable in the control standard. Commercial standards are also available for these compounds.

6. PROCEDURE

6.1.~~1~~ For systems collecting the samples via impingers, a~~A~~n absorbing solution is prepared by dissolving 0.11 - 0.13 grams of recrystallized DNPH in 1 ~~liter (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 ~~addition of~~ contaminant-free dilute solution of DNPH and analyzing by ~~ed in the~~ HPLC. ~~Cartridges should be sealed and refrigerated at less than 40°F.~~

6.1.1~~2~~. In the laboratory, pipette 15 mL of the DNPH absorbing solution into each of the 30 mL ~~midget~~ impingers for each emission test. Add 0.1 mL of 2.85 N sulfuric acid or 0.15 mL of 3.8M perchloric acid to each impinger.

~~6.1.3 DNPH impregnated cartridges may also be used to collect carbonyl samples. At the volumes being sampled (1 L/minute), no back-up cartridge is needed. Leave the cartridges capped.~~

6.2 For systems collecting the samples via cartridges, DNPH-impregnated cartridges shall be sealed and refrigerated, at a temperature less than 40°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.

~~6.2 Connect the impinger pairs in series and cap the open ends to prevent contamination. (These sets of impingers (cartridges) are picked up by the automotive test personnel for sampling.)~~

6.3 ~~After the sampling has been completed, cap the impingers or cartridges and return them to the laboratory~~. After sampling ~~At the laboratory,~~ uncap and place all the impingers ~~and the field blank impinger~~ 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 ~~sampling with~~ 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: ~~configured as follows~~:

Primary System:

Columns:	4.6 ~~millimeters (~~mm~~)~~ ID x 250 mm x 1/4 inches OD Dupont Zorbax ODS two columns in series, Guard column - 2 cm long packed with C18 5 µm pellicular
Column temperature:	40ºC
Detector:	UV/VIS at 360 ~~nanometers~~ nm
Sample volume:	~~20~~ 10 ~~microliters~~ 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 ~~5~~ 2 min
	100 percent A, 0 percent B ~~5~~ 2 to ~~35~~ 22 min
	50 percent A, 50 percent B ~~35~~ 22 to ~~36~~ 37 min
	~~50 percent A, 50 percent B~~ ~~36 to 46 " (hold~~)

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:	40ºC
Detector:	UV/VIS at 360 nm
Sample volume:	10 µL
Solvent A:	purified water
Solvent B:	acetonitrile
Flow:	1.5 mL/min
Program -	65 percent A, 35 percent B (initial time)
	65 percent A, 35 percent B 0 - 5.5 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 The target carbonyl peaks at or above the ~~maximum allowable limit of detection~~ LOD are reported (Section 8.10). ~~At the laboratory's discretion, peaks at or above the LOD calculated in section 8.10 may be reported. The calculated LOD must be lower than the maximum allowable LOD~~.

7. CALCULATIONS

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

7.2 The mass of each carbonyl compound, ~~µg~~ per ~~15 mL~~ impinger or cartridge, is determined by the following calculation:

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

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:

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

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 Reagent Blanks. The solvents used are of the highest HPLC grade and are ~~checked at least daily for impurities by conducting blank analyses.~~ 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.

8.2 Carbonyl/2,4-DNPH ~~Phenylhydrazone~~ Purity. The carbonyl/ 2,4-~~dinitrophenylhydrazones~~ 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 ~~phenylhydrazone~~ must yield only the peak of interest. No contaminant peaks above the LOD should be observed.

8.3 Calibration Run. One run of the calibration standard is performed ~~at least~~ daily to generate the response ~~calibration~~ factors needed for quantifying sample analyses.

8.4 Control Standard Run. One run of the quality control standard is performed ~~at least~~ daily after the calibration run. Measurements of all compounds in the control standard, except acrolein, must fall within the control limits before sample analysis may proceed. To meet this requirement, it may be necessary to rerun the calibration and control standards, and inspect and repair the HPLC.

8.5 Control Charts. A ~~Q~~quality control chart~~(s)~~ is ~~are~~ maintained for each component of the control sample, except acrolein. The control charts, used on a daily basis, establishes that the method is "in- ~~"statistical~~ control." The following describes how to construct a typical control chart:

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

~~The control sample must be "in control" for~~ 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. Due to the low variability of the carbonyl control standard measurements, a ~~A~~ control standard ~~sample~~ 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 ~~sample~~ measurements of the same analyte exceed the 2s limit. No control requirements have been established for acrolein, since it has been shown to degrade over time.

8.6 Field Blanks. One field blank is analyzed for each set of impingers for each emission test. One cartridge for each ~~per~~ batch number used is analyzed as a field blank.

8.7 At least ~~O~~one cartridge per batch is analyzed as a batch blank.

8.8 Duplicates. A duplicate analysis of one sample is performed at least once a 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, 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 must be reanalyzed. If the criteria are still not met, all sample results analyzed during the day from this instrument must be deleted and the samples reanalyzed.

8.9 Linearity. A multipoint calibration to confirm ~~check for~~ instrument linearity is performed for all target analytes for new instruments, after making instrument modifications which can affect linearity, and at least once every year. ~~six months.~~ 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, ~~evenly~~ distributed over the range of expected sample concentration ~~linearity of the instrument~~. 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.

8.10 Limit of Detection. The ~~limit of detection~~ 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. ~~every six months~~. To make the ~~necessary~~ calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the LOD. The LOD must be calculated using the following equation [Ref. 7] ~~(Ref. 9.3~~):

$$\text{LOD} = \frac{|b| + (t \times s)}{m}$$

~~LOD = |A| + 3.3(S)~~

where ~~each term in the equation is expressed in concentration units, and |A| is the absolute value of the least squares X-intercept calculated from the multipoint data. S~~ |b| is the absolute value of the y-intercept, m is the slope of the linear regression, s is the standard deviation 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

~~At least three replicates are required.~~ The lowest standard must be of a concentration of ~~at~~ one to five times the estimated LOD ~~detection limit~~. ~~If data is not available in the concentration range near the detection limit, S may be estimated by:~~

~~S = RSD x |A|~~

~~RSD is the relative standard deviation of the lowest standard analyzed.~~

~~An example of typical LODs is given in the table below:~~

~~Compound~~	~~LOD (ug/ml)~~
~~Formaldehyde/2,4-dinitrophenylhydrazone~~	~~0.048~~
~~Acetaldehyde/2,4-dinitrophenylhydrazone~~	~~0.011~~
~~Acrolein/2,4-dinitrophenylhydrazone~~	~~0.006~~
~~Acetone/2,4-dinitrophenylhydrazone~~	~~0.004~~
~~Propionaldehyde/2,4-dinitrophenylhydrazone~~	~~0.016~~
~~Butyraldehyde/2,4-dinitrophenylhydrazone~~	~~0.06*~~
~~Hexanal/2,4-dinitrophenylhydrazone~~	~~0.019~~
~~Benzaldehyde/2,4-dinitrophenylhydrazone~~	~~0.027~~
~~Methyl ethyl ketone/2,4-dinitrophenylhydrazone~~	~~__*~~
~~Methacrolein/2,4-dinitrophenylhydrazone~~	—
~~Crotonaldehyde/2,4-dinitrophenylhydrazone~~	~~0.016~~
~~Valeraldehyde/2,4-dinitrophenylhydrazone~~	~~0.009~~
~~m or p-Tolualdehyde/2,4-dinitrophenylhydrazone~~	—

~~CAS Nos.~~	~~Compound~~	~~LOD (ug/ml)~~
~~00050-00-0~~	~~Formaldehyde~~	~~0.007~~
~~00075-07-0~~	~~Acetaldehyde~~	~~0.002~~
~~00107-02-8~~	~~Acrolein~~	~~0.002~~
~~00067-64-1~~	~~Acetone~~	~~0.001~~

~~00123-38-6~~	~~Propionaldehyde~~	~~0.004~~	
~~00123-72-8~~	~~Butyraldehyde*~~	~~0.019~~	
~~00066-25-1~~	~~Hexanal~~	~~0.007~~	
~~00100-52-7~~	~~Benzaldehyde~~	~~0.010~~ ~~0.004~~	
~~00078-93-3~~	~~Methyl Ethyl Ketone*~~	~~—~~	
~~00078-85-3~~	~~Methacrolein~~	—	
~~04170-30-3~~	~~Crotonaldehyde~~	~~0.016~~	
~~00110-62-3~~	~~Valeraldehyde~~	~~0.009~~	
~~00104-87-0~~	~~p-Tolualdehyde~~	~~**~~	~~or~~
~~00620-23-5~~	~~m-Tolualdehyde~~	~~**~~	

~~* Butyraldehyde may co-elute with methyl ethyl ketone~~

~~**p-Tolualdehyde may co-elute with m-Tolualdehyde and o-Tolualdehyde~~

8.10.1 The maximum allowable LOD is 0.06 μg carbonyl derivative/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 either the maximum allowable LOD or the calculated laboratory LOD.

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

~~9. REFERENCES~~

~~9.1 Hull, L.A., Procedures for 2,4-Dinitrophenylhydrazone Aldehyde-Ketone Air Analysis, Internal Report at U.S. EPA.~~

~~9.2 Shriner, R.L. and Fuson, R.C., Identification of Organic Compounds, 2nd. Ed., John Wiley and Sons, Inc., 1940, p. 143.~~

~~9.3 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.~~

Part G

DETERMINATION OF NMOG MASS EMISSIONS

1. INTRODUCTION

1.1 ~~Non-methane organic gases (~~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:

$$NMOG_{wm} = \Sigma NMHC_{wm} + \Sigma ROH_{wm} + \Sigma RHO_{wm}$$

Non-methane hydrocarbon weighted mass emissions ($NMHC_{wm}$) can be determined by either ~~flame ionization detection (~~FID~~)~~ or ~~gas chromatography (~~GC~~)~~. If the FID method is used to calculate $NMHC_{wm}$, 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 $NMHC_{wm}$, refer to ~~the~~ section 3. "Speciated Hydrocarbon Mass Emissions Calculation" ~~section~~ contained herein. Carbonyl weighted mass emissions (RHO_{wm}) are to be calculated according to ~~the~~ section 5 "Carbonyl Mass Emissions Calculation" ~~section~~ contained herein. For alcohol fueled vehicles, alcohol weighted mass emissions (ROH_{wm}) are to be calculated according to ~~the~~ section 4 "Alcohol Mass Emissions Calculation" ~~section~~ contained herein.

3. SPECIATED HYDROCARBON MASS EMISSIONS CALCULATION

1. INTRODUCTION

1.1 Vehicular exhaust emissions are measured according to the ~~Federal Test Procedure~~ FTP [Ref. 1] ~~(1)~~. For each of the three phases of the FTP, a tedlar bag of 0.5 ft^3 capacity is used to collect a dilute exhaust sample. A fourth 0.5 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.

2. HC MASS EMISSIONS CALCULATION PER TEST PHASE

2.1 $HC_{mass\ n} = (HC_{conc} * HC_{dens} * VMIX * 10^{-6}) / (\text{Carbon No.})$

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. WEIGHTED HC MASS EMISSIONS CALCULATION

3.1
$$HC_{wm} = 0.43 * \frac{(HC_{mass\ 1} + HC_{mass\ 2})}{(D_{phase\ 1} + D_{phase\ 2})} + 0.57 * \frac{(HC_{mass\ 3} + HC_{mass\ 2})}{(D_{phase\ 3} + D_{phase\ 2})}$$

4. SAMPLE CALCULATION

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_{phasen} (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 / ~~10.88~~ 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: $HC_{mass} = 5.7\ \text{mg}$

and for Phase 3: $HC_{mass} = 4.2\ \text{mg}$

Therefore,

$$HC_{wm} = 0.43 * \frac{(HC_{mass\ 1} + HC_{mass\ 2})}{(D_{phase\ 1} + D_{phase\ 2})} + 0.57 * \frac{(HC_{mass\ 3} + HC_{mass\ 2})}{(D_{phase\ 3} + D_{phase\ 2})}$$

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

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

4. ALCOHOL MASS EMISSIONS CALCULATION

1. INTRODUCTION

1.1 Vehicular emissions are measured according to the ~~Federal Test Procedure~~ (FTP)[Ref. 1] ~~(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.

2. ALCOHOL MASS EMISSIONS CALCULATION PER TEST PHASE

2.1 $\text{ROH}_{\text{mass n}} = (\text{ROH}_{\text{conc}} * \text{ROH}_{\text{dens}} * \text{VMIX} * 10^{-6}) / (\text{Carbon No.})$

2.2 $\text{ROH}_{\text{conc}} = \text{ROH}_{e} - (\text{ROH}_{d} * (1 - (1 / \text{DF})))$

NOTE: If ROH_{conc} is calculated to be less than zero, then $\text{ROH}_{\text{conc}} = 0$.

2.3 $\text{ROH}_{e} = (\text{Imass}_{e} / \text{Ivol}_{e}) * (\text{Mol. Vol.} / \text{Mol. Wt.})$

2.4 $\text{Imass}_{e} = (\text{Iconc}_{e1} + \text{Iconc}_{e2}) * \text{Dens}_{\text{ROH}} * \text{Ivol}_{r}$

2.5 $\text{Ivol}_{e} = \text{Ivol}_{em} *$ ~~$(\text{Itemp}_{e} / 293.16° \text{K}) * (760 \text{ mm Hg} / P_{B})$~~
$(293.16°\text{K} / \text{Itemp}_{e}) * (P_{B} / 760 \text{ mm Hg})$

2.6 $\text{ROH}_{d} = (\text{Imass}_{d} / \text{Ivol}_{d}) * (\text{Mol. Vol.} / \text{Mol. Wt.})$

2.7 $\text{Imass}_{d} = (\text{Iconc}_{d1} + \text{Iconc}_{d2}) * \text{Dens}_{\text{ROH}} * \text{Ivol}_{r}$

2.8 $\text{Ivol}_{d} = \text{Ivol}_{dm} *$ ~~$(\text{Itemp}_{d} / 293.16° \text{K}) * (760 \text{ mm Hg} / P_{B})$~~
$(293.16°\text{K} / \text{Itemp}_{d}) * (P_{B} / 760 \text{ mm Hg})$

3. WEIGHTED ALCOHOL MASS EMISSIONS CALCULATION

$$\text{ROH}_{wm} = 0.43 * \frac{(\text{ROH}_{\text{mass 1}} + \text{ROH}_{\text{mass 2}})}{(D_{\text{phase 1}} + D_{\text{phase 2}})} + 0.57 * \frac{(\text{ROH}_{\text{mass 3}} + \text{ROH}_{\text{mass 2}})}{(D_{\text{phase 3}} + D_{\text{phase 2}})}$$

4. SAMPLE CALCULATION

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)	$Iconc_{e1}$ (ppmC)	$Iconc_{e2}$ (ppmC)	$Ivol_{em}$ (liter)	$Iconc_{d1}$ (ppmC)	$Iconc_{d2}$ (ppmC)	$Ivol_{dm}$ (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 ppmC + 0.05 ppmC) * 0.7914 g/mL * 15 mL * 10^6 µg/g
= 27.2 µg

Mol. Wt. of CH_3OH = (1 * 12.01115) + (4 * 1.00797) + (1 * 15.9994)
= 32.0428 g/mole

$Ivol_e$ = $Ivol_{em}$ * ~~($Itemp_e$ / 293.16° K) * (760 mm Hg / P_B)~~
(293/16° K / $Itemp_e$) * (P_B / 760 mm Hg)

= 3.90 liter * ~~(295° K / 293.16° K)~~ (293.16°K / 295° K) *
(760 mm Hg / 760 mm Hg)
= ~~3.92~~ 3.88 liter

ROH_e = ($Imass_e$ / $Ivol_e$) * (Mol. Vol. / Mol. Wt.)
= (27.2*10^{-6} g / ~~3.92~~ 3.88 liter)*(24.055 liter/mole / 32.0428 g/mole)
= ~~5.20~~ 5.27 ppmC

$Imass_d$ = $(Iconc_{d1} + Iconc_{d2}) * Dens_{ROH} * Ivol_r$
= $(0.07 \text{ ppmC} + 0.01 \text{ ppmC}) * 0.7914 \text{ g/ml} * 15 \text{ ml} * 10^6\ \mu\text{g/g}$
= $0.95\ \mu\text{g}$

$Ivol_d$ = $Ivol_{dm}$ * ~~(Itemp~~ $\cancel{(Itemp_e / 293.16^\circ K) * (760 \text{ mm Hg} / P_B)}$
$\underline{(293.16^\circ K / Itemp_d) * (P_B / 760 \text{ mm Hg})}$
= 13.50 liter * $\cancel{(294^\circ K / 293.16^\circ K)}$ $\underline{(293.16^\circ K / 294^\circ K)}$ *
(760 mm Hg / 760 mm Hg)
= ~~13.54~~ $\underline{13.46}$ liter

ROH_d = $(Imass_d / Ivol_d) * (\text{Mol. Vol.} / \text{Mol. Wt.})$
= $(0.95*10^{-6}$ g/ ~~13.54~~ $\underline{13.46}$ liter)*(24.055 liter/mole / 32.0428 g/mole)
= 0.05 ppmC

DF = $12.02 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}]$
(see $\underline{\text{section 6,}}$ 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)
= ~~73~~ $\underline{69}$ 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

$$DF = \frac{12.02}{1.5\% + (\cancel{73}\ \underline{69} \text{ ppmC} + 9 \text{ ppmC} + 237 \text{ ppmC} + \cancel{5.30}\ \underline{5.27} \text{ ppmC} + 0.81 \text{ ppm}) * 10^{-4}}$$

= ~~7.85~~ $\underline{7.84}$

ROH_{conc} = $ROH_e - (ROH_d * (1 - (1 / DF)))$
= ~~5.20~~ $\underline{5.27}$ ppmC - (0.05 ppmC * (1 - (1 / 7.84)))
= ~~5.15~~ $\underline{5.23}$ 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

$ROH_{mass\ n}$ = $(ROH_{conc} * ROH_{dens} * VMIX * 10^{-6}) / (\text{Carbon No.})$
$ROH_{mass\ 1}$ = (~~5.15~~ $\underline{5.23}$ ppmC * 37.719 g/ft^3 * 2834 ft^3 * 10^{-6}) / 1

$$= \cancel{0.55}\ \underline{0.56}\ \text{g}$$

Similarly, for Phase 2:

$$\text{ROH}_{\text{mass 2}} = 0.08\ \text{g}$$

and for Phase 3:

$$\text{ROH}_{\text{mass 3}} = \cancel{0.07}\ \underline{0.08}\ \text{g}$$

Therefore,

$$\text{ROH}_{\text{wm}} = 0.43 * \frac{(\text{ROH}_{\text{mass 1}} + \text{ROH}_{\text{mass 2}})}{(\text{D}_{\text{phase 1}} + \text{D}_{\text{phase 2}})} + 0.57 * \frac{(\text{ROH}_{\text{mass 3}} + \text{ROH}_{\text{mass 2}})}{(\text{D}_{\text{phase 3}} + \text{D}_{\text{phase 2}})}$$

$$\text{ROH}_{\text{wm}} = 0.43 * \frac{(\cancel{0.55}\ \underline{0.56}\ \text{mg} + 0.08\ \text{mg})}{(3.581\ \text{mile} + 3.845\ \text{mile})} + 0.57 * \frac{(\cancel{0.07}\ \underline{0.08}\ \text{mg} + 0.08\ \text{mg})}{(3.583\ \text{mile} + 3.845\ \text{mile})}$$

$$\text{ROH}_{\text{wm}} = 0.05\ \text{g (methanol weighted mass emissions)}$$

5. CARBONYL MASS EMISSIONS CALCULATIONS

1. INTRODUCTION

1.1 Vehicular emissions are measured according to the ~~Federal Test Procedure~~ (FTP~~)~~[Ref. 1] ~~(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.

2. CARBONYL MASS EMISSIONS CALCULATION PER TEST PHASE

2.1 $\text{RHO}_{\text{mass n}} = (\text{RHO}_{\text{conc}} * \text{RHO}_{\text{dens}} * \text{VMIX} * 10^{-6})$

2.2 $\text{RHO}_{\text{conc}} = \text{RHO}_e - (\text{RHO}_d * (1 - (1 / \text{DF})))$
NOTE: If RHO_{conc} is calculated to be less than zero, then $\text{RHO}_{\text{conc}} = 0$.

2.3 $\text{RHO}_e = (\text{Imass}_e / \text{Ivol}_e) * (\text{Mol. Vol.} / \text{Mol. Wt.})$

2.4 $\text{Ivol}_e = \text{Ivol}_{em} *$ ~~$(\text{Itemp}_e / 293.16° \text{K}) * (760 \text{ mm Hg} / P_B)$~~
$(293.16°\text{K} / \text{Itemp}_e) * (P_B / 760 \text{ mm Hg})$

2.5 $\text{RHO}_d = (\text{Imass}_d / \text{Ivol}_d) * (\text{Mol. Vol.} / \text{Mol. Wt.})$

2.6 $\text{Ivol}_d = \text{Ivol}_{dm} *$ ~~$(\text{Itemp}_d / 293.16° \text{K}) * (760 \text{ mm Hg} / P_B)$~~
$(293.16°\text{K} / \text{Itemp}_d) * (P_B / 760 \text{ mm Hg})$

3. WEIGHTED CARBONYL MASS EMISSIONS CALCULATION

$$\text{RHO}_{\text{wm}} = 0.43 * \frac{(\text{RHO}_{\text{mass 1}} + \text{RHO}_{\text{mass 2}})}{(D_{\text{phase 1}} + D_{\text{phase 2}})} + 0.57 * \frac{(\text{RHO}_{\text{mass 3}} + \text{RHO}_{\text{mass 2}})}{(D_{\text{phase 3}} + D_{\text{phase 2}})}$$

4. SAMPLE CALCULATION

4.1 Carbonyl emissions from a ~~compressed natural gas (~~CNG~~)~~ vehicle are collected in three sets of dilute exhaust impingers and one set of dilution air impingers during the FTP. ~~High performance liquid chromatography~~ 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$_e$ (°K)	Itemp$_d$ (°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)	D$_{phase\ n}$ (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$_{em}$ * ~~(Itemp$_e$ / 293.16° K) * (760 mm Hg / P$_B$)~~
(293/16° K / Itemp$_e$) * (P$_B$ / 760 mm Hg)

= 8.49 liter * ~~(295° K / 293.16° K)~~ (293.16° K / 295° K) *
(760 mm Hg / 760 mm Hg)
= ~~8.54~~ 8.44 liter

RHO$_e$ = (Imass$_e$ / Ivol$_e$) * (Mol. Vol. / Mol. Wt.)
= ($2.45*10^{-6}$ g / ~~8.54~~ 8.44 liter)*(24.055 liter/mole / 30.0268 g/mole)
= ~~230~~ 233 ppb

Ivol$_d$ = Ivol$_{dm}$ * ~~(Itemp$_d$ / 293.16° K) * (760 mm Hg / P$_B$)~~
(293.16°K / Itemp$_d$) * (P$_B$ / 760 mm Hg)
= 31.57 liter * ~~(292° K / 293.16° K)~~ 293.16° K / 292° K) *
(760 mm Hg / 760 mm Hg)
= ~~31.45~~ 31.70 liter

RHO_d = (Imass$_d$ / Ivol$_d$) * (Mol. Vol. / Mol. Wt.)
= (0.17*10^{-6} g / ~~31.45~~ 31.70 liter)*(24.055 liter/mole / 30.0268 g/mole)
= 4 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 - ~~0.02900~~ 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)))
= ~~230~~ 233 ppb - (~~4.33~~ 4 ppb * (1 - (1 / 10.69)))
= ~~226~~ 229 ppb

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

$RHO_{mass\ n}$ = (RHO_{conc} * RHO_{dens} * VMIX * 10^{-6})
$RHO_{mass\ 1}$ = (~~226~~ 229 ppb * 35.35 g/ft^3 * 2866 ft^3 * 10^{-6})
= ~~22.9~~ 23.2 mg

Similarly, for Phase 2:
$RHO_{mass\ 2}$ = ~~6.3~~ 6.6 mg
and for Phase 3:
$RHO_{mass\ 3}$ = ~~12.2~~ 12.7 mg

Therefore,

$$RHO_{wm} = 0.43 * \frac{(RHO_{mass\ 1} + RHO_{mass\ 2})}{(D_{phase\ 1} + D_{phase\ 2})} + 0.57 * \frac{(RHO_{mass\ 3} + RHO_{mass\ 2})}{(D_{phase\ 3} + D_{phase\ 2})}$$

$$RHO_{wm} = 0.43 * \frac{(\cancel{22.9}\ \underline{23.2}\ \text{mg} + \cancel{6.3}\ \underline{6.6}\ \text{mg})}{(3.581\ \text{mile} + 3.845\ \text{mile})} + 0.57 * \frac{(\cancel{12.2}\ \underline{12.7}\ \text{mg} + \cancel{6.3}\ \underline{6.6}\ \text{mg})}{(3.583\ \text{mile} + 3.845\ \text{mile})}$$

RHO_{wm} = $\cancel{3.1}$ $\underline{3.2}$ *g* ***<u>mg/mi</u>*** (formaldehyde weighted mass emissions)

6. DILUTION FACTOR CALCULATION

1. DILUTION FACTORS

1.1 For Non-Alcohol Fueled Vehicles:

1.1.1
$$DF = \frac{100 * \dfrac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e\ ) * 10^{-4}}$$

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

1.1.2 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a\ ) * CO_{em}$

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

~~b~~c) For LPG, $CH_{\cancel{2.66}\ 2.64}$, where x = 1, y = ~~2.66~~ 2.64, z = 0:
$DF = \cancel{11.64}\ 11.68 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e\ ) * 10^{-4}$
$CO_e = (1 - \cancel{0.02330}\ 0.02320 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

~~e~~d) For CNG, $CH_{\cancel{3.80}\ 3.78}$, where x = 1, y = ~~3.80~~ 3.78, and z = 0.016:
$DF = \cancel{9.77}\ 9.83\ / [[CO_{2e} + (NMHC_e + CH_{4e} + CO_e\ ) * 10^{-4}\ ]$
$CO_e = (1 - \cancel{0.02900}\ 0.02890 * CO_{2e} - 0.000323 * R_a\ ) * CO_{em}$

1.2 For Alcohol Fueled Vehicles:

1.2.1
$$DF = \frac{100 * \dfrac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e\ ) * 10^{-4}}$$

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

1.2.2 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$

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:
$DF = 12.29 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}]$
$CO_e = (1 - 0.02500 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

~~Attachment~~ APPENDIX 1

LIST OF COMPOUNDS

CAS #	COMPOUND	MIR
	Alcohols	
00067-56-1	methanol	0.56
00064-17-5	ethanol	1.34
	Light End and Mid-Range Hydrocarbons (Listed in approximate elution order)	
00074-85-1	ethene	7.29
00074-86-2	ethyne	0.50
00074-84-0	ethane	0.25
00115-07-1	propene	9.40
00074-98-6	propane	0.48
00463-49-0	1,2-propadiene	10.89
00074-99-7	1-propyne	4.10
00075-28-5	2-methylpropane	1.21
00115-11-7	2-methylpropene	5.31
00106-98-9	1-butene	8.91
00106-99-0	1,3-butadiene	10.89
00106-97-8	n-butane	1.02
00624-64-6	trans-2-butene	9.94
00463-82-1	2,2-dimethylpropane	0.37
00107-00-6	1-butyne	9.24
00590-18-1	cis-2-butene	9.94
00563-45-1	3-methyl-1-butene	6.22
00078-78-4	2-methylbutane	1.38
00503-17-3	2-butyne	9.24
00109-67-1	1-pentene	6.22
00563-46-2	2-methyl-1-butene	4.90
00109-66-0	n-pentane	1.04
00078-79-5	2-~~mehtyl~~methyl-1,3-butadiene	9.08
00646-04-8	trans-2-pentene	8.80
00558-37-2	3,3-dimethyl-1-butene	4.42
00627-20-3	cis-2-pentene	8.80
00689-97-4	1-buten-3-yne	9.24
00513-35-9	2-methyl-2-butene	6.41
00542-92-7	1,3-cyclopentadiene	7.66
00075-83-2	2,2-dimethylbutane	0.82
00142-29-0	cyclopentene	7.66
00691-37-2	4-methyl-1-pentene	4.42

CAS #	COMPOUND	MIR
00760-20-3	3-methyl-1-pentene	4.42
00287-92-3	cyclopentane	2.38
00079-29-8	2,3-dimethylbutane	1.07
01634-04-4	1-methyl-tert-butyl-ether	0.62
00691-38-3	4-methyl-cis-2-pentene	6.69
00107-83-5	2-methylpentane	1.53
00674-76-0	4-methyl-trans-2-pentene	6.69
00096-14-0	3-methylpentane	1.52
00763-29-1	2-methyl-1-pentene	4.42
00592-41-6	1-hexene	4.42
00110-54-3	n-hexane	0.98
13269-52-8	trans-3-hexene	6.69
07642-09-3	cis-3-hexene	6.69
04050-45-7	trans-2-hexene	6.69
00616-12-6	3-methyl-trans-2-pentene	6.69
00625-27-4	2-methyl-2-pentene	6.69
01120-62-3	3-methylcyclopentene	5.65
07688-21-3	cis-2-hexene	6.69
00637-92-3	1-ethyl-tert-butyl-ether	1.98
00922-62-3	3-methyl-cis-2-pentene	6.69
00590-35-2	2,2-dimethyl~~hexane~~pentane	1.40
00096-37-7	methylcyclopentane	2.82
00108-08-7	2,4-dimethylpentane	1.78
00464-06-2	2,2,3-trimethylbutane	1.32
07385-78-6	3,4-dimethyl-1-pentene	3.48
00693-89-0	1-methylcyclopentene	7.66
00071-43-2	benzene	0.42
03404-61-3	3-methyl-1-hexene	3.48
00562-~~0~~49-2	3,3-dimethylpentane	0.71
00110-82-7	cyclohexane	1.28
00591-76-4	2-methylhexane	1.08
00565-59-3	2,3-dimethylpentane	1.51
00110-83-8	cyclohexene	5.67
00589-34-4	3-methylhexane	1.40
02532-58-3	cis-1,3-dimethylcyclopentane	2.55
00617-78-7	3-ethylpentane	1.40
00822-50-4	trans-1,2-dimethylcyclopentane	1.85
00592-76-7	1-heptene	3.48
00540-84-1	2,2,4-trimethylpentane	0.93
14686-14-7	trans-3-heptene	5.53
00142-82-5	n-heptane	0.81

CAS #	COMPOUND	MIR
02738-19-4	2-methyl-2-hexene	5.53
03899-36-3	3-methyl-trans-3-hexene	5.53
14686-13-6	trans-2-heptene	5.53
00816-79-5	3-ethyl-~~cis-~~2-pentene	5.53
00107-39-1	2,4,4-trimethyl-1-pentene	2.69
10574-37-5	2,3-dimethyl-2-pentene	5.53
06443-92-1	cis-2-heptene	5.53
00108-87-2	methylcyclohexane	1.85
00590-73-8	2,2-dimethylhexane	1.20
00107-40-4	2,4,4-trimethyl-2-pentene	5.29
01640-89-7	ethylcyclopentane	2.31
00592-13-2	2,5-dimethylhexane	1.63

CAS #	COMPOUND	MIR
03221-61-2	2-methyloctane	1.14
02216-33-3	3-methyloctane	1.14
00100-42-5	styrene(ethenylbenzene)	2.22
00095-47-6	o-xylene	6.46
00124-11-8	1-nonene	2.23
00111-84-2	n-nonane	0.54
00098-82-8	(1-methylethyl)benzene	2.24
15869-87-1	2,2-dimethyloctane	1.01
04032-94-4	2,4-dimethyloctane	1.01
00103-65-1	n-propylbenzene	2.12
00620-14-4	1-methyl-3-ethylbenzene	7.20
00622~~0~~-96-8	1-methyl-4-ethylbenzene	7.20
00108-67-8	1,3,5-trimethylbenzene	10.12
00611-14-3	1-methyl-2-ethylbenzene	7.20
00095-63-6	1,2,4-trimethylbenzene	8.83
00124-18-5	n-decane	0.47
00538-93-2	(2-methylpropyl)benzene	1.87
00135-98-8	(1-methylpropyl)benzene	1.89
00535-77-3	1-methyl-3-(1-methylethyl)benzene	6.45
005~~7~~26-73-8	1,2,3-trimethylbenzene	8.85
00099-87-6	1-methyl-4-(1-methylethyl)benzene	6.45
00496-11-7	2,3-dihydroindene(indan)	1.06
00527-84-4	1-methyl-2-(1-methylethyl)benzene	6.45
00141-93-5	1,3-diethylbenzene	6.45
00105-05-5	1,4-diethylbenzene	6.45
01074-43-7	1-methyl-3-n-propylbenzene	6.45
01074-55-1	1-methyl-4-n-propylbenzene	6.45
00135-01-3	1,2-diethylbenzene	6.45
01074-17-5	1-methyl-2-n-propylbenzene	6.45
01758-88-9	1,4-dimethyl-2-ethylbenzene	9.07
00874-41-9	1,3-dimethyl-4-ethylbenzene	9.07
00934-80-5	1,2-dimethyl-4-ethylbenzene	9.07
02870-04~~0~~-4	1,3-dimethyl-2-ethylbenzene	9.07
01120-21-4	n-undecane(hendecane)	0.42
00933-98-2	1,2-dimethyl-3-ethylbenzene	9.07
00095-93-2	1,2,4,5-tetramethylbenzene	9.07
03968-85-2	(2-methylbutyl)benzene	1.70
00527-53-7	1,2,3,5-tetramethylbenzene	9.07
~~27138-21-2~~01074-92-6	1-(1,1-dimethylethyl)-2-methylbenzene	5.84
00488-23-3	1,2,3,4-tetramethylbenzene	9.07
00538-68-1	n-pentylbenzene	1.70

CAS #	COMPOUND	MIR
00098-19-1	1-(1,1-dimethylethyl)-3,5-DMbenzene	7.50
00091-20-3	naphthalene	1.18
00112-40-3	n-dodecane	0.38
	Carbonyl Compounds	
00050-00-0	formaldehyde	7.15
00075-07-0	acetaldehyde	5.52
00107-02-8	acrolein	6.77
00067-64-1	acetone	0.56
00123-38-6	propionaldehyde	6.53
00123-72-8	butyraldehyde	5.26
00066-25-1	hexanaldehyde	3.79
00100-52-7	benzaldehyde	-0.55
00078-93-3	methyl ethyl ketone (2-butanone)	1.18
00078-85-3	methacrolein	6.77
04170-30-3	crotonaldehyde	5.42
00110-62-3	valeraldehyde	4.41
00620-23-5	m-tolualdehyde	-0.55

List of ~~Light End and Mid Range Hydrocarbons~~ Compounds
(Listed by CAS number)

00050-00-0	formaldehyde
00620-23-5	m-tolualdehyde
00064-17-5	ethanol
00066-25-1	hexanal
00067-56-1	methanol
00067-64-1	acetone
00071-43-2	benzene
00074-84-0	~~ethyane~~ 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
00103-65-1	n-propylbenzene
00104-87-0	p-tolualdehyde
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
00110-62-3	valeraldehyde
00109-66-0	n-pentane
00109-67-1	1-pentene
00110-54-3	n-hexane
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
00123-33-6	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
00563-78-0	2,3-dimethyl-1-butene
00565-59-3	2,3-dimethylpentane
00565-75-3	2,3,4-trimethylpentane
~~00576-73-8~~	~~1,2,3-trimethylbenzene~~
00583-48-2	3,4-dimethylhexane
00584-94-1	2,3-dimethylhexane
00589-34-4	3-methylhexane

00934-80-5	1,2-dimethyl-4-ethylbenzene
~~00992-62-3~~	~~3-methyl-cis-2-pentene~~
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
01120-21-4	n-undecane
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
~~10~~01758-88-9	1,4-dimethyl-2-ethylbenzene
02051-30-1	2,6-dimethyloctane
02091-95-6	2,2,5-trimethylheptane
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
02532-58-3	~~cos~~cis-1,3-dimethylcyclopentane
02738-19-4	2-methyl-2-hexene
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
03968-85-2	(2-methylbutyl)benzene
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	~~1-cis,2-trans,~~ (1a,2a,3b)-1,2,3-trimethylcyclopentane

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.

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

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

Ivol_{e} = total volume of dilute exhaust bubbled through the impingers per test phase corrected to standard conditions (293.16° K and 760 mm Hg), liter.

Ivol_{em} = total volume of dilute exhaust bubbled through the impingers 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°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° K and 760 mm Hg assuming a C:H ratio of 1:1.85 for gasoline; 16.78 g/ft^3 at 293.16° 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° K and 760 mm HG assuming a C:H ratio of 1:3.78 for natural gas; and ~~17.28~~ 17.26 g/ft^3 for LPG at 293.16° 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°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°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° K and 760 mm Hg), ft^3

II. The following list is commonly used measurement abbreviations:
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.