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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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 oC 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.

1.3   Total olefins are determined from 0.05 to 28 mass percent.

1.4   This procedure is based on American Society for Testing and Materials (ASTM) Method D6839-15[1].

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.

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 X 10-12 g carbon/second.

3.2.4   Linearity: $>10^7$.

3.3   Digital data acquisition system: provided by the instrument manufacturer.

4   Reagents

4.1   Pentane, reagent grade or equivalent.

4.2   Commercial test mixture(s) covering the range of hydrocarbon types and carbon numbers expected in gasoline, plus ethanol.

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 the instrument manufacturer. 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 measures oxygenates, paraffins, olefins, naphthenes, and aromatics.

7.3   0.1 µL of each sample is injected via autosampler into the instrument.

7.4   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 provided in ASTM D6839-15

9.2.1 The factors for olefins are 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:

$$T = A_{ic}$$

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, Vi, 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 chosen sample of National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) is run at least once per quarter. The total olefin concentration reported must agree with the certified value within twice 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.

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

# of Carbon	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	0.7649	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

Table 4. A sample Excel spreadsheet for a test

Sample:			1-100		
Analysis Date:			3/22/2012		
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	

11   **References**

11.1   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 D6839-15.

11.2   Instrument manual.

12.   **Revision History**

12.1   Revision 1.1:   Effective Date: 1/1/1997

12.2   Version 2.0:   Effective Date: 4/1/2000

        Referenced ASTM D6293

        Significant Changes:

        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.

12.3   Version 3.0:   Effective Date: 4/1/2001

        Significant Changes:

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

12.4   Revision 3.1:   Effective Date: 10/1/2001

        Significant Changes:

        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.

12.5   Revision 3.2:   Effective Date: 4/1/2007

Significant Changes:

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 repeatability equation.

12.6   Version 4.0:   Effective Date: 2/10/2012

Significant Changes:

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.

12.7   Revision 4.1:   Effective Date: 9/1/2014

Significant Changes:

Changed 9.2 to remove reference to "Table R", which does not exist.

Changed 10.2 to bring SRM requirements in line with other FAMES test methods.

Corrected the revision history for Revision 3.2, which now refers to repeatability rather than reproducibility.

12.8   Version 5.0:   Effective Date: 5/1/2017

Significant Changes:

Renumbered sections 1.3 and 1.4.

Changed 1.4 to reflect the latest version of the ASTM test method.

Removed all references to brands and models in sections 3.1, 3.3, 4.2, 5, 7.2, 9.2, 11.1, and 11.2.

12.9   Version 5.1:   Effective Date: 12/1/2019

       SOP format updated for ADA compliance