

AIR RESOURCES BOARD

Effective Date: February 10, 2012

PROCEDURE FOR THE DETERMINATION OF OXYGENATES AND  
PARAFFIN, OLEFIN, NAPHTHENE, AND AROMATIC HYDROCARBON  
TYPE ANALYSIS IN GASOLINE BY MULTI-DIMENSIONAL GAS CHROMATOGRAPHY

SOP NO. MLD 131

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CALIFORNIA AIR RESOURCES BOARD  
MONITORING AND LABORATORY DIVISION

Procedure for the Determination of Oxygenates and Paraffin, Olefin, Naphthene, and Aromatic Hydrocarbon Type Analysis in Gasoline by Multi-Dimensional Gas Chromatography

**1 Introduction**

- 1.1 This document describes an automated method for the determination of paraffins, iso-paraffins, olefins, naphthenes, and aromatics by carbon number in gasoline. Hydrocarbons with carbon numbers higher than 10 are reported as a single group, C11+. Oxygenates are also determined by this method.
- 1.2 This test method covers gasolines and similar hydrocarbon streams with final boiling points of 200 °C or less. Oxygenates determined include t-butyl methyl ether (MTBE), t-butyl ethyl ether (ETBE), t-amyl methyl ether (TAME), diisopropyl ether (DIPE), methanol, ethanol, n-propanol, isopropanol, isobutanol, t-butanol, s-butanol and n-butanol.
- 1.4 Total olefins are determined from 0.05 to 28 mass percent.
- 1.3 This procedure is based on ASTM D6839-02<sup>1</sup>.

**2 Method**

- 2.1 A representative sample is introduced into a gas chromatographic system containing a series of columns, traps, and switching valves.
- 2.2 The columns and traps selectively separate the sample into different chemical types which then elute to a detector and are quantified.
- 2.3 The mass concentration of each compound or chemical type is determined by multiplication of peak areas by detector response factors and normalization to 100 percent.
- 2.4 The liquid volume concentration of each compound or chemical type is determined by multiplication of the mass concentration by a density factor and normalizing to 100

percent.

### 3 **Instrumentation**

3.1 Gas chromatograph, autosampler, columns and valves: Bruker PIONA+ analyzer.

#### 3.2 **Detector**

3.2.1 A flame ionization detection system optimized for use with packed columns.

3.2.2 Sensitivity: >0.015 coulombs/gram.

3.2.3 Minimum detectability:  $5 \times 10^{-12}$  g carbon/second.

3.2.4 Linearity:  $>10^7$ .

3.3 Digital data acquisition system: Bruker CompassCDS Workstation.

### 4 **Reagents**

4.1 Pentane, reagent grade or equivalent.

4.2 Bruker PIONA+ test mixtures.

4.3 Air, "Zero" grade.

4.4 Helium, 99.995%.

4.5 Hydrogen, 99.99%.

### 5 **Preparation of Instrument**

The instrument is set up and optimized by Bruker. Column temperatures and valve times may need adjustment as traps age.

## 6 Calibration

This test method is based on normalization. No calibration is required.

## 7 Procedure

- 7.1 Transfer 2 mL of each sample into a glass autosampler vial and cap the vial.
- 7.2 For each sample, the appropriate test method is determined and specified in the software's sample list. Ordinarily, this method is OPONA-90 (oxygenates, paraffins, olefins, naphthenes, and aromatics.)
- 7.2 0.1 µL of each sample is injected via autosampler into the instrument.
- 7.3 Peak groupings and identifications provided by the data system are checked and corrected, if necessary.

## 8 Safety

- 8.1 Gasoline and many of its various components are toxic. Persons using this method must wear protective gloves and eyewear when working with reagents and samples. Reagents and samples are kept in a fume hood with adequate ventilation.

## 9 Calculations

### 9.1 Response Factor

- 9.1.1 For each hydrocarbon group, the following formula is used to calculate a detector response factor:

$$F_i = \frac{(C_{aw} \times C_n) + (H_{aw} \times H_n) \times 0.7487}{(C_{aw} \times C_n)}$$

where  $F_i$  is the relative response factor,  $C_{aw}$  is the atomic weight of carbon,  $C_n$  is the

number of carbon atoms in the group,  $H_{aw}$  is the atomic weight of hydrogen, and  $H_n$  is the number of hydrogen atoms in the group.

9.2 Response factors for hydrocarbons are given in table R.

9.25 The factors for olefins are be corrected for the hydrogenation which occurs as part of the method.

9.3 Response factors for oxygenates are given in table 1.

9.4 A corrected area is calculated for each group:

$$A_{ic} = A_i \times F_i$$

where  $A_{ic}$  is the corrected area for each group  $i$  and  $F_i$  is the detector response factor.

9.5 The total of all collected areas,  $T$ , is determined:

$$T = \sum A_{ic}$$

9.6 The mass percent for each group,  $M_i$ , is then calculated:

$$M_i = A_{ic} \times 100 / T$$

9.7 The non-normalized corrected liquid volume for each group,  $V_{ic}$ , is calculated by dividing each group's mass percent by the appropriate average relative density value  $D_i$  from table 2 or table 3:

$$V_{ic} = M_i / D_i$$

9.8 The total volume  $T_v$  is calculated by adding the  $V_{ic}$  values of all groups.

9.9 The liquid volume percent of each group,  $V_i$ , is calculated by the following equation:

$$V_i = V_{ic} / T_v$$

9.10 The total olefin content is determined by adding the volume percents of C4-C10 olefin groups (both cyclic and non-cyclic).

- 9.11 Weight percent carbon, hydrogen, and oxygen can be calculated by multiplying the mass percent of each component by the percentage of carbon, hydrogen, and oxygen in that component and adding the results. A sample Excel spreadsheet for performing this calculation is shown in table 4.

## 10 **Quality Control**

- 10.1 A "blank" sample containing no oxygenates, aromatics, or olefins (typically pentane or air), is analyzed at least once per quarter. If the blank chromatogram shows more than 0.1 volume percent of any oxygenate, total olefins, or total aromatics then the blank is repeated or the instrument hardware checked.
- 10.2 A NIST SRM is run at least once per quarter. The total olefin concentration reported must agree with the certified value within the repeatability of the test method (see 10.4). For SRMs 2294, 2296, and 2297, the repeatability is approximately 0.13 vol%.
- 10.3 A control standard is analyzed at the beginning of each set of samples. The total olefin content of the control standard analyses is recorded on a quality control chart. A result is considered to be out of control if its difference from the mean is greater than twice the repeatability (see 10.4). In this event, corrective action must be taken prior to analyzing samples.
- 10.4 For total olefin measurements, the repeatability is given by the following equation:

$$r = 0.13(X)^{0.46}$$

where r is the repeatability and X is the measured concentration in weight percent.

## 11 **References**

1. Standard Test Method for Hydrocarbon Types, Oxygenated Compounds and Benzene In Spark Ignition Engine Fuels by Gas Chromatography, American Society for Testing and Materials, Method D6839-02.
2. PIONA+ Analyzer User Manual, Bruker Daltonics Inc., 2011.

## 12. Standard Operating Procedure Revision History

Version 1.1: 1/1/97

Version 2.0: 4/1/00

Referenced ASTM D6293

Changed olefin scope to reflect D6293.

Removed specific AC test sample numbers, as they are subject to change.

Updated the quality control section to conform to current practices, including the use of NIST SRMs.

Version 3.0: 4/1/01

Added the procedure for correcting the olefin response factors (sections 6.5 and 9.25). Also changed references to "PONAX" method to "Gasoline" method.

Version 3.1: 10/1/01

Changed section 6.1 and 9.25 to make the olefin response factor optional, depending on whether it improves the accuracy of the analysis of the NIST SRM.

Version 3.2: 4/1/07

Changed section 1.3 to reflect the new underlying ASTM method. Deleted section 6.5.1, which was redundant and confusing. Section 10.4 updated with new reproducibility equation.

Version 4.0: 2/10/12

Changed various sections to reflect the replacement of the Reformulyzer by the Bruker PIONA+. Added an example of the spreadsheet used for calculating C/H/O percentage as table 4. Removed most of sections 5 and 6, which were specific to the Reformulyzer.

Table 1  
Response Factors for Oxygenates

| Compound   | Response Factor |
|------------|-----------------|
| methanol   | 3.030           |
| ethanol    | 1.910           |
| n-propanol | 1.867           |
| I-propanol | 1.742           |
| n-butanol  | 1.546           |
| I-butanol  | 1.390           |
| s-butanol  | 1.609           |
| t-butanol  | 1.229           |
| MTBE       | 1.334           |
| DIPE       | 1.317           |
| ETBE       | 1.313           |
| TAME       | 1.242           |

Table 2. Average density, g/mL at 20 °C of hydrocarbon type groups

| Number of Carbons | Naphthenes | Paraffins | Cycloolefins | Olefins | Aromatics |
|-------------------|------------|-----------|--------------|---------|-----------|
| 3                 |            | 0.5005    |              | 0.5139  |           |
| 4                 |            | 0.5788    |              | 0.6037  |           |
| 5                 | 0.7454     | 0.6262    | 0.7720       | 0.6474  |           |
| 6                 | 0.7636     | 0.6594    | 0.7803       | 0.6794  | 0.8789    |
| 7                 | .7649      | 0.6837    | 0.7854       | 0.7023  | 0.8670    |
| 8                 | 0.7747     | 0.7025    | 0.8000       | 0.7229  | 0.8681    |
| 9                 | 0.7853     | 0.7176    | 0.8073       | 0.7327  | 0.8707    |
| 10                | 0.8103     | 0.7300    | 0.8123       | 0.7430  | 0.8724    |

The densities used for polynaphthenes and compounds with more than ten carbons are 0.8832 and 0.8400 respectively.

Table 3. Densities, g/mL at 20 °C of oxygenates

| Oxygenate  | Density |
|------------|---------|
|            |         |
| methanol   | 0.7965  |
| ethanol    | 0.7967  |
| n-propanol | 0.8111  |
| i-propanol | 0.7925  |
| n-butanol  | 0.8147  |
| i-butanol  | 0.8052  |
| s-butanol  | 0.8144  |
| t-butanol  | 0.7910  |
| MTBE       | 0.7459  |
| DIPE       | 0.7240  |
| ETBE       | 0.7440  |
| TAME       | 0.7710  |

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| Sample:        | 1-100   |        |           |        |        |
|----------------|---------|--------|-----------|--------|--------|
| Analysis Date: | 3/22/12 |        |           |        |        |
| Fraction       | frac C  | frac H | mass %    | wt. C  | wt. H  |
| C4 P           | 0.827   | 0.173  | 0.570     | 0.471  | 0.099  |
| C5 P           | 0.832   | 0.168  | 9.080     | 7.558  | 1.522  |
| C6 P           | 0.836   | 0.164  | 10.740    | 8.981  | 1.759  |
| C7 P           | 0.839   | 0.161  | 10.640    | 8.927  | 1.713  |
| C8 P           | 0.841   | 0.159  | 11.540    | 9.707  | 1.833  |
| C9 P           | 0.843   | 0.157  | 3.220     | 2.714  | 0.506  |
| C10 P          | 0.844   | 0.156  | 0.700     | 0.591  | 0.109  |
| C11+ P         | 0.845   | 0.155  | 3.670     | 3.102  | 0.568  |
|                |         |        |           |        |        |
| C6 A           | 0.923   | 0.077  | 0.760     | 0.701  | 0.059  |
| C7 A           | 0.912   | 0.088  | 5.750     | 5.247  | 0.503  |
| C8 A           | 0.905   | 0.095  | 8.580     | 7.765  | 0.815  |
| C9 A           | 0.899   | 0.101  | 7.530     | 6.772  | 0.758  |
| C10 A          | 0.895   | 0.105  | 2.650     | 2.371  | 0.279  |
| C11+ A         | 0.891   | 0.109  | 1.020     | 0.909  | 0.111  |
|                |         |        |           |        |        |
| O/N            | 0.856   | 0.144  | 11.880    | 10.172 | 1.708  |
|                |         |        |           |        |        |
| C5 cyc O       | 0.882   | 0.118  | 0.070     | 0.062  | 0.008  |
| C6 cyc O       | 0.877   | 0.123  | 0.280     | 0.246  | 0.034  |
| C7 cyc O       | 0.874   | 0.126  | 0.260     | 0.227  | 0.033  |
| C8 cyc O       | 0.872   | 0.128  | 0.070     | 0.061  | 0.009  |
| C9 cyc O       | 0.870   | 0.130  | 0.000     | 0.000  | 0.000  |
| poly-N         | 0.869   | 0.131  | 0.000     | 0.000  | 0.000  |
|                |         |        |           |        |        |
| MTBE           | 0.681   | 0.137  | 0.000     | 0.000  | 0.000  |
| Ethanol        | 0.521   | 0.131  | 10.990    | 5.730  | 1.443  |
| TAME           | 0.705   | 0.138  | 0.000     | 0.000  | 0.000  |
|                |         |        |           |        |        |
| Total %        |         |        | 100.000   | 82.315 | 13.868 |
|                |         |        | C/H Ratio | 5.94   |        |
|                |         |        | Wt% O     | 3.817  |        |

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