



Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100–Metre Capillary (with Precolumn) High- Resolution Gas Chromatography¹

This standard is issued under the fixed designation D 6730; 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

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 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 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 mass % of olefins. However, some interfering co-elution with the olefins above C₇ 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, toluene, 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 D 1319 (volume %) or other test methods, such as those based on multidimensional 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 D 1744 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 D 4815 and D 5599 for oxygenates, and Test Method D 5623 for sulfur compounds, or equivalent.

1.6 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

- D 1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption²
- D 1744 Test Method for Determination of Water in Liquid Petroleum Products by Karl Fisher Reagent³
- D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder⁴
- D 4057 Practice for Manual Sampling of Petroleum and

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² *Annual Book of Standards*, Vol 05.01.

³ Discontinued; see 1999 *Annual Book of ASTM Standards*, Vol 05.01.

⁴ *Annual Book of Standards*, Vol 05.02.

- Petroleum Products⁴
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products⁴
- D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards⁴
- D 4626 Practice for Calculation of Gas Chromatographic Response Factors⁴
- D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, *tertiary*-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography⁴
- D 5580 Test Method for Determination of Benzene, Toluene, Ethylbenzene, *p/m*-Xylene, *o*-Xylene, C₉ and Heavier Aromatics and Total Aromatics in Finished Gasoline by Gas Chromatography⁵
- D 5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection⁵
- D 5623 Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection⁵
- E 355 Practice for Gas Chromatography Terms and Relationships⁶
- E 594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography⁶
- E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatography⁶

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 E 355.

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 mass % is determined by normalization of the peak areas after correction with detector response factors. Unknown components are reported as a total unknown 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.^{7,8,9,10} 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).

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 D 1744. 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 D 4815 and D 5599 for oxygenates, Test Method D 5580 for aromatics, and Test Method D 5623 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

⁷ Johansen, N.G., and Etre, L.S., "Retention Index Values of Hydrocarbons on Open Tubular Columns Coated with Methyl Silicone Liquid Phases," *Chromatographia*, Vol 5, No. 10, October 1982.

⁸ Johansen, N.G., Etre, L.S., and Miller, R.L., "Quantitative Analysis of Hydrocarbons by Structural Group Type in Gasolines and Distillates. Part 1," *Journal of Chromatography*, 256, 1983, pp. 393-417.

⁹ 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.

¹⁰ 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 *Annual Book of Standards*, Vol 05.03.

⁶ *Annual Book of Standards*, Vol 14.02.

detector, with associated gas controls and electronics, designed for optimum response with open tubular columns, shall conform to the specifications as described in Practice E 594, 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 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 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, <i>t</i> -butanol and 2-methylbutene-2 at 35°C | 3.25 to 5.25 |
| Peak symmetry, <i>t</i> -butanol at 35°C | > 1.0 to < 5.0 |

6.4.2 *Precolumn*—A variable length (1 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 Society¹¹ 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 D 4307, 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 D 4057 and D 4177). 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 D 3700 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 D 4057 for instructions on manual sampling from bulk storage into open containers. Stopper the container immediately after taking a sample.

¹¹ *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.

TABLE 1 System and Column Evaluation Mixture

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

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

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 E 1510 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 ± 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.*

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

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 $P = (\text{head pressure (psig)} + \text{ambient pressure}) / \text{ambient pressure.}$

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

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

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

9.5.1.5 $\text{Flow rate (cm}^3\text{/min)} = u_o \times A_c \times 60.$

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

9.5.3.2 $P = 40 \text{ psig} + 12.0 / 12.0 = 4.33.$

9.5.3.3 $j = 3/2((18.778-1)/(81.370-1)) = 0.33$

9.5.3.4 $u_o = 23.88 / 0.33 = 71.96 \text{ cm/s.}$

9.5.3.5 $A_c = \pi(0.025/2)^2 = 4.9 \times 10^{-4} \text{ cm}^2.$
9.5.3.6 $\text{Flow rate} = 71.96 \times 4.9 \times 10^{-4} \times 60 = 2.12 \text{ cm}^3\text{/min.}$

9.5.3.7 $\text{Split Ratio} = (192 + 2.12) / 2.12 = 91.6:1.$

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.

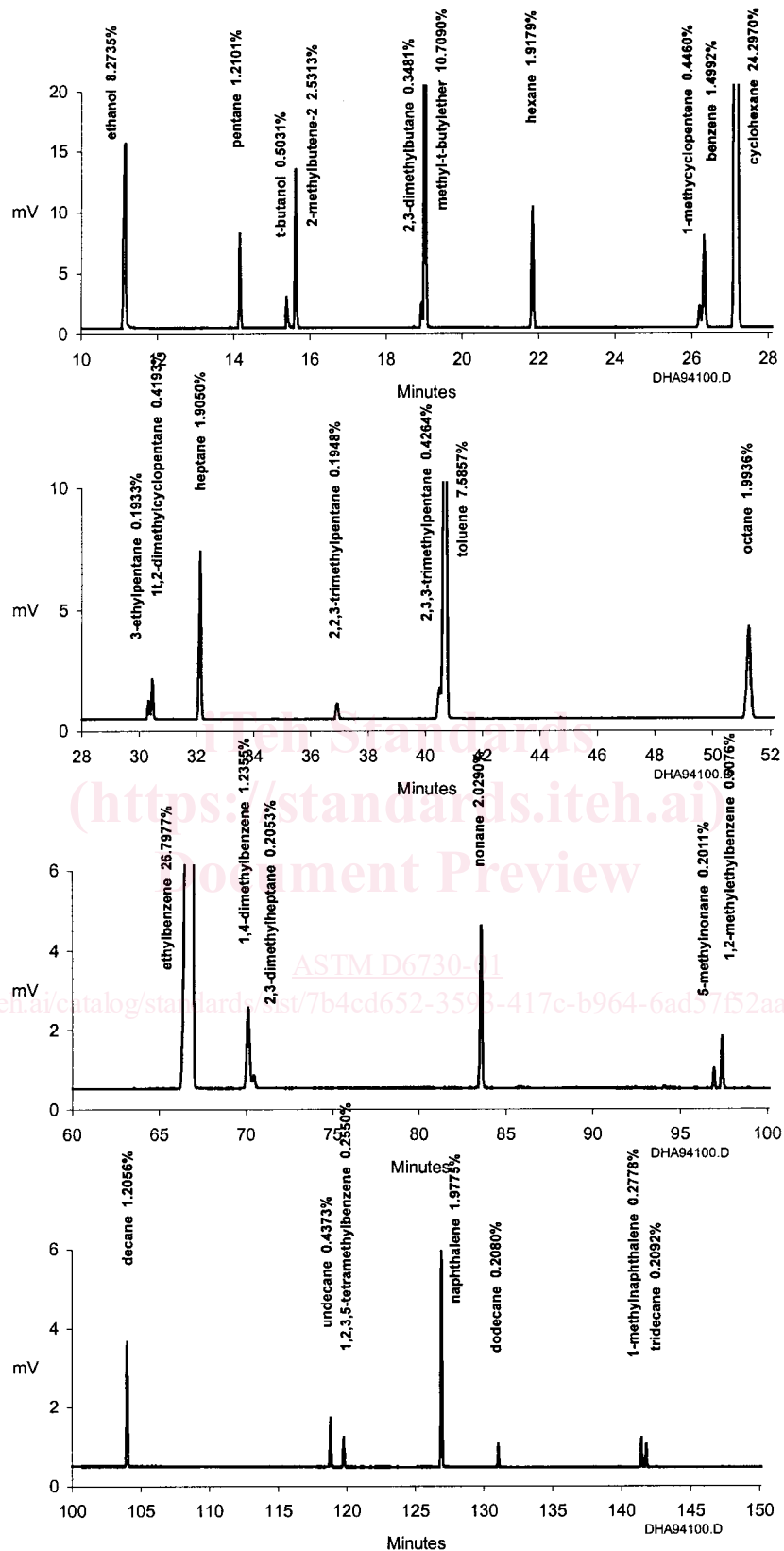


FIG. 1 DHA Speciation Analysis—System and Column Evaluation Mixture (7.5.5)

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 - 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 |

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

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

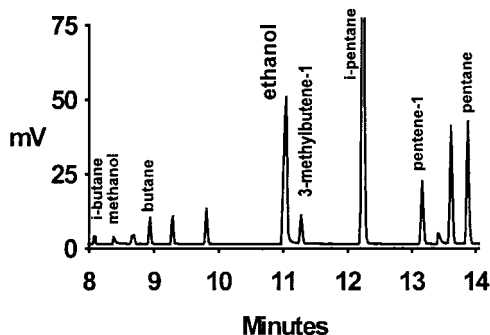


FIG. 2 *i*-butane/methanol and ethanol/3-methyl-butene-1

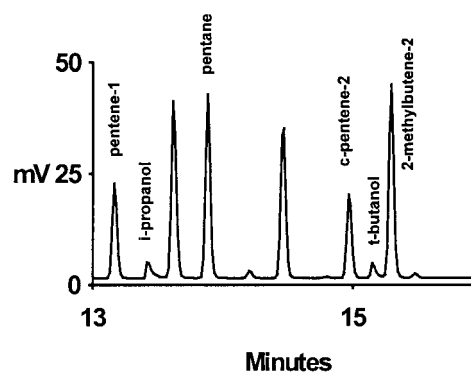


FIG. 3 *i* propanol/2-methylbutene-1 and *t* butanol/2-methylbutene-2

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-DMC₄, use a 9 min initial hold. If too close to the 2-MC₅ 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.

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 *117 (Unknown)/1,2-methylethylbenzene*—The unknown isoparaffin (117) appears to be a component of alkylate

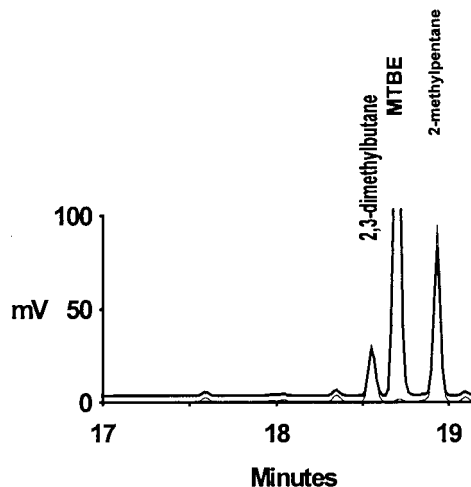


FIG. 4 2,3-dimethylbutane/methyl-*t* butylether

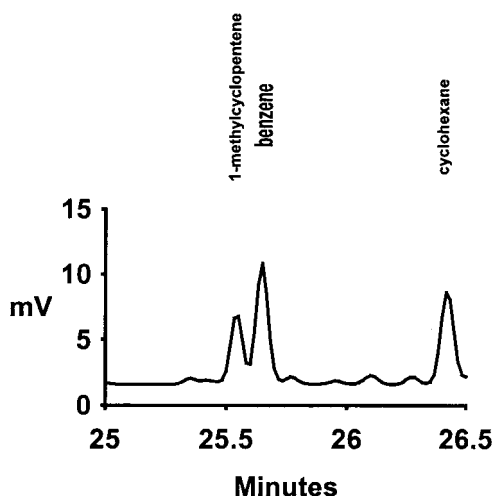


FIG. 5 1-methylcyclopentene/benzene

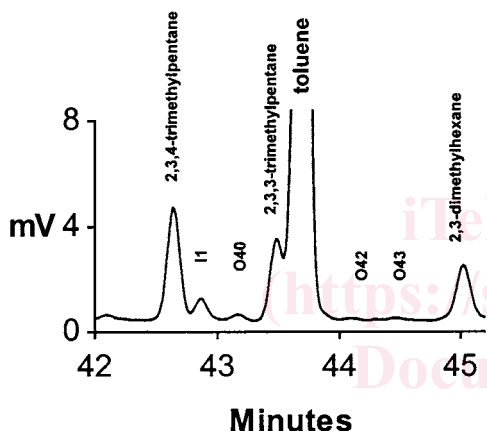


FIG. 6 2,3,3-trimethylpentane/toluene

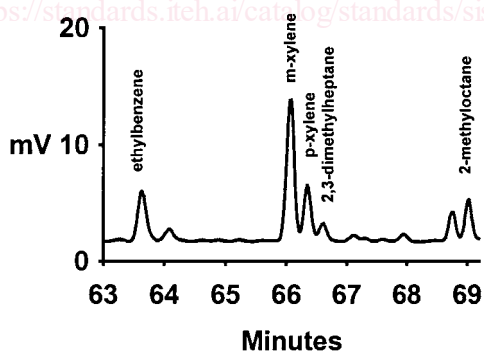


FIG. 7 p-xylene/2,3-dimethylheptane

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).

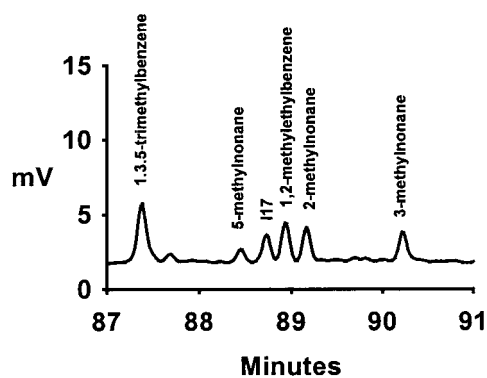


FIG. 8 I17 (unknown)/1,2-methylethylbenzene

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*-C₁₃ 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).

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 standards and calculated using Practice D 4626. The response factors, as listed in Table 3, are relative to that calculated for heptane. Calculations are based on the following equation:

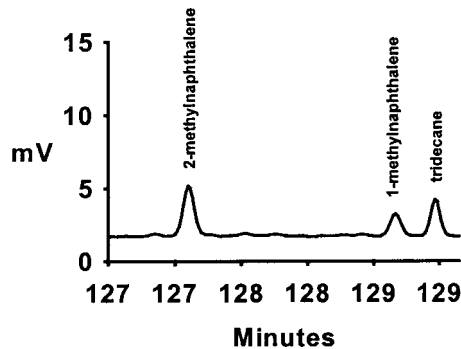


FIG. 9 1-methylnaphthalene/tridecane

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 |

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

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.

13.3 Quantitative, Oxygenates—Determine response factors for methanol, ethanol, and other oxygenated compounds experimentally. The principles in Practice D 4626 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 D 1744, 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.

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

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 ¹²

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

¹² Supporting data is available from ASTM International Headquarters in the form of a research report. Request RR: D02-1518.

Oxygenates Relative Response Factors

| | Lab1 | Lab 2 | Lab 3 | Lab4 | 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 | 408.5989 | 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 | | |
| | 0.7845 | 86.0985 | 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 | 374.7085 | 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 | 890.9965 | 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 | 861.5785 | 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

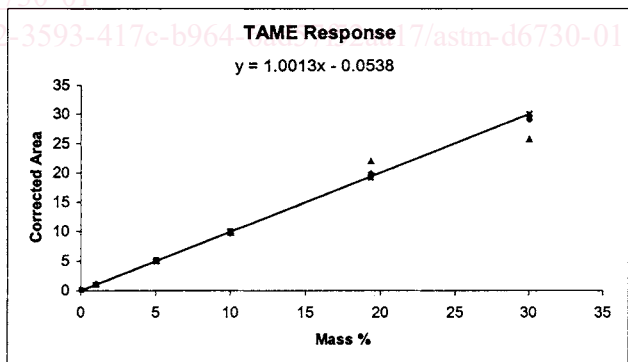
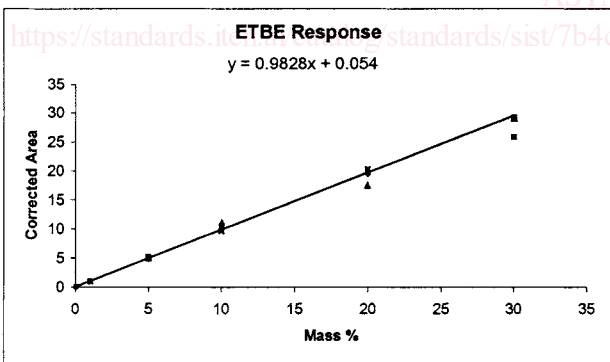
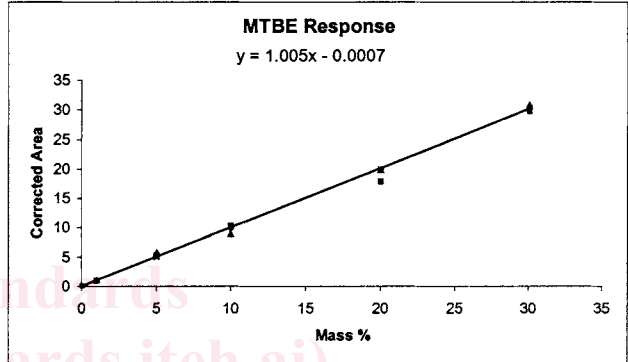
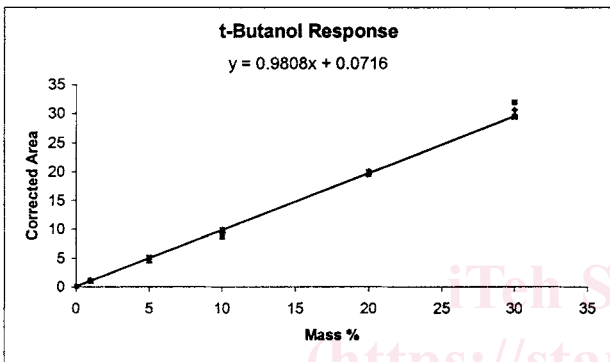
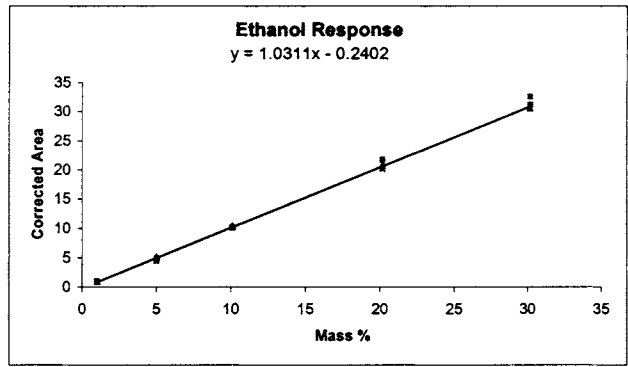
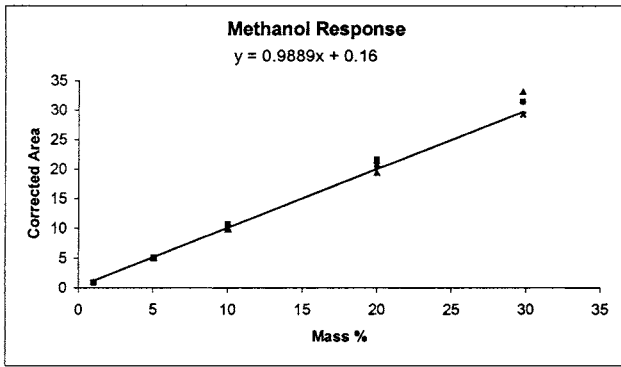


FIG. 11 Graphical Representation Determination of Oxygenate Response - DHA Speciation Analysis

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.

18. Keywords

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

TABLE 4 Repeatability and Reproducibility of DHA Determinations

NOTE 1—The following is a partial list of precision data that has been prepared by statisticians of CS94 in accordance with RR: D2-1007, and represents their best estimate of the cooperative study data. The complete precision data set appears in Annex A1., Table A1.3.

NOTE 2—For each analyte to qualify for a precision statement, it must be present in at least six samples, and detected by at least six laboratories, at least once. The (repeatability standard deviation)/mean value for each analyte/sample combination must be less than or equal to 0.1, as per LOQ requirements which, while not a standard, is what CS94 is recommending.

NOTE 3—

Legend:

- r_{min} = lower 95 % confidence limit of r_{est} ,
- r_{est} = repeatability estimate in percent of concentration,
- r_{max} = upper 95 % confidence limit of r_{est} ,
- R_{min} , R_{est} , R_{max} = for reproducibility,
- C_{min} = lower concentration limit that r_{est} , R_{est} is applicable, and
- C_{max} = upper concentration limit that r_{est} , R_{est} is applicable.

| Component | Average RI | r_{min} | r_{est} | r_{max} | R_{min} | R_{est} | R_{max} | C_{min} | C_{max} |
|----------------------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| n-butane | 400.00 | 6.8 | 9.9 | 13.9 | 15.3 | 32.4 | 59.1 | 1.02 | 3.75 |
| i-pentane | 477.45 | 5.9 | 7.2 | 8.7 | 8.5 | 14.8 | 23.8 | 2.48 | 13.38 |
| Pentene-1 | 490.83 | 5.2 | 7.5 | 10.5 | 9.7 | 13.8 | 19 | 0.06 | 0.43 |
| n-pentane | 500.00 | 5.2 | 6.5 | 8.1 | 7.1 | 10.4 | 14.8 | 1.06 | 3.49 |
| Cyclopentane | 566.84 | 3.8 | 4.9 | 6.2 | 7 | 10.1 | 14 | 0.07 | 0.59 |
| 2,3-dimethylbutane | 569.24 | 2.9 | 3.2 | 3.5 | 5.1 | 8.5 | 13.1 | 0.7 | 1.91 |
| n-hexane | 600.00 | 2 | 2.4 | 2.9 | 3.6 | 5.1 | 6.9 | 0.33 | 2.52 |
| Methylcyclopentane | 625.86 | 2.2 | 2.6 | 3.1 | 4.5 | 6.4 | 8.7 | 0.37 | 2.35 |
| 1-methylcyclopentene | 648.71 | 1.9 | 2.7 | 3.7 | 7.9 | 8.7 | 9.6 | 0.17 | 0.82 |
| Benzene | 649.92 | 2.6 | 3.6 | 4.8 | 5.5 | 9 | 13.7 | 0.17 | 1.58 |
| Cyclohexane | 657.81 | 2.7 | 3.7 | 4.9 | 8.2 | 14.8 | 24.3 | 0.07 | 0.9 |
| 2-methylhexane | 667.61 | 1.6 | 2.2 | 2.9 | 5.1 | 6.1 | 7.2 | 0.39 | 1.09 |
| 2,2,4-trimethylpentane | 688.48 | 2.4 | 3.2 | 4.1 | 7.4 | 11.4 | 16.7 | 0.1 | 11.26 |
| n-heptane | 700.00 | 2.5 | 3.4 | 4.5 | 7.7 | 10.8 | 14.7 | 0.21 | 1.06 |
| Methylcyclohexane | 717.89 | 2.8 | 3.4 | 4 | 4.1 | 5.9 | 8.2 | 0.11 | 1.2 |
| 2,3,4-trimethylpentane | 746.83 | 2.3 | 3.8 | 6 | 5.8 | 7.8 | 10.3 | 0.08 | 4.26 |
| Toluene | 751.77 | 1.9 | 2.7 | 3.8 | 10.8 | 13.5 | 16.5 | 1.99 | 10.34 |
| 2-methylheptane | 764.14 | 3.5 | 4.9 | 6.6 | 4.8 | 6.1 | 7.5 | 0.15 | 0.63 |
| n-octane | 800.00 | 2.2 | 3.6 | 5.5 | 6.5 | 15.7 | 30.9 | 0.14 | 0.75 |
| Ethylbenzene | 854.65 | 2.2 | 3.2 | 4.4 | 7.2 | 10.6 | 14.9 | 0.62 | 2.62 |
| 1,3-dimethylbenzene | 864.22 | 2.6 | 3.3 | 4.2 | 9.7 | 12.5 | 15.7 | 1.55 | 6.66 |
| 3-methyloctane | 880.24 | 5.1 | 8.5 | 13 | 8.7 | 15.5 | 24.9 | 0.07 | 0.29 |
| n-nonane | 900.20 | 3.9 | 6.4 | 9.8 | 8.6 | 10.3 | 12.2 | 0.06 | 0.34 |
| n-propylbenzene | 946.33 | 2.8 | 5 | 8.1 | 7.6 | 11.9 | 17.7 | 0.21 | 0.77 |
| 1,4-methylethylbenzene | 956.22 | 3.5 | 5.3 | 7.7 | 5.1 | 7.7 | 11.1 | 0.32 | 1.19 |
| 1,3,5-trimethylbenzene | 961.92 | 3.7 | 5.5 | 7.7 | 5.4 | 8.3 | 12.1 | 0.39 | 1.21 |
| 2-methylnonane | 971.77 | 6.5 | 10.6 | 16.2 | 17.5 | 25.9 | 36.6 | 0.03 | 0.19 |
| 1,2,4-trimethylbenzene | 983.40 | 4.2 | 5.7 | 7.5 | 7.8 | 10.6 | 13.9 | 1.19 | 4.32 |
| n-decane | 1000.20 | 7.5 | 9.2 | 11.1 | 12.1 | 17.9 | 25.3 | 0.03 | 0.25 |
| 1,2,3-trimethylbenzene | 1006.88 | 3.8 | 5.8 | 8.5 | 7.2 | 8.5 | 10 | 0.28 | 0.96 |
| n-undecane | 1100.00 | 8.6 | 13.9 | 21 | 24.4 | 40 | 61.2 | 0.03 | 0.18 |
| 1,2,3,5-tetramethylbenzene | 1108.79 | 6.4 | 7.8 | 9.3 | 10.2 | 13.9 | 18.3 | 0.21 | 0.51 |
| Naphthalene | 1168.01 | 6.1 | 8.5 | 11.3 | 12.9 | 16.9 | 21.5 | 0.13 | 0.4 |
| n-dodecane | 1200.00 | 12.2 | 16.7 | 22.1 | 20.2 | 32.9 | 50 | 0.01 | 0.11 |
| 2-methylnaphthalene | 1282.57 | 7.6 | 11.1 | 15.4 | 17.5 | 22.3 | 28 | 0.05 | 0.5 |

(Mandatory Information)

A1. PROCEDURE FOR ADJUSTING THE SELECTIVITY OF A DHA METHYL SILICONE OPEN TUBULAR COLUMN

A1.1 The successful application of this test method is highly dependent upon the selectivity of the column used. New 100 m × 0.25 mm 0.5 μm methyl silicone open tubular fused silica columns will likely not have sufficient selectivity for aromatics to function properly. Critical to the successful analysis of *reformulated* and oxygenated spark engine motor fuels is column inertness and component selectivity. Inertness of the primary 100–m column affects the retention and adsorption of the oxygenates such as alcohols and ethers, while selectivity for the aromatic compounds is controlled by the liquid phase. Until adequate commercial columns are available, it will be necessary to slightly increase the column selectivity, which is accomplished by the addition of a short precolumn containing a moderately selective liquid phase.

A1.2 Prior to making any precolumn additions to the 100–m methyl silicone capillary column, determine that the main column meets the column specifications outlined in 6.4.1 and determined in Section 9. Section 9 describes the preliminary evaluation of the 100–m methyl silicone capillary column, using a 35°C isothermal analysis to determine the basic column characteristics of efficiency, retention factor, inertness, and selectivity. Figs. A1.1-A1.3 provide examples of the column quality specification determinations. These determinations may also be made with a precolumn attached, since the precolumn has little if any affect on the results. Fig. A1.4 illustrates that the addition of different lengths of precolumn has negligible influence on the retention characteristics of oxygenated compounds. Poor peak shape and resolution of these oxygenates cannot be corrected by the addition of the precolumn. Tailing peaks may also be the result of an active injector liner or packing material, or both, in the injector liner. An increase in retention of the oxygenates is likely due to column activity. The relative position of the oxygenates to the hydrocarbons is dependent upon column temperature, thus a faulty column oven temperature control could also result in shifted peaks.

A1.3 When necessary, a precolumn is added to the primary 100–m column to adjust the column selectivity for aromatic compounds. Precolumns that have been used successfully are variable lengths of 0.25 mm internal diameter fused silica open tubular column containing a 1.0 μm film thickness of 5 % phenyl methyl silicone. The film thickness is likely not critical, only the total amount of phase. Lengths ranging from 1 to more than 3 m have been necessary to provide sufficient selectivity, depending on the initial selectivity of the methyl silicone column used. One metre of 1.0 μm precolumn is equivalent to a 100–m column with 0.5 μm of 0.1 % phenyl methyl silicone liquid phase.

A1.4 Figs. A1.5-A1.8 illustrate the resolution of the methylcyclopentene-1 and benzene pair with a new column and one, two, and three metres of precolumn. The key segment of the chromatogram is expanded to better illustrate the resolution of this component pair.

A1.5 The preliminary evaluation of the 100–m column will provide the user with information regarding the initial length of precolumn with which to start the tuning process. Dependent upon the methylcyclopentene-1 and benzene resolution, an initial precolumn of between 1 and 4 m is selected; which ever provides a resolution greater than 1.2.

A1.6 The final tuning will consist of reducing the precolumn length, probably in increments of 0.25 m, until the proper resolution is achieved between 2,3,3-trimethylpentane and toluene, and 1,4-dimethylbenzene and 2,3-dimethylheptane; using the actual analysis temperature conditions.

A1.7 Fig. A1.9 illustrates graphically the effect of different lengths of precolumn, attached to the same 100–m column. The key component separations are shown. These analyses were made using the conditions given in Table 2. In this case, the use

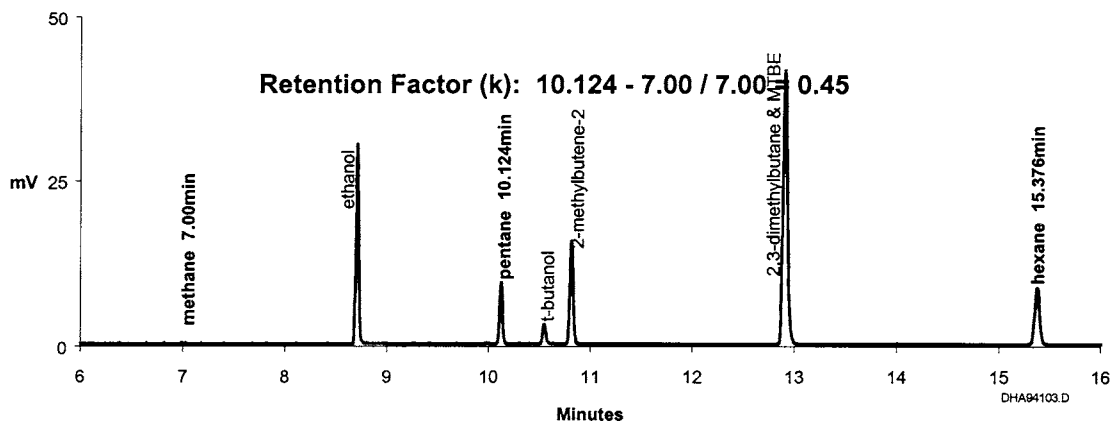


FIG. A1.1 Column Retention Factor Calculation (9.1)

Efficiency (n): $5.545 (10.124 / 0.032)^2 = 555,016$
 Resolution (R): $2(10.817 - 10.547) / 1.699(0.034 + 0.034) = 4.673$

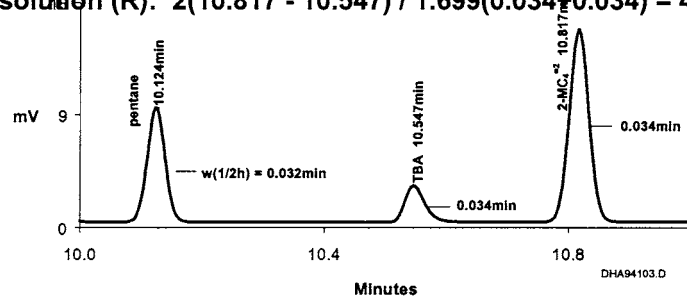


FIG. A1.2 Column Efficiency and Resolution Calculations (9.2 and 9.3)

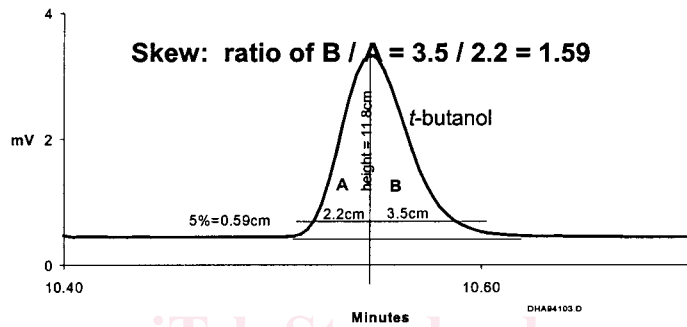


FIG. A1.3 Column Inertness - Peak Skewness Calculation (11.5)

of the 1.25-m precolumn provides the best compromise for the three key separations.

ent 100-m columns. The final precolumn length will provide adequate resolution of all three of the key separations.

A1.8 Fig. A1.10 illustrates the use of different lengths of precolumn to achieve the specified selectivity for three differ-

A1.9 Figs. A1.11-A1.17 illustrate DHA analyses.