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Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by ~~100–Metre~~100-Metre Capillary (with Precolumn) High-Resolution Gas Chromatography[1]

This standard is issued under the fixed designation D6730; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. ~~Scope~~ Scope*

1.1 This test method covers the determination of individual hydrocarbon components of spark-ignition engine fuels and their mixtures containing oxygenate blends (MTBE, ETBE, ethanol, and so forth) with boiling ranges up to 225 °C. Other light liquid hydrocarbon mixtures typically encountered in petroleum refining operations, such as blending stocks (naphthas, reformates, alkylates, and so forth) may also be analyzed; however, statistical data was obtained only with blended spark-ignition engine fuels.

1.2 Based on the cooperative study results, individual component concentrations and precision are determined in the range from 0.01 % to approximately 30 % by mass. The test method may be applicable to higher and lower concentrations for the individual components; however, the user must verify the accuracy if the test method is used for components with concentrations outside the specified ranges.

1.3 This test method also determines methanol, ethanol, *t*-butanol, methyl *t*-butyl ether (MTBE), ethyl *t*-butyl ether (ETBE), and *t*-amyl methyl ether (TAME) in spark ignition engine fuels in the concentration range from 1 % to 30 % by mass. However, the cooperative study data provided insufficient statistical data for obtaining a precision statement for these compounds.

1.4 Although a majority of the individual hydrocarbons present are determined, some co-elution of compounds is encountered. If this test method is utilized to estimate bulk hydrocarbon group-type composition (PONA), the user of such data should be cautioned that some error will be encountered due to co-elution and a lack of identification of all components present. Samples containing significant amounts of naphthenic (for example, virgin naphthas) constituents above *n*-octane may reflect significant errors in PONA-type groupings. Based on the gasoline samples in the interlaboratory cooperative study, this test method is applicable to samples containing less than 25 % by mass of olefins. However, some interfering co-elution with the olefins above C_7 is possible, particularly if blending components or their higher boiling cuts such as those derived from fluid catalytic cracking (FCC) are analyzed, and the total olefin content may not be accurate. Annex A1 of this test method compares results of the test method with other test methods for selected components, including olefins, and several group types for several interlaboratory cooperative study samples. Although benzene, toulene, and several oxygenates are determined, when doubtful as to the analytical results of these components, confirmatory analyses can be obtained by using the specific test methods listed in the reference section.

1.4.1 Total olefins in the samples may be obtained or confirmed, or both, if necessary, by Test Method D1319 (percent by volume) or other test methods, such as those based on multidimentional PONA-type of instruments.

1.5 If water is or is suspected of being present, its concentration may be determined, if desired, by the use of Test Method D1744 or equivalent. Other compounds containing oxygen, sulfur, nitrogen, and so forth, may also be present, and may co-elute with the hydrocarbons. If determination of these specific compounds is required, it is recommended that test methods for these specific materials be used, such as Test Methods D4815 and D5599 for oxygenates, and Test Method D5623 for sulfur compounds, or equivalent.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate ~~safety~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

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***A Summary of Changes section appears at the end of this standard**

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
D1744 Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent (Withdrawn 2016)[3]
D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
D4626 Practice for Calculation of Gas Chromatographic Response Factors
D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography
D5580 Test Method for Determination of Benzene, Toluene, Ethylbenzene, *p/m*-Xylene, *o*-Xylene, C_9 and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography
D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection
D5623 Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection
E355 Practice for Gas Chromatography Terms and Relationships
E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography
E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions can be found in Practice E355.

4. Summary of Test Method

4.1 A representative sample of the petroleum liquid is introduced into a gas chromatograph equipped with an open tubular (capillary) column coated with a methyl silicone liquid phase, modified with a capillary precolumn. Helium carrier gas transports the vaporized sample through the column, in which it is partitioned into individual components which are sensed with a flame ionization detector as they elute from the end of the column. The detector signal is presented on a strip chart recorder or digitally, or both, by way of an integrator or integrating computer. Each eluting component is identified by comparing its retention time to that established by analyzing reference standards or samples under identical conditions. The concentration of each component in percent by mass is determined by normalization of the peak areas after correction with detector response factors. Unknown components are reported as a total unknown percent by mass.

5. Significance and Use

5.1 Knowledge of the individual component composition (speciation) of gasoline fuels and blending stocks is useful for refinery quality control and product specification. Process control and product specification compliance for many individual hydrocarbons can be determined through the use of this test method.

5.2 This test method is adopted from earlier development and enhancement.[4,5,6,7] The chromatographic operating conditions and column tuning process, included in this test method, were developed to provide and enhance the separation and subsequent determination of many individual components not obtained with previous single-column analyses. The column temperature program profile is selected to afford the maximum resolution of possible co-eluting components, especially where these are of two different compound types (for example, a paraffin and a naphthene).

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Johansen, N.G., and Ettre, L.S., "Retention Index Values of Hydrocarbons on Open Tubular Columns Coated with Methyl Silicone Liquid Phases," *Chromatographia*, Vol 5, No. 10, October 1982.

[5] Johansen, N.G., Ettre, L.S., and Miller, R.L., "Quantitative Analysis of Hydrocarbons by Structural Group Type in Gasolines and Distillates. Part 1," *Journal of Chromatography*, Vol 256, 1983, pp. 393–417.

[6] Kopp, V.R., Bones, C.J., Doerr, D.G., Ho, S.P., and Schubert, A.J., "Heavy Hydrocarbon/Volatility Study: Fuel Blending and Analysis for the Auto/Oil Air Quality Improvement Research Program," SAE Paper No. 930143, March 1993.

[7] Schubert, A.J. and Johansen, N.J., "Cooperative Study to Evaluate a Standard Test Method for the Speciation of Gasolines by Capillary Gas Chromatography," SAE Paper No. 930144, March 1993.

5.3 Although a majority of the individual hydrocarbons present in petroleum distillates are determined, some co-elution of compounds is encountered. If this test method is utilized to determine bulk hydrocarbon group-type composition (PONA), the user of such data should be cautioned that some error will be encountered due to co-elution and a lack of identification of all components present. Samples containing significant amounts of olefinic or naphthenic, or both, constituents above octane may reflect significant errors in PONA-type groupings.

5.4 If water is or is suspected of being present, its concentration is determined by the use of Test Method D1744. Other compounds containing oxygen, sulfur, nitrogen, and so forth may also be present, and may co-elute with the hydrocarbons. When known co-elution exists, these are noted in the test method data tables. If determination of these specific compounds is required, it is recommended that test methods for these specific materials be used, such as Test Method D4815 and D5599 for oxygenates, Test Method D5580 for aromatics, and Test Method D5623 for sulfur compounds.

6. Apparatus

6.1 *Gas Chromatograph*—Instrumentation capable of column oven temperature programming, from subambient (5 °C) to at least 200 °C, in 0.1 °C/min or less rate increments, is required. Multi-step column oven temperature programming is required, consisting of an initial hold time, an initial temperature program followed by an isothermal temperature hold and another programmed temperature rise. A heated flash vaporizing injector designed to provide a linear sample split injection (that is, 200:1) is required for proper sample introduction. The associated carrier gas controls must be of sufficient precision to provide reproducible column flows and split ratios in order to maintain analytical integrity. A hydrogen flame ionization detector, with associated gas controls and electronics, designed for optimum response with open tubular columns, shall conform to the specifications as described in Practice E594, as well as having an operating temperature range of up to at least 250 °C.

6.2 *Sample Introduction*—Manual or automatic liquid sample injection to the splitting injector may be employed. Automated injections are highly recommended. Micro-syringes, auto-syringe samplers, or valves capable of 0.1 µL to 0.5 µL. injections are suitable. It should be noted that some syringes and improper injection techniques as well as inadequate splitter design could result in sample fractionation. This must be determined in accordance with Section 10.

6.3 *Electronic Integrator*—Any electronic integration device used for quantitating these analyses shall meet or exceed these minimum requirements:

6.3.1 Capacity to handle 400 or more peaks per analysis.

6.3.2 Normalized area percent calculation with response factors.

6.3.3 Noise and spike rejection.

6.3.4 Accurate area determination of fast (1 s to 2 s) peaks (10 Hz or greater sampling rate).

6.3.5 Maintain peak detection sensitivity for narrow and broad peaks.

6.3.6 Positive and negative sloping baseline correction.

6.3.7 Perpendicular drop and tangent skimming as needed.

6.3.8 Display of baseline used to ensure correct peak area determination.

6.4 *Open Tubular Column*—The column used for this test method consists of a primary (100 m) analytical column and a precolumn. The ability to provide the required component separations is dependent on the precise control of the column selectivity, which is typically slightly more than that exhibited by current commercially available columns. Some older columns, and columns that have a sample residue from repeated use without conditioning, may exhibit the required polarity. Until adequate columns are commercially available, the currently used methyl silicone columns can be modified or *tuned* to meet the method column specifications. See Section 11 for a description of the column performance specifications and Annex A1 for a description of the column modification procedure.

6.4.1 The primary gas chromatographic column used for this test method will meet the following specifications.

Material	fused silica
Length	100 m
Internal diameter	0.25 mm
Liquid phase	methyl silicone
Film thickness	0.50 µm
Theoretical plates, n, pentane at 35 °C	~ 400 000 to 500 000
Retention factor, k, pentane at 35 °C	0.45 to 0.50
Resolution, R, *t*-butanol and 2-methylbutene-2 at 35 °C	3.25 to 5.25
Peak symmetry, *t*-butanol at 35 °C	> 1.0 to < 5.0

6.4.2 *Precolumn*—A variable length (1 m to 4 m) of 5 % phenyl/95 % dimethylpolysiloxane fused silica open tubular column (0.25 mm inside diameter) is added to the front (injector) end of the 100 m column, as described in Annex A1.

7. Reagents and Materials

7.1 *Carrier Gas*—Helium, 99.999 % pure. (**Warning—**Helium, air, nitrogen, compressed gas under pressure.)

7.2 *Oxidant*—Air, 99.999 % pure. (**Warning—**see 7.1.)

7.3 *Detector Makeup Gas*—Nitrogen, 99.999 % pure. (**Warning—**see 7.1.)

7.4 *Fuel Gas*—Hydrogen, 99.999 % pure. (**Warning—**Hydrogen, flammable gas under high pressure.)

7.5 *Reference Standards:*

7.5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society[8] where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.5.2 *Methanol*—(**Warning—**These materials are flammable and may be harmful or fatal, if ingested or inhaled.).

7.5.3 *Ethanol*—Only absolute ethanol of 99.5 minimum percent meets the requirements of this test method. (**Warning—**see 7.5.2.)

7.5.4 *Hydrocarbon and Other Component References*—Individual and mixed component reference materials are commercially available and may be used to establish qualitative and quantitative calibration. (**Warning—**see 7.5.2.)

7.5.5 *System and Column Evaluation Mixture*—A quantitatively prepared mixture, complying with Practice D4307, of individual hydrocarbons and oxygenates of interest is used for system and column evaluation (see Table 1). (**Warning—**see 7.5.2.) Fig. 1 is a chromatogram of the recommended mixture in Table 1.

8. Sampling

8.1 Hydrocarbon liquids with Reid vapor pressures of 110 kPa (16 psi) or less may be sampled either into a floating piston cylinder or into an open container (Practices D4057 and D4177). If the sample as received does not meet the upper boiling range requirements of 1.1, it may be necessary to extend the analysis time and raise the upper column temperature of this test method to ensure complete elution of higher boiling range sample material from the column.

8.1.1 *Piston Cylinder Sampling*—Refer to Practice D3700 for instructions on transferring a representative sample of a hydrocarbon fluid from a source into a floating piston cylinder. Add inert gas to the ballast side of the floating piston cylinder to achieve a pressure of 350 kPa (45 psi) above the vapor pressure of the sample.

8.1.2 *Open Container Sampling*—Refer to Practice D4057 for instructions on manual sampling from bulk storage into open containers. Stopper the container immediately after taking a sample.

8.2 Preserve the sample by cooling to approximately 4 °C and maintaining that temperature prior to analysis.

TABLE 1 System and Column Evaluation Mixture

	%
Ethanol	8.00
n-pentane	2.00
t-butanol	0.50
2-methylbutene-2	2.50
2,3-dimethylbutane	0.50
Methyl-*t*-butyl ether	10.00
n-hexane	2.00
1-methylcyclopentene	0.50
Benzene	1.00
Cyclohexane	28.90
3-ethylpentane	0.20
1,2*t*-dimethylcyclopentane	0.50
n-heptane	2.00
2,3,3-trimethylpentane	0.50
Toluene	7.00
n-octane	2.00
Ethylbenzene	25.00
p-xylene	1.00
2,3-dimethylheptane	0.20
n-nonane	2.00
5-methylnonane	0.20
1-methyl-2-ethylbenzene	0.50
n-decane	1.00
n-undecane	0.50
1,2,3,5-tetramethylbenzene	0.25
Naphthalene	0.50
n-dodecane	0.25
1-methylnaphthalene	0.25
n-tridecane	0.25

[8] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

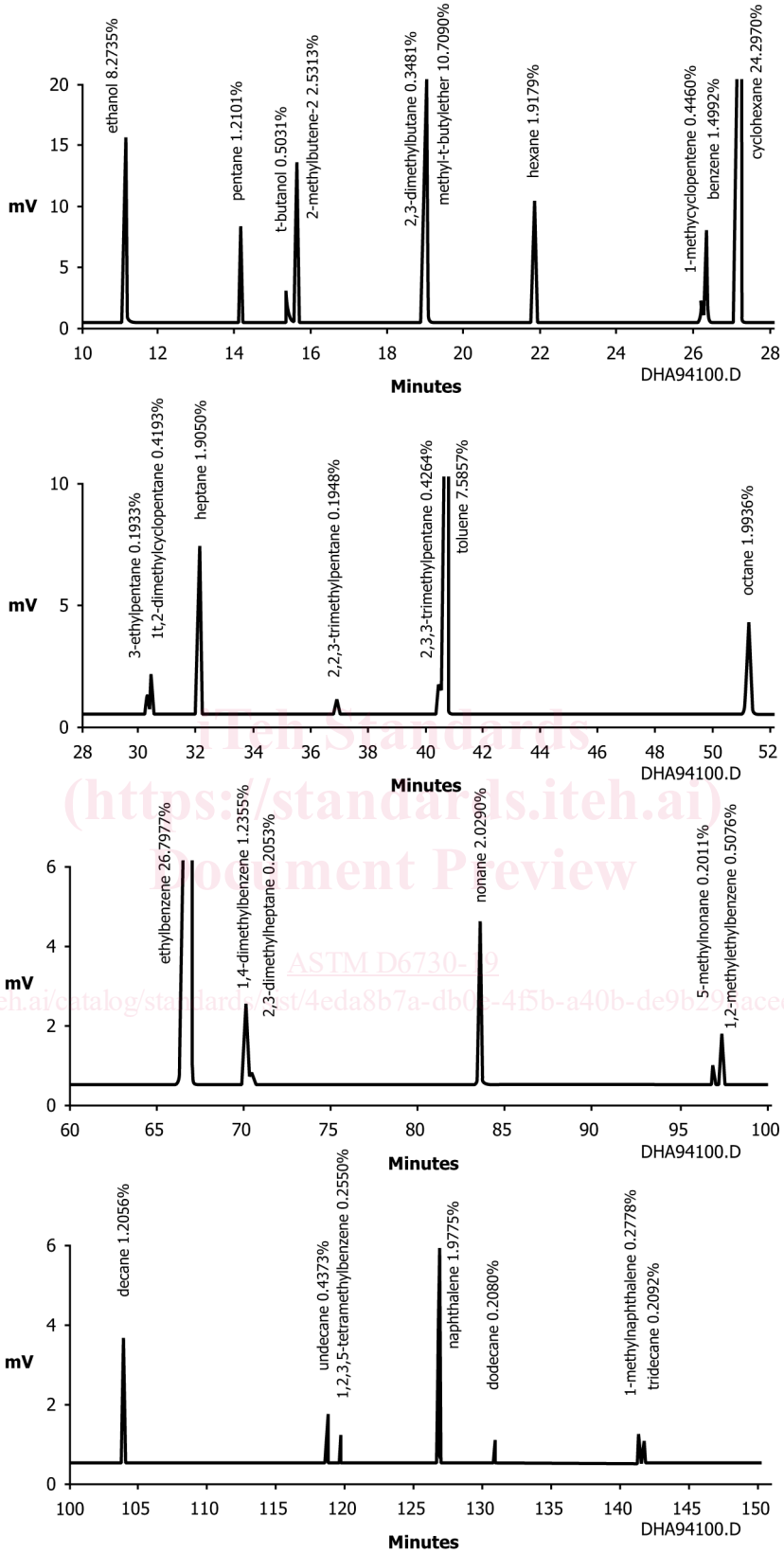


FIG. 1 DHA Speciation Analysis—System and Column Evaluation Mixture (7.5.5)

8.3 Transfer an aliquot of the cooled sample to a precooled septum vial and seal immediately.

8.4 Obtain the test specimen for analysis directly from the sealed septum vial, for either manual or automatic injection.

9. Preparation of Apparatus

9.1 Install the 100 m column and, if required, a precolumn according to the manufacturer's or supplier's instructions and Annex A1. See Practice E1510/8 for recommended installation procedures.

9.2 Determine the required length of the precolumn in accordance with Annex A1. Adjust the operating conditions of the gas chromatograph to those listed in Table 2 or as determined by Section 12 and Annex A1.

9.3 During setup and, when not performing analyses, it is advisable to turn off the cryogenic operation and set the column oven temperature at 35 °C. Attach the column outlet to the flame ionization detector inlet and check for leaks throughout the system. If leaks are found, tighten or replace fittings before proceeding.

9.4 Confirm or adjust, or both, the column carrier gas flow rate by making injections of methane or natural gas. *The methane retention time shall be 7.00 min ± 0.02 min with the column oven temperature at 35 °C*, which results in an average linear velocity of 24 cm⁄s, as determined using Eq 1. This will result in a methane retention time of 6.53 min at 5 °C. Raising or lowering the carrier gas pressure to the injector makes flow rate adjustment. A starting point of 277 kPa (40 psig) helium pressure is recommended, although columns requiring as high as 332 kPa (48 psig) helium have been encountered.

$$\text{average linear gas velocity: } u_{ave}\,(\text{cm/s}) = \text{column length (cm)}/t_{M(s)} \quad (1)$$

9.5 After final adjustment of the carrier gas flow rate, note the carrier gas inlet pressure. Measure and, if necessary, readjust the injector split flow rate to give the specified or desired split ratio. Calculate the column outlet flow rate using 9.5.1 and the split ratio using 9.5.2.

9.5.1 *Column Carrier Gas Flow Rate (at outlet):*

9.5.1.1 P = (head pressure (psig) + ambient pressure)/ambient pressure.

9.5.1.2 j = compressibility factor = $3/2((P^2-1)/(P^3-1))$.

9.5.1.3 $u_o = u_{ave}/j$ = column outlet velocity.

9.5.1.4 $A_c = \text{pi}(r)^2$ = column cross-sectional area (cm^2).

where r = column internal radius (cm).

9.5.1.5 Flow rate (cm^3/min) = $u_0 \times A_c \times 60$.

9.5.2 *Injection Split Ratio*—(Split flow rate + column flow rate)/column flow rate.

9.5.3 *Example*—Using a 100 m × 0.25 mm capillary column:

9.5.3.1 $U_{ave} = 100 \times 100/6.98 \times 60 = 23.88$ cm/s.

9.5.3.2 $P = 40$ psig + 12.0/12.0 = 4.33.

9.5.3.3 $j = 3/2((18.778\text{-}1)/(81.370\text{-}1)) = 0.33$

9.5.3.4 $u_o = 23.88/0.33 = 71.96$ cm/s.

9.5.3.5 $A_c = \text{pi}(0.025/2)^2 = 4.9 \times 10^{-4}$ cm^2.

9.5.3.6 Flow rate = $71.96 \times 4.9 \times 10^{-4} \times 60 = 2.12$ cm^3/min.

9.5.3.7 Split Ratio = (192 + 2.12)/2.12 = 91.6:1.

TABLE 2 GC Operating Conditions

Column Temperature Program	
Initial temperature	5 °C
Initial time	10 min.
First program rate	5.0 °/min
First hold temperature	50 °C
First hold time	to the elution of ethylbenzene (~50 min)
Second program rate	1.5 °/min
Final temperature	200 °C
Final hold time	5 min
Injector	
Temperature	250 °C
Split ratio	150:1
Sample size	0.1 µL – 0.2 µL
Detector	
Type	flame Ionization
Temperature	250 °C
Use manufacturers recommended detector gas flows or:	
Fuel gas	hydrogen at 30 mL/min
Oxidant	air at 300 mL/min
Make-up gas, where required	nitrogen at 20 mL/min
Carrier Gas	
Type	helium
Pressure	~ 277 kPa (40 psig)
Average linear velocity	24 cm/s at 35 °C

9.6 Make a blank analysis (no sample injection) run to ensure proper instrument operation and further condition the column and instrumentation. If stray peaks or a rising baseline signal is observed, the column oven shall be kept at the upper temperature until the baseline becomes steady and returns to within approximately 5 % of the starting temperature detector signal.

9.7 After any extended conditioning period, or if the instrument has been shut down, it is advisable to repeat 9.4, 9.5, and 9.6 to ensure proper carrier gas flows are being used and the column is clean.

10. Split Injection Linearity

10.1 Splitting injector linearity must be established to determine proper quantitative parameters and limits. The split ratio used is dependent upon the split linearity characteristics of the particular injector and the sample retention factor of the column. The retention factor of a particular column for a sample component is proportional to the amount of liquid phase (loading or film thickness) and the ratio of the column temperature to the component boiling point (vapor pressure). Overloading of the column may cause loss of resolution for some components and, since overloaded peaks are skewed, variance in retention times. This can lead to erroneous component identification. During column evaluations and split linearity studies, be aware of any peaks that may appear *front skewed*, indicating column overload. Note the component size and avoid conditions leading to this problem during actual analyses.

10.2 Set the injector temperature and split ratio to the following values and, for each set of conditions inject the listed quantities of the system and column evaluation mixture (7.5.5), using the operating conditions listed in Table 2 or as determined in Section 12.

injector temperature: 250 °C<	split: 100:1 split: 200:1	> sample: 0.2 µL, 0.5 µL, 1.0 µL
injector temperature: 300 °C<	split: 100:1 split: 200:1	> sample: 0.2 µL, 0.5 µL, 1.0 µL

10.3 Compare the calculated concentrations to the known standard concentrations after calculating the corrected area normalization using the response factors from 13.2 and Table A1.1.

$$\%\ \text{relative error} = 100 \times (\text{concentration determined} - \text{concentration known})/\text{concentration known} \quad (2)$$

10.4 Report and use only those combinations of conditions from 10.2 that result in 3 % or less relative error. This is the splitter linearity range.

11. Column Evaluation

11.1 In order to establish that a column will perform as required, the following specifications shall be determined for new column acceptability and are useful for periodic evaluation of column deterioration. These specification determinations can be made with or without a precolumn, since the precolumn will have little effect on their values. See Annex A1, Fig. A1.1, for examples of these determinations. After performing the steps in Sections 9 and 10, analyze the column performance mixture (7.5.5) at 35 °C isothermal, at least through heptane. The remainder of the analysis may be ignored, but the remaining components must be eluted from the column prior to performing another analysis. Setting the column temperature to 220 °C for an additional 20 min will be sufficient.

11.2 Calculate the retention factor (k) for pentane at 35 °C:

$$k = (t_R - t_M)/t_M \quad (3)$$

where:

t_M = gas holdup time (methane), and
t_R = retention time for pentane, min.

11.2.1 The retention factor must be between 0.45 and 0.50 for proper application of this test method.

11.3 Calculate the column efficiency using the pentane peak:

$$n = 5.545\ (t_R/w_{1/2h})^2 \quad (4)$$

where:

n = column efficiency (theoretical plates),
t_R = retention time of pentane, and
$w_{1/2h}$ = peak width at half height.

11.3.1 The column efficiency must be at least 400 000 plates for proper application of this test method.

11.4 The selectivity of apparently identical columns toward hydrocarbons may vary regarding oxygenated compounds; either due to extraneous materials in the liquid phase, or due to activity of the column wall surface. The addition of a precolumn has little if any affect on the selectivity toward oxygenates (see Annex A1, Fig. A1.4). The relative resolution of oxygenates is inherent to the quality of the primary 100 m column, and is specified by the resolution of *t*-butanol from 2-methylbutene-2 at 35 °C. Calculate the resolution:

$$R = 2(t_{R2-M-Butene-2} - t_{RTBA})/1.699(w_{1/2h2-M-Butene-2} + w_{1/2hTBA}) \quad (5)$$

11.4.1 The resolution for this pair at 35 °C must be between 3.25 and 5.25.

11.5 Extraneous column effects, or instrumental effects such as an active injector liner, may cause adsorption of oxygenated compounds, commonly seen and referred to as *tailing*, and may increase their retention. If this effect is caused by instrumental activity, the problem should be corrected. If the column is inherently active, a new column should be obtained. A measure of the tailing can be made and specified by applying a *skewness* calculation, which determines a ratio of the distances from the peak apex perpendicular to the front and back of the peak at 5 % of the peak height. See Annex A1, Fig. A1.3 for an example of this calculation.

$$\text{skewness} = B/A \quad (6)$$

11.5.1 This test method shall be made using the *t*-butanol peak (0.5 %) in the analysis of the column performance mixture (7.5.5) at 35 °C isothermal. The skewness ratio must be greater than 1.0 and not more than 5.0.

12. Optimization of Instrument Operating Conditions

12.1 The column temperature programming profile is dependent upon the individual column characteristics. Table 2 lists the programming profile determined for a 100 m methyl silicone column with a precolumn as determined in Annex A1. The profile is determined by establishing satisfactory separations for the sets of sample components listed in 12.3. It is not practical to expect complete separation of all components, so the optimum for each column may contain some compromises, also dependent upon any particular other separations deemed important.

12.2 The use of retention indices to numerically express the relative location of components among themselves and to surrounding normal paraffins is a convenient convention. The indices are also useful in providing a system of component identification with complex analyses such as this. There are several schemes for calculating retention indices, the first of which is the Kovats method, developed to express the logarithmic relationship of retention times of a homologous series of compounds when chromatographed isothermally. While this test method is not an isothermal column temperature procedure, it does contain isothermal steps and the longer temperature program step is a slow rate. The use of the Kovats indices provides a closer relationship to previous work in this field than using the linear index format.

12.2.1 The formula for the calculation of Kovats retention indices is:

$$RI_i = 100 \times (n + (\log(t_i) - \log(t_n))/(\log(t_{n+1}) - \log(t_n))) \quad (7)$$

where:

RI = retention index,
n = carbon number of *n*-paraffin,
t_i = retention time of component,
t_n = retention time of preceding *n*-paraffin, and
t_{n+1} = retention time of next *n*-paraffin.

12.3 The following examples show the key or critical separations required for this analysis. Typical retention indices are given, and a description of the effect of instrumental conditions on the separation is provided.

12.3.1 *i-butane/methanol and ethanol/3-methylbutene-1*—The initial starting temperature of 5 °C is dictated by these separations. A lower starting temperature is not necessary and a higher temperature would effect the next set. The retention indices should be about 380 for methanol and 456.5 for ethanol (Fig. 2).

12.3.2 *i-propanol/2-methylbutene-1* and *t-butanol/2-methylbutene-2*—*i*-propanol will appear resolved between pentene-1 and 2-methyl-butene-1, *t*-butanol will appear resolved between *c*-pentene-2 and 2-methylbutene-2.

12.3.2.1 Higher temperatures will move the alcohols into the peaks ahead of them. At 35 °C the alcohols will be located ahead of the pentene-1 and *c*-pentene-2, respectively (Fig. 3).

12.3.3 *2,3-dimethylbutane/methyl-t-butylether*—This separation is critical and the 5 °C hold for 10 min determines its success. The retention indices should be about 569.5, 571.5, and 574.0 for 2,3-dimethylbutane, MTBE, and 2-methylpentane, respectively. If the MTBE is too close to the 2,3-DMC_4, use a 9 min initial hold. If too close to the 2-MC_5 use an 11 min hold (Fig. 4).

12.3.4 *1-methylcyclopentene/benzene*—This is a key separation that is used to specify the column selectivity. Changing column temperature produces only slight differences in this resolution (Fig. 5).

12.3.4.1 The 50 °C column temperature is held isothermal until the elution of ethylbenzene. This is variable due to slight differences in the column retention factor.

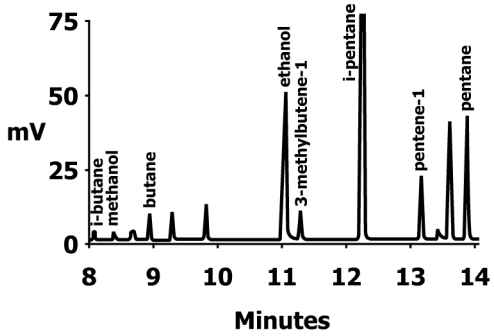


FIG. 2 *i*-butane/methanol and ethanol/3-methyl-butene-1

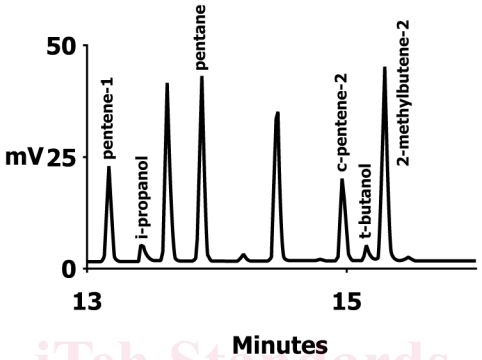


FIG. 3 *i*propanol/2-methyl/butene-1 and *t*butanol/2-methylbutene-2

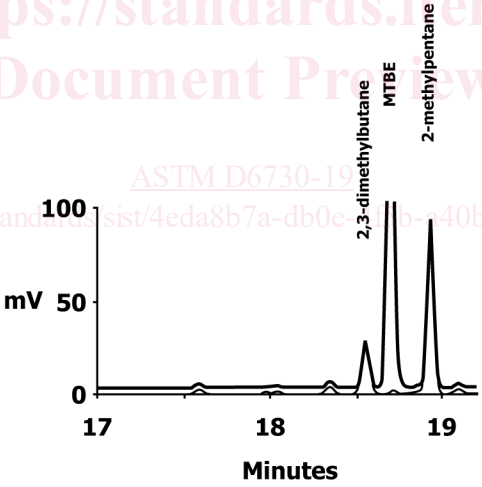


FIG. 4 2,3-dimethylbutane/methyl-*t*butylether

12.3.5 *2,3,3-trimethylpentane/toluene*—This is a key separation that is used to specify the column selectivity. Column temperature has very little effect on this resolution, which is controlled by the column selectivity for aromatics (Fig. 6).

12.3.6 *p-xylene/2,3-dimethylheptane* —This is a key separation which limits the maximum length of the precolumn. If the column selectivity is too great the aromatics are retained and this separation is not achieved. If this resolution is excessive and the separation in 12.3.5 is insufficient, the precolumn should be lengthened slightly. Lowering the 50 °C hold temperature to 48 °C will increase this separation (Fig. 7).

12.3.7 *l17 (Unknown)/1,2-methylethylbenzene* —The unknown isoparaffin (l17) appears to be a component of alkylate and must be resolved from the aromatic. If the resolution is incomplete the final column temperature program rate of 1.5 °/min. is adjusted to provide sufficient separation. Increase the rate in 0.1 °/min increments to increase the resolution. This rate is also dictated by the separation requirements in 12.3.8. The proper rate will provide for both separations (Fig. 8).

12.3.8 *1-methylnaphthalene/tridecane* —The recommended final column temperature program rate of 1.5 °/min. should also provide this separation. If the 1-MeNaph/*n*-C_{13} resolution is incomplete this rate may be adjusted to provide sufficient separation. Lower the rate in 0.1 °/min. increments to increase the resolution (Fig. 9).

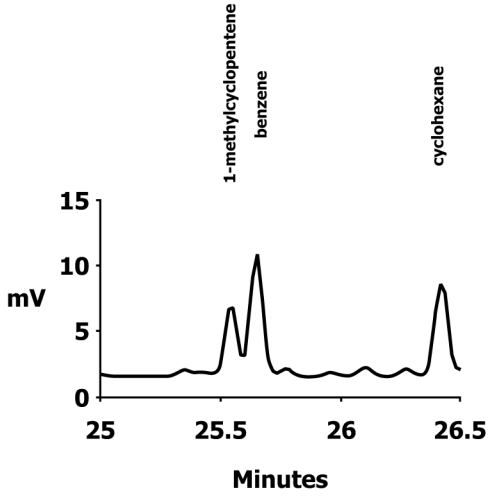


FIG. 5 1-methylcyclopentene/benzene

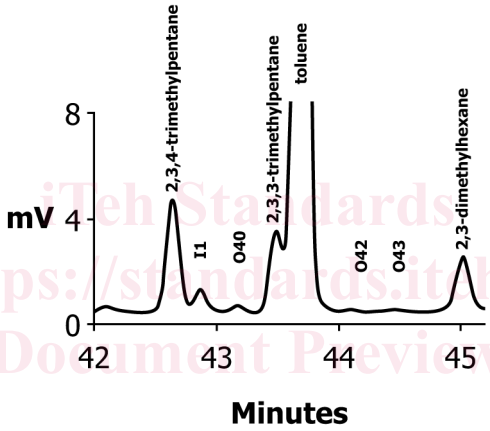


FIG. 6 2,3,3-trimethylpentane/toluene

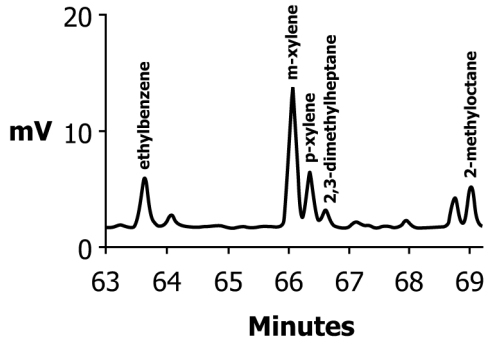


FIG. 7 *p*-xylene/2,3-dimethylheptane

13. Calibration

13.1 *Qualitative*—Determine the retention times of components by analyzing known reference mixtures or samples under identical conditions. Calculate retention indices from these data using 12.2. Table A1.1 provides a listing of typical values for this test method.

13.2 *Quantitative, Hydrocarbons*—Use theoretical response factors for correction of the detector response of hydrocarbons determined by this test method, unless response factors have been determined experimentally. The response of an FID to hydrocarbons is determined by the ratio of the molecular weight of the carbon in the analyte to the total molecular weight of the analyte. If experimentally determined response factors are to be used, they must be determined using known purity individual

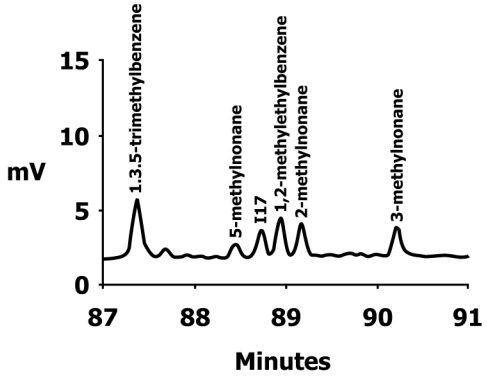


FIG. 8 I17 (unknown)/1,2-methylethylbenzene

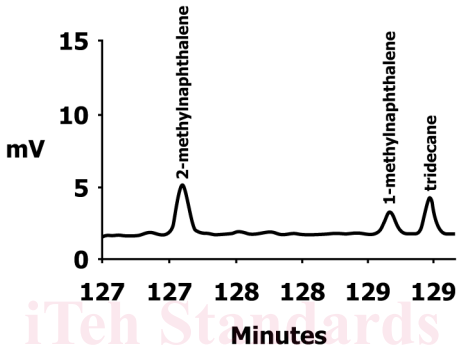


FIG. 9 1-methylnaphthalene/tridecane

standards and calculated using Practice D4626. The response factors, as listed in Table 3, are relative to that calculated for heptane. Calculations are based on the following equation:

$$F_i = (((((C_{aw} \times C_n) + (H_{aw} \times H_n)) / C_n) \times 0.83905) / C_{aw}) \quad (8)$$

where:

F_i = relative response factor for a hydrocarbon type group of a particular carbon number.
C_{aw} = atomic weight of carbon 12.011,
C_n = number of carbon molecules in the group,
H_{aw} = atomic weight of hydrogen, 1.008,
H_n = number of hydrogen molecules in the group,
0.83905 is the correction factor with heptane as unity (1.0000), and
0.7487 is used with methane as unity.

TABLE 3 Theoretical FID Relative Response Factors

Carbon No.	Saturated Paraffins	Unsaturated Paraffins	Saturated Naphthenes	Unsaturated Naphthenes	Aromatics
1	1.1207	-	-	-	-
2	1.0503	-	-	-	-
3	1.0268	0.9799	-	-	-
4	1.0151	0.9799	-	-	-
5	1.0080	0.9799	0.9799	0.9517	-
6	1.0034	0.9799	0.9799	0.9564	0.9095
7	1.0000	0.9799	0.9799	0.9598	0.9195
8	0.9975	0.9799	0.9799	0.9623	0.9271
9	0.9955	0.9799	0.9799	0.9642	0.9329
10	0.9940	0.9799	0.9799	0.9658	0.9376
11	0.9927	0.9799	0.9799	0.9671	0.9415
12	0.9916	0.9799	0.9799	0.9681	0.9447
13	0.9907	0.9799	0.9799	0.9690	0.9474
14	0.9899	0.9799	0.9799	0.9698	0.9497
15	0.9893	0.9799	0.9799	0.9705	0.9517

13.3 *Quantitative, Oxygenates*—Determine response factors for methanol, ethanol, and other oxygenated compounds experimentally. The principles in Practice D4626 should be applied when determining these response factors. The response of the flame ionization detector for oxygenated compounds is not directly (theoretically) related to mass concentration. A study has indicated that the FID response is linear for the conditions of this test method (see Figs. 10 and 11). Each individual apparatus must be calibrated using gravimetrically prepared standards, covering the sample concentration ranges expected and the scope of this test method. Standards used must comply with the requirements in Section 7. Figs. 10 and 11 present calibration data for six oxygenates as determined in a preliminary cooperative study report for calibration of this test method. Precision data will be prepared when more data becomes available.

14. Sample Analysis Procedure

14.1 Adjust the instrument operating variables to the values specified in Table 1 or as determined in Section 12.

14.2 Set the recorder or integration device, or both, for accurate presentation and collection of the data.

14.3 Inject an appropriate size sample (as determined in Section 10) into the injection port and start the analysis. Obtain a chromatogram and a peak integration report.

15. Calculation

15.1 Identify each peak by matching retention indices (or retention times) with those for known reference standards or sample components. If a computing integrator is used, examine the chromatographic data for proper peak integration. Examine the report to ensure peaks are properly identified.

15.1.1 Proper component identification using retention indices requires the use of *windows* surrounding each RI value in order to account for the analysis to analysis variations. The following windows have been found to provide satisfactory identification for this test method.

Indices	Window
100 – 300	± 15
300 – 400	± 2.6
400 – 500	± 1.5
500 – 885	± 0.6
885 – 900	± 0.5
> 900	± 0.6

15.2 Obtain the area for each peak. Multiply each peak area by its appropriate response factor, taken from Table 2 or determined separately with standards, to obtain corrected peak areas. Use a response factor of 1.000 for unknown peaks.

15.3 If required, determine the concentration of water in the sample using Test Method D1744, or an equivalent method. The total concentration of any other materials not determined by this test method should also be obtained.

15.4 The corrected peak areas are normalized to 100 % or to 100 % minus the concentrations determined in 15.3.

$$\text{component \% (m/m)} = \text{corrected peak area} \times (100 - \text{\% undetected})/\text{total corrected peak area} \quad (9)$$

16. Report

16.1 Report the concentration of each component as mass %, % (m/m), to the nearest 0.001 % (m/m).

16.2 These individual component data may be grouped by summing the concentration of compounds in each particular group type such as paraffin, isoparaffin, olefin, aromatic, naphthene, oxygenates, and unknowns. Commercially available software may be used to provide this function, as well as calculation of other properties of petroleum liquids. See the caution in 5.3.

17. Precision and Bias[9]

17.1 *Repeatability*—The difference in two test results obtained by the same operator with the same apparatus in a given laboratory under constant operating conditions on test samples taken from the same laboratory sample should, in the long run, in the normal and correct operation of the test method not exceed the values given in Table 4 and Table A1.3 for the gasoline components.

17.2 *Reproducibility*—The difference between two single and independent measurements on test samples taken from the same bulk sample should, in the long run, in the normal and correct operation of the test method, not exceed the values given in Table 4 and Table A1.3 for the gasoline components.

17.3 *Bias*—No information can be presented on the bias of the procedure in this test method for measuring hydrocarbon concentrations because no material having an accepted reference value is available.

[9] Supporting data is available from ASTM International Headquarters in the form of a research report. Request RR:D02-1518. Contact ASTM Customer Service at service@astm.org.

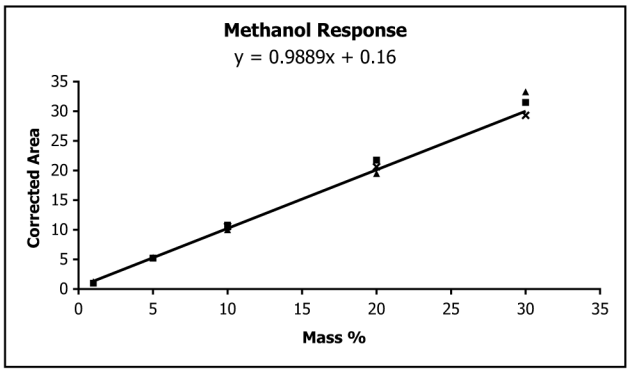
Oxygenates Relative Response Factors

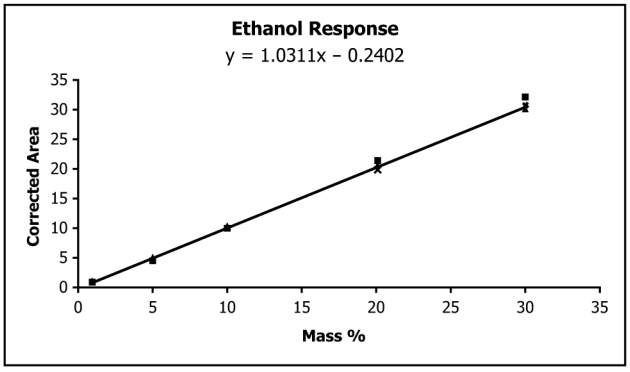
	Lab 1	Lab 2	Lab 3	Lab 4	Ave.	Std. Dev.	%SD	Auto/Oil RRF
Methanol	3.0760	3.0477	2.9779	2.9230	3.0062	0.0691	2.30	3.0965
Ethanol	2.1888	2.0797	2.1755	2.0640	2.1270	0.0642	3.02	2.0953
t-Butanol	1.2975	1.3189	1.3312	1.2989	1.3116	0.0163	1.24	1.3368
MTBE	1.5279	1.5590	1.4860	1.5024	1.5188	0.0318	2.09	1.5016
ETBE	1.3848	1.3720	1.3804	1.3720	1.3773	0.0064	0.46	1.4032
TAME	1.3383	1.2993	1.3598	1.3340	1.3329	0.0250	1.88	1.3775

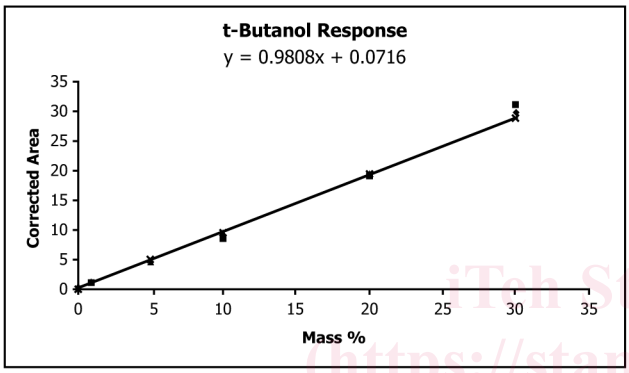
DHA Method Oxygenate Linearity Cooperative Study - peak area
Laboratory 4

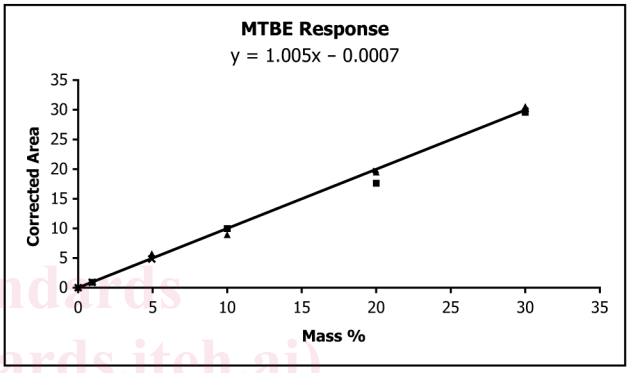
Spl							Ave. RF	RRF
MeOH	0.0100	1.0100	5.0500	10.0200	20.0100	29.8300		
	0.4037	34.7643	174.8862	340.9069	717.4781	1046.1427		
	0.3599	33.8017	179.9043	353.4087	717.1507	980.1566		
ave.	0.3818	34.2830	177.3953	347.1578	717.3144	1013.1496		
RF	0.0262	0.0295	0.0285	0.0289	0.0279	0.0294	0.0288	2.9230
EtOH	0.0100	1.0000	5.0000	10.1000	20.1500	30.1800		
	0.2883	50.5190	237.7223	495.9717	967.7888	1526.2755		
	0.4095	46.7438	242.3003	500.4514	1007.0434	1537.3776		
ave.	0.3489	48.6314	240.0113	498.2116	987.4161	1531.8265		
RF	0.0287	0.0206	0.0208	0.0203	0.0204	0.0197	0.0204	2.0640
TBA	0.0099	0.9640	4.9692	9.9583	19.8768	29.7953		
	1.0363	77.5423	408.5969	757.2307	1546.4197	2241.0530		
	1.1869	72.7672	392.8649	775.5192	1550.7498	2346.4085		
ave.	1.1116	75.1548	400.7309	766.3749	1548.5847	2293.7307		
RF	0.0089	0.0128	0.0124	0.0130	0.0128	0.0130	0.0128	1.2989
MTBE	0.0100	0.9992	5.0362	9.9724	20.0248	30.0471		
	0.7645	66.0865	345.4606	713.3773	1332.2069	2041.1591		
	0.5890	65.8994	325.8215	679.7792	1348.4042	2052.4822		
ave.	0.6767	65.9929	335.6411	696.5783	1340.3055	2046.8206		
RF	0.0148	0.0151	0.0150	0.0143	0.0149	0.0147	0.0148	1.5024
ETBE	0.0099	0.9851	4.9255	9.8707	19.6724	29.5727		
	0.4527	69.3251	374.3939	732.8740	1537.9746	2144.9023		
	0.6242	72.7316	374.7065	695.3345	1462.4055	2173.4412		
ave.	0.5384	71.0283	374.5502	714.1042	1500.1901	2159.1718		
RF	0.0183	0.0139	0.0132	0.0138	0.0131	0.0137	0.0135	1.3720
TAME	0.0100	0.9997	4.9788	9.8883	19.1530	29.7144		
	0.3702	75.3456	363.7452	762.9970	1488.8626	2346.1907		
	0.0072	75.1503	380.0280	763.6254	1420.3514	2230.3657		
ave.	0.1887	75.2480	371.8866	763.3112	1454.6070	2288.2782		
RF	0.0530	0.0133	0.0134	0.0130	0.0132	0.0130	0.0132	1.3340
C6	8.5050	8.4750	8.4400	8.4525	8.4525	8.6950		
	890.3467	843.5383	836.5459	803.1739	843.6532	847.7344		
	847.7681	854.2333	840.8679	834.8488	841.6083	802.3011		
ave.	869.0574	848.8858	838.7069	819.0113	842.6307	825.0177		
RF	0.0098	0.0100	0.0101	0.0103	0.0100	0.0105	0.0101	1.0262
C7	8.5050	8.4750	8.4400	8.4525	8.4525	8.6950		
	893.5123	847.7426	868.0640	834.6944	880.9965	869.6032		
	846.4708	858.0901	862.0443	871.7571	882.1653	834.0419		
ave.	869.9916	852.9164	865.0541	853.2258	881.5809	851.8225		
RF	0.0098	0.0099	0.0098	0.0099	0.0096	0.0102	0.0099	1.0000
C8	8.5050	8.4750	8.4400	8.4525	8.4525	8.6950		
	889.7205	846.6591	877.1065	838.8929	890.2631	873.8851		
	839.2188	855.2006	862.7846	884.2601	895.4804	854.5747		
ave.	864.4697	850.9298	869.9455	861.5765	892.8718	864.2299		
RF	0.0098	0.0100	0.0097	0.0098	0.0095	0.0101	0.0098	0.9944
C9	8.5050	8.4750	8.4400	8.4525	8.4525	8.6950		
	883.5337	843.1968	870.7139	832.1808	883.3178	868.7531		
	829.0626	849.0969	854.1742	881.9661	889.9074	860.0512		
ave.	856.2982	846.1469	862.4440	857.0734	886.6126	864.4021		
RF	0.0099	0.0100	0.0098	0.0099	0.0095	0.0101	0.0099	1.0003

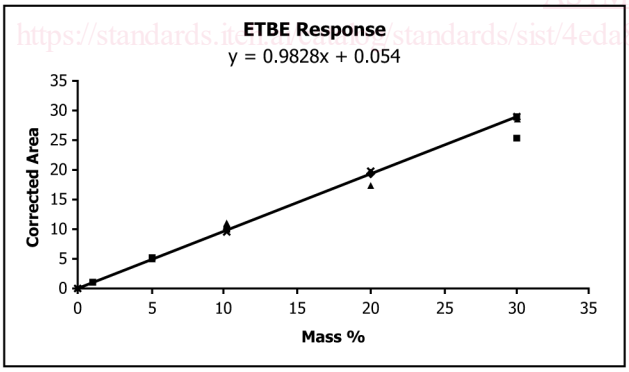
FIG. 10 Determination of Oxygenate Response—DHA Speciation Analysis











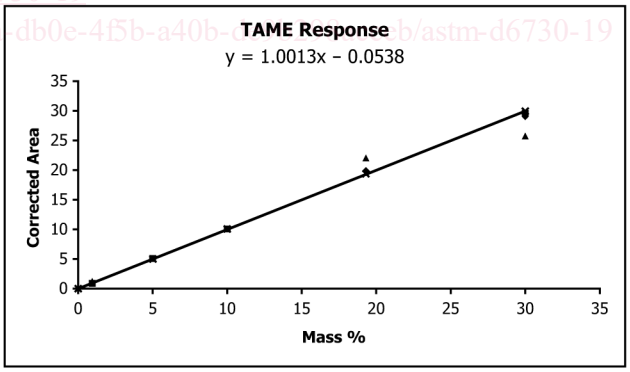


FIG. 11 Graphical Representation Determination of Oxygenate Response—DHA Speciation Analysis

18. Keywords

18.1 detailed hydrocarbon analysis; DHA; gas chromotography; hydrocarbons; open tubular column; oxygenates; PIONA; PONA