

AIR RESOURCES BOARD

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

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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 D6839-02¹, with the addition of the olefin response factor correction described in sections 6 and 9.

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, columns and valves: Analytical Controls Reformulyzer.

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: 5×10^{-12} g carbon/second.

3.2.4 Linearity: > 10^7 .

3.3 Liquid Autosampler: Hewlett-Packard model 6890 injector.

3.4 Digital data acquisition system: Hewlett-Packard Chemstation with Analytical Controls Reformulyzer software.

4 **Reagents**

4.1 2,2,4-trimethylpentane (isooctane), reagent grade or equivalent.

4.2 Analytical Controls Reformulyzer test mixtures.

4.3 Air, "Zero" grade.

4.4 Helium, 99.995%.

4.5 Hydrogen, 99.99%.

5 **Preparation of Instrument**

5.1 **Gas flow settings**

- 5.1.1 Carrier gas A: 22 mL/min.
- 5.1.2 Carrier gas B: 14 mL/min.
- 5.1.3 Hydrogenation gas: 14 mL/min.
- 5.1.4 Detector air: 450 mL/min.
- 5.1.5 Detector hydrogen: 50 mL/min.

5.2 **Timing**

- 5.2.1 Cut and backflush times vary from instrument to instrument and may require adjustment.
- 5.2.2 These times may require adjustment as the columns and traps age.
- 5.2.3 Analytical Controls test mixtures are used to check and, if necessary, adjust valve timing.
- 5.2.4 Details of the timing procedure are given in the proposed ASTM D6293-98.

6 **Calibration**

- 6.1 This test method is based on normalization. No calibration is required.
- 6.2 As discussed in section 5.2, cut and backflush timing may require periodic adjustment.
- 6.3 Analysis of an appropriate AC test mixture is performed once per quarter, or when an instrument problem is suspected. Irregular results in this analysis may indicate for instrument repair.
- 6.4 Any necessary adjustments to timing are made in the analytical method being used (typically method Gasoline).

- 6.5 Corrected olefin response factors may be calculated in order to obtain accurate olefin results. These response factors are calculated by the instrument's software using the analyses of an fcc gasoline in the PNA and PHONA modes. The correction can correct inaccuracy due to incomplete desorption of olefins from the olefin trap. However, the correction can also cause inaccuracy, apparently depending on the specific trap being used.

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 PONAX (paraffins, olefins, naphthenes, aromatics, and oxygenates).
- 7.2 0.1 µL of each sample is injected via autosampler into the Reformulyzer.
- 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 may be corrected for the hydrogenation which occurs as part of the method and for the incomplete desorption of olefins from the olefin trap (see section 6.5).

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).

10 Quality Control

- 10.1 A "blank" sample containing no oxygenates, aromatics, or olefins (typically isooctane 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 SRM 2294 and 2296, 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 are 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.

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.

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