California Environmental Protection Agency
AIR RESOURCES BOARD

# CALIFORNIA NON-METHANE ORGANIC GAS TEST PROCEDURES FOR 2017 AND SUBSEQUENT MODEL YEAR VEHICLES

Adopted: September 2, 2015

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## Part A

## GENERAL APPLICABILITY AND REQUIREMENTS

1. These test procedures shall apply to all 2017 and subsequent model-year vehicles.

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 Emissions

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

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

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

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

Note: Alternatives to direct measurement of carbonyls under certain conditions are presented in the "California 2015 and Subsequent Model Criteria Pollutant Exhaust Emission Standards and Test Procedures and 2017 and Subsequent Model Greenhouse Gas Exhaust Emission

Standards and Test Procedures for Passenger Cars, Light-duty Trucks, and Medium-duty Vehicles," Section D.1.10.

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) |

Note: NMHC by GC is included for research purposes only, should any lab wish to speciate the hydrocarbons in the emissions. Its use is not mandated by these test procedures.

4. For natural gas-fueled vehicles, the methane concentration in the exhaust sample shall be measured with a methane analyzer. A GC combined with a FID is used for direct measurement of methane concentrations. SAE Recommended Practice J1151 [Ref. 4] 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 NMOG emissions as specified in the "California 2015 and Subsequent Model Criteria Pollutant Exhaust Emission Standards and Test Procedures and 2017 and Subsequent Model Greenhouse Gas Exhaust Emission Standards and Test Procedures for Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles," incorporated by reference in Section 1961.2, title 13, California Code of Regulations (CCR).

5. The mass of NMOG emissions shall be calculated in accordance with part G, "Determination of NMOG Emissions" and 40 CFR 1066.635, "NMOG determination" [Ref. 1]. 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. Motor vehicles and/or engines are tested and the results calculated according to 40 CFR Parts 86 [Ref. 2], 1065 [Ref. 3], and 1066 [Ref. 1], as applicable.

2. The above procedures describe a method for determining NMHC exhaust mass emissions from motor vehicles.

3. 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.

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

## 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 source samples for alcohols

1.2 This procedure is based on a method developed by the U. S. Environmental Protection Agency, (U.S. EPA) [Ref. 5] which involves flowing diluted engine exhaust through deionized or purified water contained in glass impingers and analyzing this solution by gas chromatography.

1.3 The "target" alcohols (compounds of interest) that shall be measured by this method are methanol and ethanol in the range of 1 to 1200 µg per 15 mL of impinger solution. These alcohols, when measured in concentrations above the LOD, shall be reported.

1.3.1 For the purpose of calculating NMOG for vehicles tested on exhaust emission test fuel containing ethanol (see Part G, Determination of NMOG Mass Emissions):

1.3.1.1 The only alcohol that needs to be reported from this method is ethanol.

1.3.1.2 The analysis of methanol is also within the scope of this analytical method and its measurement may provide meaningful information to the laboratory. However, its measurement is not required.

1.4 Other applicable forms of instrumentation and analytical techniques may be used if shown to yield results equivalent to those specified in this procedure and if approved in advance by the Executive Officer of the Air Resources Board.

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

### 2. METHOD SUMMARY

2.1 The samples are received by the laboratory in impingers. Compound separation and analysis are performed using a GC. The sample is injected into the GC by means of a liquid autosampler. Separation of the sample mixture into its

components is performed by a temperature-programmed capillary column. A FID is used for alcohol detection and quantification.

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

## 3. INTERFERENCES AND LIMITATIONS

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

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

3.3 To avoid sample loss and/or contamination, samples should be analyzed or transferred from the impingers to tightly sealed storage bottles as soon as possible after collection.

## 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 type column [typically 30 m, 0.53 mm ID (Megabore), 1.0 µ film thickness] and FID, is used. Other columns may be used, provided the alternate(s) can be demonstrated to the ARB to be equivalent or better with respect to precision, accuracy and resolution of all the target alcohols.

4.1.2 A liquid injection autosampler is required.

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

## 5. REAGENTS AND MATERIALS

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

5.2 Ethanol shall be absolute, ACS reagent grade.

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

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

5.4.1 A **calibration standard** within the expected concentration range of the samples is prepared by successive dilutions of the stock solution with deionized or purified water.

5.4.1.1 Typical calibration standards range from 3 to 100 µg/mL for exhaust emission testing, depending on fuel type.

5.4.1.2 Evaporative emission testing may require calibration standards as high as 1000 µg/mL due to higher sample concentration.

5.4.1.3 Calibration standards must be replaced frequently to avoid degradation of the standard. Standards with concentrations of 100 µg/mL or less should be replaced weekly.

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

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

5.4.4 Standards may also be purchased (e.g., NIST).

5.4.5 All standards should be refrigerated at a temperature below 40$^{o}$F during storage.

5.5 Gas requirements.

5.5.1 Air shall contain less than 50 ppbC hydrocarbon contamination.

5.5.2 Nitrogen shall have a minimum purity of 99.998 percent.

5.5.3 Helium shall have a minimum purity of 99.995 percent.

5.5.4 Hydrogen shall have a minimum purity of 99.995 percent.

## 6. PROCEDURE

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

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

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

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

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

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

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

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

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

## 7. CALCULATIONS

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

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

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

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

7.2 Sample batches that span a broad concentration range (several orders of magnitude) should use more than one calibration level.

7.2.1 Each sample concentration would then be calculated by using a standard of similar concentration to calculate the response factor, as in Section 7.1.

7.2.2 A multipoint calibration curve calculated by the GC software (e.g., Varian Star 6.0) may be used instead of the one-point calibration described in Section 7.1.

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

Mass (µg) = Concentration (µg/mL) x Impinger volume (mL)

7.4 An internal standard method may also be used.

## 8. QUALITY CONTROL

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

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

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

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

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

1. Obtain at least 20 daily control standard results;

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

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

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

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

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

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

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

8.6 Linearity - A multipoint calibration to confirm instrument linearity is performed for all target alcohols for new instruments, after making instrument modifications that can affect linearity, and at least once every year. The multipoint calibration consists of at least five concentration or mass loading levels, each above the LOD,

distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one point calibrations.

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

$$s = s_a \div m$$

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

The LOD must be calculated using the following equation:

$$LOD = t * s$$

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

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

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

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

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

## Part D

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

## METHOD NO. 1002

### 1. INTRODUCTION

1.1 This document describes a gas chromatographic method of measuring $C_2$ to $C_5$ hydrocarbons (light-end hydrocarbons) in the ppbC range from automotive source samples. This method does not include sample collection procedures.

1.2 This test method is included for research purposes only, should any lab wish to speciate the hydrocarbons in the emissions. Its use is not mandated by these test procedures.

1.3 The "target" hydrocarbons (compounds of interest) that are typically analyzed and reported by this method and Method 1003 are listed in Appendix 1. All compounds on this list, when measured in concentrations above the LOD, should be measured and reported ("targeted") by either Method 1002 or Method 1003. Each laboratory should divide the list into light-end (Method 1002) and mid-range (Method 1003) hydrocarbons in the manner that best suits the laboratory instrumentation. All compounds on the list not targeted by Method 1002 should be targeted by Method 1003.

1.4 Other applicable forms of instrumentation and analytical techniques can be used. For optimal results, an alternative method should yield results equivalent to those specified in this procedure.

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

### 2. METHOD SUMMARY

2.1 This is a method intended for routine analysis.

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

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

2.4 The sample is injected into the GC by means of gas sampling valves. Separation of the sample hydrocarbon mixture into its components takes place in the chromatographic column. The chromatographic column and the corresponding

operating parameters described in this method normally provide complete resolution of most target compounds.

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

## 3. INTERFERENCES AND LIMITATIONS

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

3.2 Sample bag material should not cause sample loss or contamination.

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

3.3.1 As allowed by Subsection 4.1, other types of sample collection materials or containers may be used. If so, sample stability must be investigated and an appropriate maximum allowable sample holding time set.

## 4. INSTRUMENTS AND APPARATUS

4.1 Sample collection bags, nominally 5 to 10 liters in capacity and equipped with quick-connect fittings, are typically used to contain the samples. Sample collection bags may be made of Tedlar® (polyvinylfluoride, or PVF), 2 mil in thickness, or of Kynar® or Solef® (polyvinylidenefluoride, or PVDF), each 4 mil in thickness. Other sample bag material or sample collection containers, such as nickel-coated stainless steel canisters, may be used, provided they are made of non-reactive material and do not cause sample loss or contamination.

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

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

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

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

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

## 5. REAGENTS AND MATERIALS

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

5.2 Hydrogen shall have a minimum purity of 99.995 percent.

5.3 Air shall contain less than 50 ppbC hydrocarbon contamination.

5.4 Nitrogen shall have a minimum purity of 99.998 percent.

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

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

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

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

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

NIST-traceable.) This verification can be performed at the laboratory performing the analysis.

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

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

## 6. PROCEDURE

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

6.2 Typical standard operating conditions for the automated gas chromatograph are:

| | |
|---|---|
| Helium carrier gas flow: | 2.2 mL/min at 200°C |
| Detector (0.010" FID) | |
| Temperature: | 250°C or higher |
| Nitrogen make-up gas flow: | sufficient such that the total flow of helium plus nitrogen is 25 mL/min |
| Hydrogen gas flow: | 25 mL/min |
| Air flow: | 300 mL/min |
| Range 12, attenuation 8 (or another suitable value) | |
| Sample loop/valve temperature: | 150°C (PLOT column) |
| Cryotrap temperature: | -180°C (hold to trap hydrocarbons)<br>200°C (heat to release) hydrocarbons) |
| Precolumn oven temperature: | 50°C |
| Analytical column valve oven temperature: | 150°C |
| Column Temperature Program: | 0°C (hold 7 min)<br>5°C/min to 200°C<br>200°C (hold 35 min) |

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

6.3.1 Samples may be injected manually by injecting an aliquot with a ground glass syringe.

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

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

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

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

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

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

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

6.11 The Alumina PLOT column is programmed to 200$^{o}$C to assure all compounds are eluted before the next run.

## 7. CALCULATIONS

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

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

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

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

## 8. QUALITY CONTROL

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$s = s_a \div m$$

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

The LOD must be calculated using the following equation:

$$LOD = t * s$$

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

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

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

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

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

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

## Part E

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

## METHOD NO. 1003

### 1. INTRODUCTION

1.1 This document describes a gas chromatographic method of measuring $C_6$ to $C_{12}$ hydrocarbons (mid-range hydrocarbons) in the ppbC range from automotive source samples. This method does not include sample collection procedures.

1.2 This test method is included for research purposes only, should any lab wish to speciate the hydrocarbons in the emissions. Its use is not mandated by these test procedures.

1.3 The target hydrocarbons (compounds of interest) that are typically analyzed and reported by this method and Method 1002 are listed in Appendix 1. All compounds on this list, when measured in concentrations above the LOD, should be measured and reported ("targeted") by either Method 1002 or Method 1003. Each laboratory should divide the list into light-end (Method 1002) and mid-range (Method 1003) hydrocarbons in the manner that best suits the laboratory instrumentation. All compounds on the list not targeted by Method 1003 should be targeted by Method 1002.

1.4 Other applicable forms of instrumentation and analytical techniques can be used. For optimal results, an alternative method should yield results equivalent to those specified in this procedure.

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

### 2. METHOD SUMMARY

2.1 This is a method intended for routine analysis.

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

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

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

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

## 3. INTERFERENCES AND LIMITATIONS

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

3.2 Sample bag material should not cause sample loss or contamination.

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

3.3.1 As allowed by Section 4.1, other types of sample collection materials or containers may be used. If so, sample stability must be investigated and an appropriate maximum allowable sample holding time set.

## 4. INSTRUMENTATION AND APPARATUS

4.1 Sample collection bags, nominally 5 to 10 liters in capacity and equipped with quick-connect fittings, are typically used to contain the samples. Sample collection bags may be made of Tedlar® (polyvinylfluoride, or PVF), 2 mil in thickness, or of Kynar® or Solef® (polyvinylidenefluoride, or PVDF), each 4 mil in thickness. Other sample bag material or sample collection containers, such as nickel-coated stainless steel canisters, may be used, provided they are made of non-reactive material and do not cause sample loss or contamination.

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

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

4.4 A non-polar capillary column [e.g., Varian DB-1 (methylsiloxane), typically 60 m x 0.32 mm ID, film thickness 1.0 µ] is used. Other columns may be used, provided the alternate(s) can be demonstrated to the ARB to be equivalent or

better with respect to precision, accuracy and resolution of all the target hydrocarbons.

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

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

## 5. REAGENTS AND MATERIALS

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

5.2 Hydrogen shall have a minimum purity of 99.995 percent.

5.3 Air shall contain less than 50 ppbC hydrocarbon contamination.

5.4 Nitrogen shall have a minimum purity of 99.998 percent.

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

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

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

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

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

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

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

## 6. PROCEDURE

6.1 The gaseous sample is analyzed for the target hydrocarbons $C_5$ through $C_{12}$.

6.2 Typical operating conditions for the automated GC are:

| | |
|---|---|
| Helium carrier gas flow flow: | 2.2 mL/min at 200$^{o}$C |
| Detector (0.010" FID) | |
| Temperature: | 275$^{o}$C or higher |
| Nitrogen make-up gas flow: | sufficient such that the total flow of helium plus nitrogen is 25 mL/min |
| Hydrogen gas flow (for FID): | 25 mL/min |
| "Zero" air gas flow (for FID): | 300 mL/min |
| Range 12, attenuation 8 (or another suitable value) | |
| Autosampler valve temperature: | 150$^{o}$C |
| Cryotrap temperature: | -180$^{o}$C (hold to trap hydrocabons)<br>200$^{o}$C (heat to release hydrocarbons) |
| Analytical column valve oven temperature: | 150$^{o}$C |
| Column temperature program: | -40$^{o}$C (hold 2.5 min)<br>3.6$^{o}$C/min to 210$^{o}$C<br>210$^{o}$C (hold 5 min) |

6.2.1 Samples may be injected manually by injecting an aliquot with a ground glass syringe.

6.3 Data Reduction

6.3.1 The results are calculated from the FID responses.

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

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

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

1. The relative retention indices from GC/MS analyses are used to help confirm peak identifications.

2. The primary peak identification is done by the computer using the relative retention times based on reference calibration runs.
3. Confirm that the relative peak heights of the sample run ("fingerprint") match the typical fingerprint seen in past sample runs.
4. Compare the relative retention times of the sample peaks with those of reference runs.
5. Any peak with a reasonable doubt is labeled 'Unidentified'.

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

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

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

## 7. CALCULATIONS

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

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

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

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

## 8. QUALITY CONTROL

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

concentration of all organic compounds except methane and propane below 2 percent of the propane standard concentration. The weekly blank run will provide a check on contamination in the propane region of the chromatograph.

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

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

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

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

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

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

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

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

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

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

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

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

8.7 Limit of Detection - The LOD for the target hydrocarbons in the control standard must be determined for new instruments and after making instrument modifications that can affect linearity and/or sensitivity and at least once every year unless a daily check of the instrument response indicates that the LOD has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in Section 8.4, except using calibration standard area counts rather than control standard concentrations. When the calibration standard area counts are out-of-control, investigation and/or corrective action(s) must be taken. To make the calculations, it is necessary to perform a multipoint

calibration consisting of at least four "low" concentration levels, each above the LOD, with at least five replicate determinations of the lowest concentration standard. A linear regression is performed and the standard deviation (in area counts) of the lowest concentration standard determined. The standard deviation is converted to concentration units using the slope of the linear regression:

$$s = s_a \div m$$

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

The LOD must be calculated using the following equation:

$$LOD = t * s$$

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

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

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

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

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

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

criteria set for the relative percent difference.

## Part F

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

## METHOD NO. 1004

## 1. INTRODUCTION

1.1 This document describes a method of analyzing automotive source samples 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 (compounds of interest) that shall be measured and reported by this method are listed in Appendix 1. All of these carbonyl compounds, when measured in concentrations above the LOD, shall be reported.

1.1.1 For the purpose of calculating NMOG for vehicles tested on exhaust emission test fuel containing ethanol (see Part G, Determination of NMOG Mass Emissions):

1.1.1.1 The only carbonyl compounds that need to be reported from this method are formaldehyde and acetaldehyde.

1.1.1.2 The additional carbonyls listed in Appendix 1 are within the scope of this analytical method and their measurement may provide meaningful information to the laboratory. However, their measurement is not required.

1.2 Other applicable forms of instrumentation and analytical techniques may be used if shown to yield results equivalent to those specified in this procedure and if approved in advance by the Executive Officer of the Air Resources Board.

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 DNPH reagent complexes the carbonyl compounds into their diphenylhydrazone derivatives. The cartridges are then extracted with acetonitrile.

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

## 3. INTERFERENCES AND LIMITATIONS

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

3.2 If samples are not analyzed the same day as received, they must be refrigerated at a temperature below 40$^{o}$F.

3.2.1 Impinger solutions must first be transferred to glass bottles and sealed.

3.2.2 If cartridges are not immediately extracted they must be refrigerated.

3.2.3 Acrolein and crotonaldehyde have been shown to degrade in acidified DNPH cartridges; hence, it is recommended to extract the cartridges as soon as possible. The extract must be refrigerated.

3.2.4 Refrigerated cartridge sample extracts and impinger solutions are stable for up to 30 days.

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

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

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

$$\text{\% of excess DNPH in sample cartridge} = \frac{\text{DNPH area counts, sample}}{\text{DNPH area counts, blank}} \times 100$$

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

## 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 system incorporates two LC-18 columns (e.g., Supelco's Supelcosil, typically 25cm x 4.6mm, 5µ silica gel particles) in tandem and a guard column (e.g., Supelco's Pelliguard, 2 cm long packed with LC18 5 µm pellicular beads). Other columns may be used, provided the alternate(s) can be demonstrated to the ARB 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 Samples are collected in glass impingers or DNPH-impregnated cartridges.

## 5. REAGENTS AND MATERIALS

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

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

5.3 Methanol, HPLC grade (Burdick and Jackson or equivalent).

5.4 Acidified DNPH-Silica cartridges (Waters Corp. or equivalent).

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

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

5. 7 The carbonyl/DNPH complexes listed in Table F1 may be purchased (e.g., Radian Corporation, in 1.2 mL ampules) or prepared in the laboratory. In-house standards must be recrystallized at least three times from 95 percent ethanol.

TABLE F-1
PROPERTIES OF CARBONYL/DNPH COMPLEXES

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

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

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

5.10 Control Standard - A quality control standard, containing all target carbonyls/DNPH complexes within the typical concentration range of real samples, is analyzed to monitor the precision of the analysis of each target carbonyl. The control standard may be purchased, prepared in the laboratory from a stock solution different from the calibration standard, or prepared by batch mixing old samples, spiking it with a stock solution of target compounds, and stirring for a minimum of 2 hours. If necessary, the solution is filtered using filter paper to remove precipitation. All target compounds except acrolein have been found to be stable in the control standard.

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

[1]This compound has been shown to decompose.

## 6. PROCEDURE

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

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

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

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

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

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

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

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:

Typical System:

| | |
|---|---|
| Columns: | Supelco Supelcosil (LC-18, 25cm x 4.6mm, 5µm silica gel particles), two columns in series, and a Supelco Pelliguard guard column (2 cm long packed with C18 5 µm pellicular beads) |
| Column temperature: | 40°C |
| Detector: | UV/VIS at 360 nm |
| Sample volume: | 10 µL |
| Solvent A: | acetonitrile |
| Solvent B: | methanol |
| Solvent C: | water |
| Flow: | 1.2 mL/min |

Program:

| | |
|---|---|
| 50 percent A, 5 percent B, 45 percent C | 0 (initial time) |
| 65 percent A, 3.5 percent B, 31.5 percent C | 0 to 30 min (linear ramp) |
| 100 percent A, 0 percent B, 0 percent C | 30 to 40 min (linear ramp) |
| 100 percent A, 0 percent B, 0 percent C | 40 to 42 min (hold) |
| 50 percent A, 5 percent B, 45 percent C | 42 to 45 min (linear ramp) |

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

6.7 If all target compounds are not separated using this configuration, a second HPLC with a different configuration must be used, in addition to the primary system, to separate the coeluting compounds.

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

## 7. CALCULATIONS

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

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

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

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

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

Note that the cartridge volume, analogous to the impinger volume, is the elution volume defined in Section 6.3.1.1.

7.3 For tolualdehyde, the sum of all isomers present is reported as m-tolualdehyde. Under the conditions of the system described in Section 6.6, the isomers coelute. The m-tolualdehyde response factor is applied to the single tolualdehyde peak. This concentration is reported as m-tolualdehyde.

7.4 An internal standard method may also be used.

## 8. QUALITY CONTROL

8.1 Blank Runs

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

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

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

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

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

8.3 Control Standard Run - The quality control standard is analyzed at least once each analysis day. Measurements of all target compounds in the control standard, except acrolein, must fall within the control limits to ensure the validity of the

sample analyses that day. To meet this requirement, it may be necessary to rerun the calibration and control standards, and inspect and repair the HPLC.

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

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

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

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

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

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 may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

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

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

$$s = s_a \div m$$

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

The LOD must be calculated using the following equation:

$$LOD = t * s$$

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

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

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

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

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

# Part G
# DETERMINATION OF NMOG EMISSIONS

## 1. INTRODUCTION

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

1.2 The mass of NMOG emissions in g/mile or mg/mile shall be calculated by summing the mass of NMHC, the mass of aldehydes and ketones, and the mass of alcohols.

1.3 This section addresses emissions, in concentration units, of each test phase. Calculations to use those concentrations to determine NMOG mass emissions for FTP testing are given in 40 CFR Part 1066, Section 1066.635, "NMOG determination."

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

## 2. NMOG WEIGHTED MASS EMISSIONS

2.1 Non-methane hydrocarbon weighted mass emissions ($NMHC_{wm}$) can be determined by either FID or GC. The GC method is included for research purposes only, should any lab wish to speciate the hydrocarbons in the emissions. Its use is not mandated by these test procedures.

2.1.1 FID Method

2.1.1.1 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," and 40 CFR Part 1065, subpart G.

2.1.1.2 If the FID method is used to determine the non-methane hydrocarbon weighted mass emissions, the NMHC sample measurement includes contributions from any oxygenated hydrocarbons that may be present in the sample. Therefore, the FID NMHC measurement must be corrected for the presence of alcohols and carbonyl compounds, to give a resultant value called non-oxygenated non-methane hydrocarbons (NONMHC). This correction is performed according to 40 CFR Part 1065, subpart G.

2.1.2 GC Method

2.1.2.1 Individual hydrocarbon concentrations ($HC_{conc}$) are determined by GC according to Section 4, "Speciated Hydrocarbon Mass Emissions Calculation," contained herein.

2.1.2.2 The individual concentrations are converted to mass according to 40 CFR Part 1066, Sub-part G, Section 1066.605, equation 1066.605-1 and summed.

2.1.2.3 In the GC method, the hydrocarbons are each measured individually and, therefore, the sum of species ($\sum HC$) does not include methane or oxygenated compounds. Thus, this method does not need the corrections that the FID method requires.

2.2 Alcohols

2.2.1 Individual alcohol concentrations ($ROH_{conc}$) are determined by GC according to Section 5, "Alcohol Mass Emissions Calculation," contained herein.

2.2.2 The individual concentrations are converted to mass according to 40 CFR Part 1066, Sub-part G, Section 1066.605, equation 1066.605-1.

2.3 Carbonyls

2.3.1 Individual carbonyl concentrations ($RHO_{conc}$) are determined by HPLC according to Section 6, "Carbonyl Mass Emissions Calculation," contained herein.

2.3.2 The individual concentrations are converted to mass according to 40 CFR Part 1066, Sub-part G, Section 1066.605, equation 1066.605-1.

2.4 Dilution factors are determined according to 40 CFR Part 1066, subpart G, Section 1066.610, equation 1066-610-2.

2.5 NMOG weighted mass emission calculations are given in 40 CFR Part 1066, Section 1066.635.

## 3. SPECIATED HYDROCARBON EMISSIONS CALCULATION

### 3.1 INTRODUCTION

Vehicular exhaust emissions are measured according to the FTP [Ref. 1, 2 and/or 3, as applicable]. For each of the three phases of the FTP, a sample collection bag, nominally 5 to 10 liters in capacity, is used to collect a dilute exhaust sample. Sample collection bags may be made of Tedlar®

(polyvinylfluoride, or PVF), 2 mil in thickness, or of Kynar® or Solef® (polyvinylidenefluoride, or PVDF), each 4 mil in thickness. A fourth bag is used to collect a composite dilution air (background) sample from all three phases of the FTP. Since PVF and PVDF films contain plasticizer or volatile organic components, all of the films are conditioned in a vented oven at 250°F for 16 hours before made into sample bags. Other sample bag material or sample collection containers, such as nickel-coated stainless steel canisters, may be used, provided they are made of non-reactive material and do not cause sample loss or contamination. 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 emissions of each hydrocarbon compound.

## 3.2 HC EMISSIONS CALCULATION PER TEST PHASE

3.2.1 For each hydrocarbon measured, the equations below and in 40 CFR Part 1066 are used to calculate the hydrocarbon mass emission over the test interval.

3.2.1.1 $HC_{conc} = HC_e - (HC_d * (1 - (1 / DF)))$

NOTE: If $HC_{conc}$ is calculated to be less than zero, then $HC_{conc} = 0$.

3.2.1.2 $HC_{dens}$ = (Mol. Wt. * conversion of liter to $ft^3$) / (Mol. Vol.)

3.2.1.3 The dilution factor, DF, is calculated according to 40 CFR Part 1066, Section 1066.610, equation 1066-610-2.

3.2.1.4 The resultant values are used to determine the individual hydrocarbon mass emission according to 40 CFR Part 1066, equation 1066.605-1.

3.2.2 The individual hydrocarbons are summed:

$$m_{NMHC} = \sum_{i}^{N} HC$$

3.2.3 This value is then used in 40 CFR Part 1066, Section 1066.635, to determine NMOG.

## 3.3 SAMPLE CALCULATION

3.3.1 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 Phase 1 benzene emissions based on the following data:

| Test Phase | $HC_e$ (ppbC) | $HC_d$ (ppbC) |
|---|---|---|
| 1 | 500 | 25 |
| 2 | 100 | 25 |
| 3 | 120 | 25 |

For Phase 1:

DF = 10.89 (as calculated in 40 Part CFR 1066, Section 1066.610, equation 1066-610-2.)

$HC_{conc}$ = $HC_e$ - ($HC_d$ * (1 - (1 / DF)))
= 500 ppbC - (25 ppbC * (1 - (1 / 10.89)))
= 477 ppbC

Mol. Wt. of $C_6H_6$ = (6 * 12.0107) + (6 * 1.00794)
= 78.1118 g/mole

$HC_{dens}$ = (Mol. Wt. * conversion of liter to $ft^3$) / (Mol. Vol.)
= (78.1118 g/mole * 28.3168 liter/$ft^3$) / 24.055 liter/mole
= 91.951 g/$ft^3$

3.3.2 $HC_{conc}$ and $HC_{dens}$ are then inserted into 40 CFR Part 1066, equation 1066.605-1 to yield the mass of the individual hydrocarbon.

3.3.3 The masses of the individual hydrocarbons are then summed and used in 40 CFR Part 1066, Section 1066.635, to determine NMOG.

## 4. ALCOHOL EMISSIONS CALCULATION

### 4.1. INTRODUCTION

Vehicular emissions are measured according to the FTP [Ref. 1, 2 and/or 3, as applicable]. 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 emissions of alcohol compounds.

## 4.2. ALCOHOL EMISSIONS CALCULATION PER TEST PHASE

4.2.1 For each alcohol measured, the equations below and in 40 CFR Part 1066 are used to calculate the alcohol mass emission over the test interval.

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

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

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

4.2.5 $Ivol_e = Ivol_{em} * (293.15 K / Itemp_e) * ( P_B / 760 mm Hg)$

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

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

4.2.8 $Ivol_d = Ivol_{dm} * (293.15 K / Itemp_d) * (P_B / 760 mm Hg)$

4.2.9 $ROH_{dens} = (Mol. Wt. * conversion of liter to ft^3) / (Mol. Vol.)$

4.2.10 The DF is calculated according to 40 CFR Part 1066, Section 1066.610, equation 1066-610-2.

4.2.11 The resultant values are used to determine the individual alcohol mass emission according to 40 CFR Part 1066, equation 1066.605-1.

4.2.12 The individual alcohol mass emission is then used in 40 CFR Part 1066, Section 1066.635, to determine NMOG.

## 4.3 SAMPLE CALCULATION

4.3.1 Alcohol emissions from an E85 fueled vehicle are collected in three sets of dilute exhaust impingers and one set of dilution air impingers during the FTP. Gas chromatography is used to determine the alcohol concentration in each impinger. This is the same vehicle test as the example in Section 3.3. Calculate the Phase 1 ethanol emissions based on the following data, along with the data presented in Section 3.3:

| Test Phase | $Ivol_r$ (mL) | $Iconc_{e1}$ (µg/mL) | $Iconc_{e2}$ (µg/mL) | $Ivol_{em}$ (liter) | $Iconc_{d1}$ (µg/mL) | $Iconc_{d2}$ (µg/mL) | $Ivol_{dm}$ (liter) | $Itemp_e$ (K) | $Itemp_d$ (K) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 15 | 4.984 | 0.106 | 8.18 | 0 | 0 | 31.16 | 294.26 | 294.26 |
| 2 | 15 | 0 | 0 | 14.65 | 0 | 0 | 31.16 | 294.26 | 294.26 |
| 3 | 15 | 0 | 0 | 8.67 | 0 | 0 | 31.16 | 294.26 | 294.26 |

| Test Phase | DF | $P_B$ (mm HG) |
|---|---|---|
| 1 | 14.27 | 760 |
| 2 | 22.15 | 760 |
| 3 | 17.33 | 760 |

Ethanol

For Phase 1:

$Imass_e$ = ($Iconc_{e1}$ + $Iconc_{e2}$) * $Ivol_r$
= (4.984 µg/mL + 0.106 µg/mL) * 15 mL
= 76.35 µg

Mol. Wt. of $C_2H_5OH$ = (2 * 12.0107) + (6 * 1.00794) + (1 * 15.9994)
= 46.0684 g/mole

$Ivol_e$ = $Ivol_{em}$ * (293.15$^o$ K / $Itemp_e$ ) * ($P_B$ / 760 mm Hg)
= 8.18 liter * (293.15$^o$ K / 294.26 K) * (760 mm Hg / 760 mm Hg)
= 8.15 liters

$ROH_e$ = ($Imass_e$ / $Ivol_e$ ) * (Mol. Vol. / Mol. Wt.)
= (76.35 µg / 8.15 liter) * (24.055 liter/mole / 46.0684 g/mole)
= 4.89 ppm

$Imass_d$ = ($Iconc_{d1}$ + $Iconc_{d2}$) * $Ivol_r$
= (0 µg/mL + 0µg/mL) * 15 mL
= 0 µg

$Ivol_d$ = $Ivol_{dm}$ * (293.15$^o$ K / $Itemp_d$ ) * ( $P_B$ / 760 mm Hg)
= 31.16 liter * (293.15$^o$ K / 294.26 K) * (760 mm Hg / 760 mm Hg)
= 31.04 liters

$ROH_d$ = ($Imass_d$ / $Ivol_d$) * (Mol. Vol. / Mol. Wt.)
= (0 µg / 31.46 liter) * (24.055 liter/mole / 46.0684 g/mole)
= 0 ppm

DF = 14.2688 (as calculated in 40 Part CFR 1066, Section 1066.610, equation 1066-610-2)

$ROH_{conc}$ = $ROH_e$ - ($ROH_d$ * (1 - (1 / DF)))
= 4.89 ppm - (0 ppmC * (1 - (1 / 14.27)))
= 4.89 ppm

$ROH_{dens}$ = (Mol. Wt. * conversion of liter to $ft^3$) / (Mol. Vol.)
= (46.0684 g/mole * 28.3168 liter/$ft^3$) / 24.055 liter/mole
= 54.2303 g/$ft^3$

4.3.2 $ROH_{conc}$ and $ROH_{dens}$ are then inserted into 40 CFR Part 1066, equation 1066.605-1 to yield the mass of the individual alcohol.

4.3.3 The mass of the individual alcohol is then used in 40 CFR Part 1066, Section 1066.635, to determine NMOG.

## 5. CARBONYL EMISSIONS CALCULATIONS

### 5.1. INTRODUCTION

Vehicular emissions are measured according to the FTP [Ref. 1, 2 and/or 3, as applicable]. 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 emissions of each carbonyl compound.

### 5.2. CARBONYL EMISSIONS CALCULATION PER TEST PHASE

5.2.1 For each carbonyl measured, the equations below and in 40 CFR Part 1066 are used to calculate the carbonyl mass emission over the test interval.

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

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

5.2.4 $Imass_e$ = $Iconc_{ce}$ * $Ivol_c$

5.2.5 $Ivol_e$ = $Ivol_{em}$ * (293.15 K / $Itemp_e$) * ($P_B$ / 760 mm Hg)

5.2.6 $RHO_d$ = ($Imass_d$ / $Ivol_d$) * (Mol. Vol. / Mol. Wt.)

5.2.7 $Imass_d$ = $Iconc_{cd}$ * $Ivol_c$

5.2.8 $Ivol_d$ = $Ivol_{dm}$ * (293.15 K / $Itemp_d$) * ($P_B$ / 760 mm Hg)

5.2.9 $RHO_{dens}$ = (Mol. Wt. * conversion of liter to $ft^3$) / (Mol. Vol.)

5.2.10 The DF is calculated according to 40 CFR Part 1066, Section 1066.610, equation 1066-610-2.

5.2.11 The resultant values are used to determine the individual carbonyl mass emission according to 40 CFR Part 1066, equation 1066.605-1.

5.2.12 The individual carbonyl mass emission is then used in 40 CFR Part 1066, Section 1066.635, to determine NMOG.

## 5.3 SAMPLE CALCULATION

5.3.1 Carbonyl emissions from an E85 vehicle are collected in three sets of dilute exhaust impingers and one set of dilution air impingers during the FTP. HPLC is used to determine the carbonyl mass in each impinger. This is the same vehicle test as the example in Section 3.3. Calculate the Phase 1 formaldehyde emissions based on the following data, along with the data presented in Section 3.3:

| Test Phase | $Ivol_c$ (mL) | Formaldehyde | | $Ivol_{em}$ (liter) | Acetaldehyde | | $Ivol_{dm}$ (liter) | $Itemp_e$ (K) | $Itemp_d$ (K) |
|---|---|---|---|---|---|---|---|---|---|
| | | $Iconc_{ce}$ (µg/mL) | $Iconc_{cd}$ (µg/mL) | | $Iconc_{ce}$ (µg/mL) | $Iconc_{cd}$ (µg/mL) | | | |
| 1 | 4.4 | 0.387 | 0.006 | 8.47 | 4.114 | 0.006 | 8.23 | 294.26 | 294.26 |
| 2 | 4.4 | 0.048 | 0.016 | 15.35 | 0.013 | 0.009 | 13.88 | 294.26 | 294.26 |
| 3 | 4.4 | 0.016 | 0.006 | 9.01 | 0.012 | 0.005 | 8.16 | 294.26 | 294.26 |

| Test Phase | DF | $P_B$ (mm HG) |
|---|---|---|
| 1 | 14.27 | 760 |
| 2 | 22.15 | 760 |
| 3 | 17.33 | 760 |

Formaldehyde

For Phase 1:

$Imass_e$ = $Iconc_{ce}$ * $Ivol_c$
= 0.387 µg/mL * 4.4 mL
= 1.70 µg

Mol. Wt. of HCHO = (1 * 12.0107) + (2 * 1.00794) + (1 * 15.9994)

$= 30.0260$ g/mole

$Ivol_e = Ivol_{em} * (293.15^o K / Itemp_e) * (P_B / 760 mm Hg)$
$= 8.47$ liter $* (293.15^o K / 294.26^o K) * (760 mm Hg / 760 mm Hg)$
$= 8.44$ liter

$RHO_e = (Imass_e / Ivol_e) * (Mol. Vol. / Mol. Wt.)$
$= (1.70 \mu g / 8.44 liter) * (24.055 liter/mole / 30.0260 g/mole)$
$= 0.16$ ppm

$Imass_d = Iconc_{cd} * Ivol_c$
$= 0.006 \mu g/mL * 4.4 mL$
$= 0.026 \mu g$

$Ivol_d = Ivol_{dm} * (293.15 K / Itemp_d) * (P_B / 760 mm Hg)$
$= 8.23$ liter $* (293.15 K / 294.26 K) * (760 mm Hg / 760 mm Hg)$
$= 8.20$ liter

$RHO_d = (Imass_d / Ivol_d) * (Mol. Vol. / Mol. Wt.)$
$= (0.026 \mu g / 8.20 liter) * (24.055 liter/mole / 30.0260 g/mole)$
$= 0.00254$ ppm

$DF = 14.2688$

$RHO_{conc} = RHO_e - (RHO_d * (1 - (1 / DF)))$
$= 0.162 ppm - (0.00258 ppm * (1 - (1 / 14.27)))$
$= 0.1596$ ppm

$RHO_{dens} = (Mol. Wt. * conversion of liter to ft^3) / (Mol. Vol.)$
$= (30.0260 g/mole * 28.3168 liter/ft^3) / 24.055 liter/mole$
$= 35.35 g/ft^3$

5.3.2 $RHO_{conc}$ and $RHO_{dens}$ are then inserted into equation 1066.605-1 to yield the mass of the individual carbonyl.

5.3.3 The mass of the individual carbonyl is then used in 40 CFR Part 1066, Section 1066.635, to determine NMOG.

## APPENDIX 1

## LIST OF COMPOUNDS

| CAS # | COMPOUND | MIR |
|---|---|---|
| | **Alcohols** | |
| 00067-56-1 | methanol | 0.67 |
| 00064-17-5 | ethanol | 1.53 |
| | **Light End and Mid-Range Hydrocarbons** (Listed in approximate elution order) | |
| 00074-85-1 | ethene | 9.00 |
| 00074-86-2 | ethyne | 0.95 |
| 00074-84-0 | ethane | 0.28 |
| 00115-07-1 | propene | 11.66 |
| 00074-98-6 | propane | 0.49 |
| 00463-49-0 | 1,2-propadiene | 8.45 |
| 00074-99-7 | 1-propyne | 6.72 |
| 00075-28-5 | 2-methylpropane | 1.23 |
| 00115-11-7 | 2-methylpropene | 6.29 |
| 00106-98-9 | 1-butene | 9.73 |
| 00106-99-0 | 1,3-butadiene | 12.61 |
| 00106-97-8 | n-butane | 1.15 |
| 00624-64-6 | trans-2-butene | 15.16 |
| 00463-82-1 | 2,2-dimethylpropane | 0.67 |
| 00107-00-6 | 1-butyne | 6.11 |
| 00590-18-1 | cis-2-butene | 14.24 |
| 00563-45-1 | 3-methyl-1-butene | 6.99 |
| 00078-78-4 | 2-methylbutane | 1.45 |
| 00503-17-3 | 2-butyne | 16.32 |
| 00109-67-1 | 1-pentene | 7.21 |
| 00563-46-2 | 2-methyl-1-butene | 6.40 |
| 00109-66-0 | n-pentane | 1.31 |
| 00078-79-5 | 2-methyl-1,3-butadiene | 10.61 |
| 00646-04-8 | trans-2-pentene | 10.56 |
| 00558-37-2 | 3,3-dimethyl-1-butene | 5.82 |
| 00627-20-3 | cis-2-pentene | 10.38 |
| 00689-97-4 | 1-buten-3-yne | 10.48 |
| 00513-35-9 | 2-methyl-2-butene | 14.08 |
| 00542-92-7 | 1,3-cyclopentadiene | 6.98 |
| 00075-83-2 | 2,2-dimethylbutane | 1.17 |
| 00142-29-0 | cyclopentene | 6.77 |
| 00691-37-2 | 4-methyl-1-pentene | 5.68 |
| 00760-20-3 | 3-methyl-1-pentene | 6.14 |

| CAS # | COMPOUND | MIR |
|---|---|---|
| 00287-92-3 | cyclopentane | 2.39 |
| 00079-29-8 | 2,3-dimethylbutane | 0.97 |
| 01634-04-4 | 1-methyl-tert-butyl-ether | 0.73 |
| 00691-38-3 | 4-methyl-cis-2-pentene | 8.12 |
| 00107-83-5 | 2-methylpentane | 1.50 |
| 00674-76-0 | 4-methyl-trans-2-pentene | 8.12 |
| 00096-14-0 | 3-methylpentane | 1.80 |
| 00763-29-1 | 2-methyl-1-pentene | 5.26 |
| 00592-41-6 | 1-hexene | 5.49 |
| 00110-54-3 | n-hexane | 1.24 |
| 13269-52-8 | trans-3-hexene | 7.57 |
| 07642-09-3 | cis-3-hexene | 7.61 |
| 04050-45-7 | trans-2-hexene | 8.62 |
| 00616-12-6 | 3-methyl-trans-2-pentene | 13.17 |
| 00625-27-4 | 2-methyl-2-pentene | 11.00 |
| 01120-62-3 | 3-methylcyclopentene | 5.10 |
| 07688-21-3 | cis-2-hexene | 8.31 |
| 00637-92-3 | 1-ethyl-tert-butyl-ether | 2.01 |
| 00922-62-3 | 3-methyl-cis-2-pentene | 12.49 |
| 00590-35-2 | 2,2-dimethylpentane | 1.12 |
| 00096-37-7 | methylcyclopentane | 2.19 |
| 00108-08-7 | 2,4-dimethylpentane | 1.55 |
| 00464-06-2 | 2,2,3-trimethylbutane | 1.11 |
| 07385-78-6 | 3,4-dimethyl-1-pentene | 4.84 |
| 00693-89-0 | 1-methylcyclopentene | 12.49 |
| 00071-43-2 | benzene | 0.72 |
| 03404-61-3 | 3-methyl-1-hexene | 4.41 |
| 00562-49-2 | 3,3-dimethylpentane | 1.20 |
| 00110-82-7 | cyclohexane | 1.25 |
| 00591-76-4 | 2-methylhexane | 1.19 |
| 00565-59-3 | 2,3-dimethylpentane | 1.34 |
| 00110-83-8 | cyclohexene | 5.00 |
| 00589-34-4 | 3-methylhexane | 1.61 |
| 01759-58-6 | trans-1,3-dimethylcyclopentane | 1.94 |
| 02532-58-3 | cis-1,3-dimethylcyclopentane | 1.94 |
| 00617-78-7 | 3-ethylpentane | 1.90 |
| 00822-50-4 | trans-1,2-dimethylcyclopentane | 1.99 |
| 00592-76-7 | 1-heptene | 4.43 |
| 00540-84-1 | 2,2,4-trimethylpentane | 1.26 |
| 14686-14-7 | trans-3-heptene | 6.32 |
| 00142-82-5 | n-heptane | 1.07 |
| 02738-19-4 | 2-methyl-2-hexene | 9.47 |
| 03899-36-3 | 3-methyl-trans-3-hexene | 9.72 |
| 14686-13-6 | trans-2-heptene | 7.14 |
| 00816-79-5 | 3-ethyl-2-pentene | 9.75 |
| 00107-39-1 | 2,4,4-trimethyl-1-pentene | 3.34 |

| CAS # | COMPOUND | MIR |
|---|---|---|
| 10574-37-5 | 2,3-dimethyl-2-pentene | 9.74 |
| 06443-92-1 | cis-2-heptene | 7.16 |
| 00108-87-2 | methylcyclohexane | 1.70 |
| 00590-73-8 | 2,2-dimethylhexane | 1.02 |
| 00107-40-4 | 2,4,4-trimethyl-2-pentene | 6.29 |
| 01640-89-7 | ethylcyclopentane | 2.01 |
| 00592-13-2 | 2,5-dimethylhexane | 1.46 |
| 00589-43-5 | 2,4-dimethylhexane | 1.73 |
| 02815-58-9 | 1,2,4-trimethylcyclopentane | 1.53 |
| 00563-16-6 | 3,3-dimethylhexane | 1.24 |
| 00565-75-3 | 2,3,4-trimethylpentane | 1.03 |
| 00560-21-4 | 2,3,3-trimethylpentane | 1.02 |
| 00108-88-3 | toluene | 4.00 |
| 00584-94-1 | 2,3-dimethylhexane | 1.19 |
| 00592-27-8 | 2-methylheptane | 1.07 |
| 00589-53-7 | 4-methylheptane | 1.25 |
| 00589-81-1 | 3-methylheptane | 1.24 |
| 15890-40-1 | (1a,2a,3b)-1,2,3-trimethylcyclopentane | 1.63 |
| 00638-04-0 | cis-1,3-dimethylcyclohexane | 1.52 |
| 02207-04-7 | trans-1,4-dimethylcyclohexane | 1.47 |
| 03522-94-9 | 2,2,5-trimethylhexane | 1.13 |
| 02613-65-2 | trans-1-methyl-3-ethylcyclopentane | 1.64 |
| 02613-66-3 | cis-1-methyl-3-ethylcyclopentane | 1.64 |
| 00111-66-0 | 1-octene | 3.25 |
| 14850-23-8 | trans-4-octene | 4.81 |
| 00111-65-9 | n-octane | 0.90 |
| 13389-42-9 | trans-2-octene | 6.00 |
| 02207-03-6 | trans-1,3-dimethylcyclohexane | 1.52 |
| 07642-04-8 | cis-2-octene | 4.81 |
| 01069-53-0 | 2,3,5-trimethylhexane | 1.22 |
| 02213-23-2 | 2,4-dimethylheptane | 1.38 |
| 02207-01-4 | cis-1,2-dimethylcyclohexane | 1.41 |
| 01072-05-5 | 2,6-dimethylheptane | 1.04 |
| 01678-91-7 | ethylcyclohexane | 1.47 |
| 00926-82-9 | 3,5-dimethylheptane | 1.56 |
| 00100-41-4 | ethylbenzene | 3.04 |
| 03074-71-3 | 2,3-dimethylheptane | 1.09 |
| 00108-38-3 | m-&p-xylene | 8.45 |
| 02216-34-4 | 4-methyloctane | 0.95 |
| 03221-61-2 | 2-methyloctane | 0.83 |
| 02216-33-3 | 3-methyloctane | 0.99 |
| 00100-42-5 | styrene (ethenylbenzene) | 1.73 |
| 00095-47-6 | o-xylene | 7.64 |
| 00124-11-8 | 1-nonene | 2.60 |
| 00111-84-2 | n-nonane | 0.78 |
| 00098-82-8 | (1-methylethyl)benzene | 2.52 |

| CAS # | COMPOUND | MIR |
|---|---|---|
| 15869-87-1 | 2,2-dimethyloctane | 0.83 |
| 04032-94-4 | 2,4-dimethyloctane | 1.03 |
| 02051-30-1 | 2,6-dimethyloctane | 1.08 |
| 00103-65-1 | n-propylbenzene | 2.03 |
| 00620-14-4 | 1-methyl-3-ethylbenzene | 7.39 |
| 00622-96-8 | 1-methyl-4-ethylbenzene | 4.44 |
| 00108-67-8 | 1,3,5-trimethylbenzene | 11.76 |
| 00611-14-3 | 1-methyl-2-ethylbenzene | 5.59 |
| 00095-63-6 | 1,2,4-trimethylbenzene | 8.87 |
| 00124-18-5 | n-decane | 0.68 |
| 00538-93-2 | (2-methylpropyl)benzene | 2.36 |
| 00135-98-8 | (1-methylpropyl)benzene | 2.36 |
| 00535-77-3 | 1-methyl-3-(1-methylethyl)benzene | 7.10 |
| 00526-73-8 | 1,2,3-trimethylbenzene | 11.97 |
| 00099-87-6 | 1-methyl-4-(1-methylethyl)benzene | 4.44 |
| 00496-11-7 | 2,3-dihydroindene (indan) | 3.32 |
| 00527-84-4 | 1-methyl-2-(1-methylethyl)benzene | 5.49 |
| 00141-93-5 | 1,3-diethylbenzene | 7.10 |
| 00105-05-5 | 1,4-diethylbenzene | 4.43 |
| 01074-43-7 | 1-methyl-3-n-propylbenzene | 7.10 |
| 01074-55-1 | 1-methyl-4-n-propylbenzene | 4.43 |
| 00135-01-3 | 1,2-diethylbenzene | 5.49 |
| 01074-17-5 | 1-methyl-2-n-propylbenzene | 5.49 |
| 01758-88-9 | 1,4-dimethyl-2-ethylbenzene | 7.55 |
| 00874-41-9 | 1,3-dimethyl-4-ethylbenzene | 7.55 |
| 00934-80-5 | 1,2-dimethyl-4-ethylbenzene | 7.55 |
| 02870-04-4 | 1,3-dimethyl-2-ethylbenzene | 10.15 |
| 01120-21-4 | n-undecane (hendecane) | 0.61 |
| 00933-98-2 | 1,2-dimethyl-3-ethylbenzene | 10.15 |
| 00095-93-2 | 1,2,4,5-tetramethylbenzene | 9.26 |
| 01595-11-5 | 1-methyl-2-n-butylbenzene | 4.73 |
| 00527-53-7 | 1,2,3,5-tetramethylbenzene | 9.26 |
| 01074-92-6 | 1-(1,1-dimethylethyl)-2-methylbenzene | 4.73 |
| 00488-23-3 | 1,2,3,4-tetramethylbenzene | 9.26 |
| 00538-68-1 | n-pentylbenzene | 2.12 |
| 00098-19-1 | 1-(1,1-dimethylethyl)-3,5-DMbenzene | 8.02 |
| 00091-20-3 | naphthalene | 3.34 |
| 00112-40-3 | n-dodecane | 0.55 |

| CAS # | COMPOUND | MIR |
|---|---|---|
| | **Carbonyl Compounds** | |
| 00050-00-0 | formaldehyde | 9.46 |
| 00075-07-0 | acetaldehyde | 6.54 |
| 00107-02-8 | acrolein | 7.45 |
| 00067-64-1 | acetone | 0.36 |
| 00123-38-6 | propionaldehyde | 7.08 |
| 00123-72-8 | butyraldehyde | 5.97 |
| 00066-25-1 | hexanaldehyde | 4.35 |
| 00100-52-7 | benzaldehyde | 0.00 |
| 00078-93-3 | methyl ethyl ketone (2-butanone) | 1.48 |
| 00078-85-3 | methacrolein | 6.01 |
| 04170-30-3 | crotonaldehyde | 9.39 |
| 00110-62-3 | valeraldehyde | 5.08 |
| 00620-23-5 | m-tolualdehyde | 0.00 |

**List of Compounds**
**(Listed by CAS number)**

| | |
|---|---|
| 00050-00-0 | formaldehyde |
| 00064-17-5 | ethanol |
| 00066-25-1 | hexanaldehyde |
| 00067-56-1 | methanol |
| 00067-64-1 | acetone |
| 00071-43-2 | benzene |
| 00074-84-0 | ethane |
| 00074-85-1 | ethene |
| 00074-86-2 | ethyne |
| 00074-98-6 | propane |
| 00074-99-7 | 1-propyne |
| 00075-07-0 | acetaldehyde |
| 00075-28-5 | 2-methylpropane |
| 00075-83-2 | 2,2-dimethylbutane |
| 00078-78-4 | 2-methylbutane |
| 00078-79-5 | 2-methyl-1,3-butadiene |
| 00078-85-3 | methacrolein |
| 00078-93-3 | methyl ethyl ketone (2-butanone) |
| 00079-29-8 | 2,3-dimethylbutane |
| 00091-20-3 | naphthalene |
| 00095-47-6 | o-xylene |
| 00095-63-6 | 1,2,4-trimethylbenzene |
| 00095-93-2 | 1,2,4,5-tetramethylbenzene |
| 00096-14-0 | 3-methylpentane |
| 00096-37-7 | methylcyclopentane |
| 00098-19-1 | 1-(1,1-dimethylethyl)-3,5-dimethylbenzene |
| 00098-82-8 | (1-methylethyl)benzene |
| 00099-87-6 | 1-methyl-4-(1-methylethyl)benzene |
| 00100-41-4 | ethylbenzene |
| 00100-42-5 | stryrene (ethenylbenzene) |
| 00100-52-7 | benzaldehyde |
| 00103-65-1 | n-propylbenzene |
| 00105-05-5 | 1,4-diethylbenzene |
| 00106-97-8 | n-butane |
| 00106-98-9 | 1-butene |
| 00106-99-0 | 1,3-butadiene |
| 00107-00-6 | 1-butyne |
| 00107-02-8 | acrolein |
| 00107-39-1 | 2,4,4-trimethyl-1-pentene |
| 00107-40-4 | 2,4,4-trimethyl-2-pentene |
| 00107-83-5 | 2-methylpentane |
| 00108-08-7 | 2,4-dimethylpentane |
| 00108-38-3 | m- & p-xylene |
| 00108-67-8 | 1,3,5-trimethylbenzene |

| | |
|---|---|
| 00108-87-2 | methylcyclohexane |
| 00108-88-3 | toluene |
| 00109-66-0 | n-pentane |
| 00109-67-1 | 1-pentene |
| 00110-54-3 | n-hexane |
| 00110-62-3 | valeraldehyde |
| 00110-82-7 | cyclohexane |
| 00110-83-8 | cyclohexene |
| 00111-65-9 | n-octane |
| 00111-66-0 | 1-octene |
| 00111-84-2 | n-nonane |
| 00112-40-3 | n-dodecane |
| 00115-07-1 | propene |
| 00115-11-7 | 2-methylpropene |
| 00123-38-6 | propionaldehyde |
| 00123-72-8 | butyraldehyde |
| 00124-11-8 | 1-nonene |
| 00124-18-5 | n-decane |
| 00135-01-3 | 1,2-diethylbenzene |
| 00135-98-8 | (1-methylpropyl)benzene |
| 00141-93-5 | 1,3-diethylbenzene |
| 00142-29-0 | cyclopentene |
| 00142-82-5 | n-heptane |
| 00287-92-3 | cyclopentane |
| 00463-49-0 | 1,2-propadiene |
| 00463-82-1 | 2,2-dimethylpropane |
| 00464-06-2 | 2,2,3-trimethylbutane |
| 00488-23-3 | 1,2,3,4-tetramethylbenzene |
| 00496-11-7 | 2,3-dihydroindene (indan) |
| 00503-17-3 | 2-butyne |
| 00513-35-9 | 2-methyl-2-butene |
| 00526-73-8 | 1,2,3-trimethylbenzene |
| 00527-53-7 | 1,2,3,5-tetramethylbenzene |
| 00527-84-4 | 1-methyl-2-(1-methylethyl)benzene |
| 00535-77-3 | 1-methyl-3-(1-methylethyl)benzene |
| 00538-68-1 | n-pentylbenzene |
| 00538-93-2 | (2-methylpropyl)benzene |
| 00540-84-1 | 2,2,4-trimethylpentane |
| 00542-92-7 | 1,3-cyclopentadiene |
| 00558-37-2 | 3,3-dimethyl-1-butene |
| 00560-21-4 | 2,3,3-trimethylpentane |
| 00562-49-2 | 3,3-dimethylpentane |
| 00563-16-6 | 3,3-dimethylhexane |
| 00563-45-1 | 3-methyl-1-butene |
| 00563-46-2 | 2-methyl-1-butene |
| 00565-59-3 | 2,3-dimethylpentane |
| 00565-75-3 | 2,3,4-trimethylpentane |
| 00584-94-1 | 2,3-dimethylhexane |

| | |
|---|---|
| 00589-34-4 | 3-methylhexane |
| 00589-43-5 | 2,4-dimethylhexane |
| 00589-53-7 | 4-methylheptane |
| 00589-81-1 | 3-methylheptane |
| 00590-18-1 | cis-2-butene |
| 00590-35-2 | 2,2-dimethylpentane |
| 00590-73-8 | 2,2-dimethylhexane |
| 00591-76-4 | 2-methylhexane |
| 00592-13-2 | 2,5-dimethylhexane |
| 00592-27-8 | 2-methylheptane |
| 00592-41-6 | 1-hexene |
| 00592-76-7 | 1-heptene |
| 00611-14-3 | 1-methyl-2-ethylbenzene |
| 00616-12-6 | 3-methyl-trans-2-pentene |
| 00617-78-7 | 3-ethylpentane |
| 00620-14-4 | 1-methyl-3-ethylbenzene |
| 00620-23-5 | m-tolualdehyde |
| 00622-96-8 | 1-methyl-4-ethylbenzene |
| 00624-64-6 | trans-2-butene |
| 00625-27-4 | 2-methyl-2-pentene |
| 00627-20-3 | cis-2-pentene |
| 00637-92-3 | 1-ethyl-tert-butyl-ether |
| 00638-04-0 | cis-1,3-dimethylcyclohexane |
| 00646-04-8 | trans-2-pentene |
| 00674-76-0 | 4-methyl-trans-2-pentene |
| 00689-97-4 | 1-buten-3-yne |
| 00691-37-2 | 4-methyl-1-pentene |
| 00691-38-3 | 4-methyl-cis-2-pentene |
| 00693-89-0 | 1-methylcyclopentene |
| 00760-20-3 | 3-methyl-1-pentene |
| 00763-29-1 | 2-methyl-1-pentene |
| 00816-79-5 | 3-ethyl-2-pentene |
| 00822-50-4 | trans-1,2-dimethylcyclopentane |
| 00874-41-9 | 1,3-dimethyl-4-ethylbenzene |
| 00922-62-3 | 3-methyl-cis-2-pentene |
| 00926-82-9 | 3,5-dimethylheptane |
| 00933-98-2 | 1,2-dimethyl-3-ethylbenzene |
| 00934-80-5 | 1,2-dimethyl-4-ethylbenzene |
| 01069-53-0 | 2,3,5-trimethylhexane |
| 01072-05-5 | 2,6-dimethylheptane |
| 01074-17-5 | 1-methyl-2-n-propylbenzene |
| 01074-43-7 | 1-methyl-3-n-propylbenzene |
| 01074-55-1 | 1-methyl-4-n-propylbenzene |
| 01074-92-6 | 1-(1,1-dimethylethyl)-2-methylbenzene |
| 01120-21-4 | n-undecane (hendecane) |
| 01120-62-3 | 3-methylcyclopentene |
| 01595-11-5 | 1-methyl-2-n-butylbenzene |
| 01634-04-4 | 1-methyl-tert-butyl-ether |

| | |
|---|---|
| 01640-89-7 | ethylcyclopentane |
| 01678-91-7 | ethylcyclohexane |
| 01758-88-9 | 1,4-dimethyl-2-ethylbenzene |
| 01759-58-6 | trans-1,3-dimethylcyclopentane |
| 02051-30-1 | 2,6-dimethyloctane |
| 02207-01-4 | cis-1,2-dimethylcyclohexane |
| 02207-03-6 | trans-1,3-dimethylcyclohexane |
| 02207-04-7 | trans-1,4-dimethylcyclohexane |
| 02213-23-2 | 2,4-dimethylheptane |
| 02216-33-3 | 3-methyloctane |
| 02216-34-4 | 4-methyloctane |
| 02532-58-3 | cis-1,3-dimethylcyclopentane |
| 02613-65-2 | trans-1-methyl-3-ethylcyclopentane |
| 02613-66-3 | cis-1-methyl-3-ethylcyclopentane |
| 02738-19-4 | 2-methyl-2-hexene |
| 02815-58-9 | 1,2,4-trimethylcyclopentane |
| 02870-04-4 | 1,3-dimethyl-2-ethylbenzene |
| 03074-71-3 | 2,3-dimethylheptane |
| 03221-61-2 | 2-methyloctane |
| 03404-61-3 | 3-methyl-1-hexene |
| 03522-94-9 | 2,2,5-trimethylhexane |
| 03899-36-3 | 3-methyl-trans-3-hexene |
| 04032-94-4 | 2,4-dimethyloctane |
| 04050-45-7 | trans-2-hexene |
| 04170-30-3 | crotonaldehyde |
| 06443-92-1 | cis-2-heptene |
| 07385-78-6 | 3,4-dimethyl-1-pentene |
| 07642-04-8 | cis-2-octene |
| 07642-09-3 | cis-3-hexene |
| 07688-21-3 | cis-2-hexene |
| 10574-37-5 | 2,3-dimethyl-2-pentene |
| 13269-52-8 | trans-3-hexene |
| 13389-42-9 | trans-2-octene |
| 14686-13-6 | trans-2-heptene |
| 14686-14-7 | trans-3-heptene |
| 14850-23-8 | trans-4-octene |
| 15869-87-1 | 2,2-dimethyloctane |
| 15890-40-1 | (1a,2a,3b)-1,2,3-trimethylcyclopentane |

## 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 |
| CCR | = | California Code of Regulations |
| CFR | = | Code of Federal Regulations |
| $C_2H_5OH$ | = | ethanol |
| 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 |
| $D_{phase\ n}$ | = | 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 (see Dilution Factor Calculation). |
| FID | = | flame ionization detector |
| 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 (293.15$^{o}$ 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.

HPLC = high performance liquid chromatography

$Iconc_{blk}$ = concentration of the blank cartridge, µg/mL

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

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

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

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

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

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

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

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

| | | |
|---|---|---|
| $Itemp_d$ | = | dilution air temperature at the flowmeter inlet for impinger/cartridge sampling, K. |
| $Itemp_e$ | = | dilute exhaust temperature at the flowmeter inlet for impinger/cartridge sampling, K. |
| $Ivol_c$ | = | elution volume of the cartridge, mL<br>(For example, the cartridge is extracted with 5 mL acetonitrile, but 0.6 mL is retained in the cartridge, so the elution volume is 4.4 mL.) |
| $Ivol_d$ | = | total volume of dilution air (background) drawn through the impingers/cartridges for all three test phases corrected to standard conditions ($293.15^o$ K and 760 mm Hg), liter. |
| $Ivol_{dm}$ | = | total volume of dilution air (background) drawn through the impingers/cartridges for all three test phases as measured during testing, liter. |
| $Ivol_e$ | = | total volume of dilute exhaust drawn through the impingers/cartridges per test phase corrected to standard conditions ($293.15^o$ K and 760 mm Hg), liter. |
| $Ivol_{em}$ | = | total volume of dilute exhaust drawn through the impingers/cartridges per test phase as measured during testing, liter. |
| $Ivol_r$ | = | volume of the reagent used in an impinger, mL. |
| LOD | = | limit of detection |
| LPG | = | liquified petroleum gas |
| MIR | = | Maximum Incremental Reactivity |
| Mol. Vol. | = | molecular volume which is 24.055 liter/mole at standard conditions ($293.15^o$ K and 760 mm Hg). |
| Mol. Wt. | = | molecular weight of the compound being measured, g/mole. |
| NIST | = | National Institute of Standards and Technology |
| NMHC | = | non-methane hydrocarbons |
| $NMHC_{wm}$ | = | the total weighted mass of non-methane hydrocarbon per mile for all three phases of the FTP, g/mile. |

| | | |
|---|---|---|
| NONMHC | = | non-oxygenated non-methane hydrocarbon |
| NMOG | = | non-methane organic gases |
| $P_B$ | = | barometric pressure during testing, mm Hg. |
| PID | = | photoionization detector |
| PLOT | = | porous layer open tubular |
| 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 ($293.15^o$ K and 760 mm Hg), $g/ft^3$. |
| $RHO_e$ | = | concentration of a carbonyl compound in the dilute exhaust per test phase, ppm. |
| $RHO_{wm}$ | = | 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 ($293.15^o$ K and 760 mm Hg), $g/ft^3$. |
| $ROH_e$ | = | concentration of an alcohol compound in the dilute exhaust per test phase, ppmC. |
| $ROH_{wm}$ | = | total weighted mass emissions of an alcohol compound per mile, g/mile. |
| SAE | = | Society of Automotive Engineers |

| | | |
|---|---|---|
| SRM | = | Standard Reference Material |

II. The following list is commonly used measurement abbreviations:

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

# APPENDIX 3

## REFERENCES


[1] Code of Federal Regulations, Title 40, Part 1066

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

[3] Code of Federal Regulations, Title 40, Part 1065

[4] SAE J1151, "Methane Measurement Using Gas Chromatography," (revised December 1991)

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