



Designation: D 6623 – 01

An American National Standard

Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by High Resolution Gas Chromatography¹

This standard is issued under the fixed designation D 6623; 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 reappraisal. A superscript epsilon (ε) indicates an editorial change since the last revision or reappraisal.

INTRODUCTION

This test method consists of three individual procedures designated as A, B, and C. Procedure A (Detailed Hydrocarbon Analysis-DHA) was the first procedure submitted to be tested and developed by ASTM. Procedure B (Individual Hydrocarbon Analysis-IHA) is derived from the revised Canadian [CAN/CGSB-3.0 No. 14-3-94](#) test method. Procedure C (DHC) is derived and is consistent with the French Standard NF M07-086. Procedures A and B employ 100 metre poly (dimethyl) siloxane open tubular capillary columns and procedure C employs a 50 metre poly (dimethyl) siloxane capillary column. In addition, Procedure A requires the use of a short precolumn (injector end) located in the GC oven and connected to the 100 metre capillary column. The precolumn is used to optimize separation selectivity. Similar samples were used to obtain the precision statements for Procedures A and B while the precision for Procedure C was obtained with a different sample set. All three procedures used similar ASTM approved statistical procedures for the calculation of the precision statements. Although the three procedures share similar instrumentation requirements and practice of the gas chromatographic art, the scope as indicated, apparatus description, reagents and materials, system optimization, calibration, calculation and precision sections are presented separately for each procedure to allow the user to perform effectively each procedure as practiced in the original interlaboratory cooperative study. It is very important that the user of this test method specify clearly which procedure (A, B, or C) was used when comparing results with other laboratories or reporting results. [Appendix X1](#) of this test method contains comparison data for Procedures A and B for several interlaboratory cooperative study samples with other types of test methods for several selected oxygenates and hydrocarbon types. Comparison data for Procedure C is not available since it used a different set of gasolines in the round robin.

1. Scope

1.1 Procedures A and B:

1.1.1 Test Procedures A and B provide for 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.

1.1.2 Based on the cooperative study results, individual component concentrations and precision are determined in the

range of 0.01 to approximately 30 % mass percent. The procedures may be applicable to higher and lower concentrations for the individual components; however, the user shall verify the accuracy if the procedures are used for components with concentrations outside the specified ranges.

1.1.3 Test Procedures A and B also determine methanol, ethanol, t-butanol methyl t-butyl ether (MTBE), ethyl t-butyl ether (ETBE), t-amyl-methyl-ether (TAME) in spark ignition engine fuels in the concentration range of 1 to 30 mass %. However, the cooperative study data provided sufficient statistical data for MTBE in Procedure B only.

1.1.4 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 olefinic or naphthenic, or both (for example, virgin naphthas) constituents

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D.02.04.0L on Hydrocarbon Analysis.

Current edition approved March 10, 2001. Published May 2001.

above *N*-octane may reflect significant errors in PONA type groupings. Based on the gasoline samples in the interlaboratory cooperative study, these procedures are applicable to concentrations of olefins to less than 25 mass %. However, some interfering coelution 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. Appendix X1 of this test method compares results of the test procedures 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 analysis can be obtained by using the specific test methods listed in the reference section.

1.1.4.1 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.

1.1.5 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.

1.2 Procedure C:

1.2.1 Test Procedure C provides for the determination of individual hydrocarbon components of spark-ignition engine fuels 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. The tables related to Procedure C enumerate the components reported. Component concentrations are determined in the range of 0.10 to 15 mass %. The procedure may be applicable to higher and lower concentrations for the individual components; however, the user shall verify the accuracy if the procedures are used for components with concentrations outside the specified ranges.

1.2.2 This test method is applicable also to spark-ignition engine fuel blends containing oxygenated components. However, in this case, the oxygenate content shall be determined by Test Methods D 5599 or D 4815.

1.2.3 Benzene co-elutes with 1-methylcyclopentene. Benzene content shall be determined by Test Method D 3606 or D 5580.

1.2.4 Toluene co-elutes with 2,3,3-trimethylpentane. Toluene content shall be determined by Test Method D 3606 or D 5580.

1.2.5 Although a majority of the individual hydrocarbons present are determined, some co-elution of compounds is encountered. If this procedure 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 olefinic (for example, cracked naphthas) or naphthenic, or both (for example, virgin naphthas) constituents above *N*-octane may reflect significant errors in PONA type groupings. Based on the interlaboratory cooperative study, this procedure is applicable to concentrations of olefins to less than 20 mass %. However, some interfering coelution with the olefins above normal heptane 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. Since many of the olefins in spark ignition fuels are at a concentration below 0.10 %, they are not reported by this test method and may bias the total olefin results low.

1.2.5.1 Total olefins in the samples may be obtained or confirmed, or both by Test Method D 1319 (volume %) or other test methods, such as those based on multidimensional PONA type of instruments.

1.2.6 If water is or is suspected of being present, its concentration may be determined, if desired, by the use of Test Method D 1744. Other compounds containing 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 Method D 5623 for sulfur compounds.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are provided for information only.

1.4 *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 3606 Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography⁴

D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder⁴

D 4057 Practice for Manual Sampling of Petroleum and 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

² Annual Book of ASTM Standards, Vol 05.01.

³ Discontinued; see 2000 Annual Book of ASTM Standards, Vol 05.01.

⁴ Annual Book of ASTM Standards, Vol 05.02.



D 4420 Test Method for Aromatics in Finished Gasoline by Gas Chromatography⁴

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 Chromatographs⁶

2.2 Other Standard:

CAN/CGSB-3.0 No. 14-3-99 Test Method for Individual Hydrocarbon Component Analysis (IHA) in Spark Ignition Engine Fuels by Gas Chromatography⁷

3. Terminology

3.1 Definitions:

3.1.1 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 Representative samples of the petroleum liquid are introduced into a gas chromatograph equipped with an open tubular (capillary) column coated with specified stationary phase(s). 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 recorded digitally by way of an integrator or integrating computer. Each eluting component is identified by comparing its retention time to those 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 of selected components with detector response factors. In Procedures A and B, the unknown components are reported individually as well as a summary total.

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 may be determined through the use of this test method.

PROCEDURE A – DETAILED HYDROCARBON ANALYSIS

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 **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. 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 each 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 selectivity.

⁵ Annual Book of ASTM Standards, Vol 05.03.

⁶ Annual Book of ASTM Standards, Vol 14.02.

⁷ Available from Canadian General Standards Board (CGSB), Ottawa, Canada K1A 1G6, Methods of Testing Petroleum and Associated Products.

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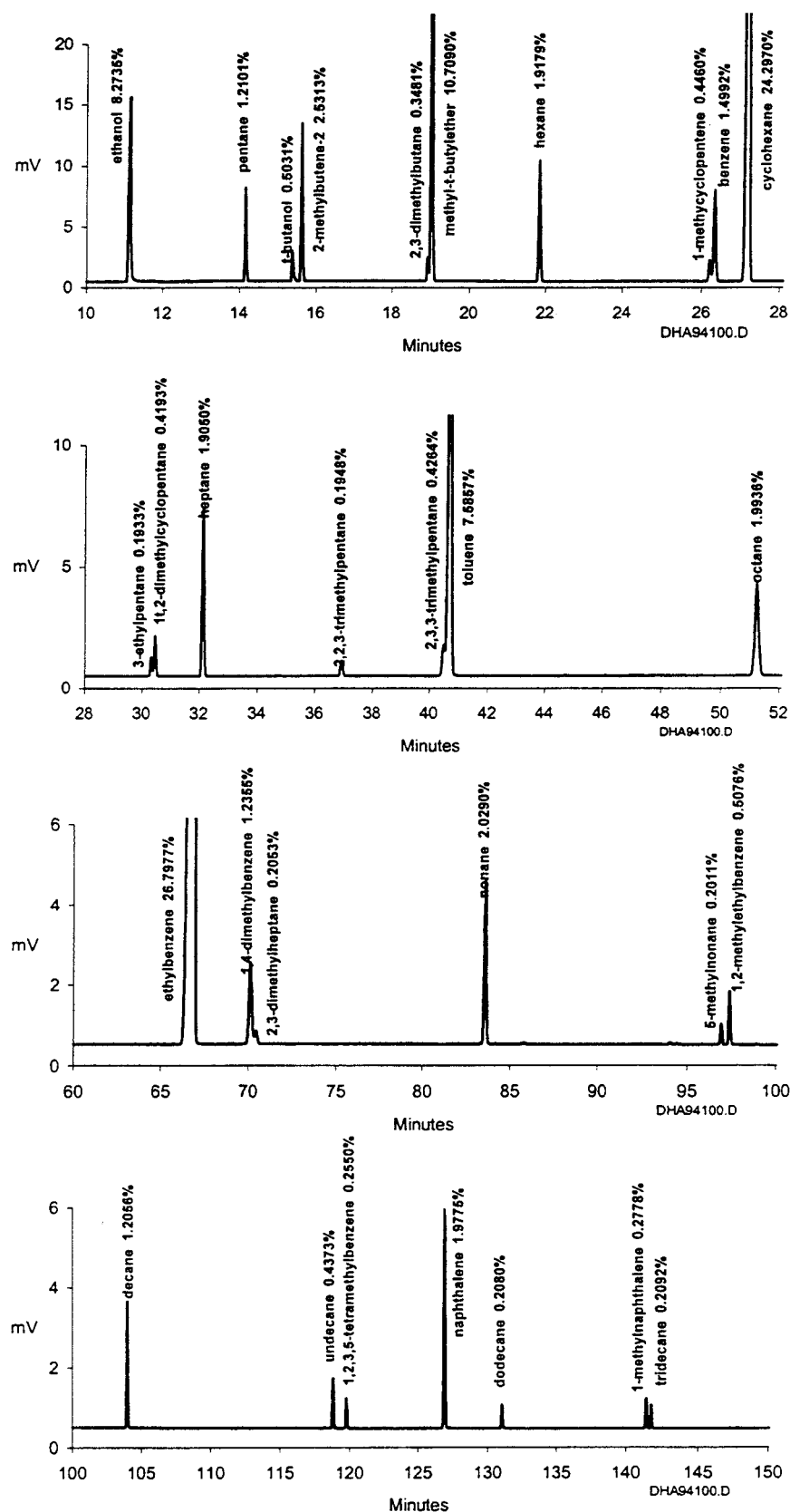


FIG. 1 DHA Speciation Analysis - System and Column Evaluation Mixture

Until adequate columns are commercially available, the currently used dimethylpolysiloxane columns can be modified or *tuned* to meet the method column specifications. See Section 10 for a description of the column 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.

Column Specifications:

Material	fus
Ed silica	
Length	10
0 metres	
Internal diameter	0.2
5 millimetre	
Liquid phase	di
Methylpolysiloxane	
Film thickness	0.5
0 micrometre	
Theoretical plates, n, pentane at 35°C	~
400 000 to 500 000	
Retention Factor, k, pentane at 35°C	0.4
5 to 0.50	
Resolution, R, <i>t</i> -butanol and 2-methylbutene-2 at 35°C	3.2
5 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 metres) of 5 % phenyl methyl silicone 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 high 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 Society⁸ 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.)

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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

TABLE 1 System and Column Evaluation Mixture (mass%)

Ethanol	8.00 %	<i>N</i> -octane	2.00 %
<i>N</i> -pentane	2.00 %	ethylbenzene	25.00 %
<i>t</i> -butanol	0.50 %	<i>p</i> -xylene	1.00 %
2-methylbutene-2	2.50 %	2,3-dimethylheptane	0.20 %
2,3-dimethylbutane	0.50 %	<i>N</i> -nonane	2.00 %
methyl- <i>t</i> -butyl ether	10.00 %	5-methylnonane	0.20 %
<i>N</i> -hexane	2.00 %	1-methyl-2-ethylbenzene	0.50 %
1-methylcyclopentene	0.50 %	<i>N</i> -decane	1.00 %
benzene	1.00 %	<i>N</i> -undecane	0.50 %
cyclohexane	28.90 %	1,2,3,5-tetramethylbenzene	0.25 %
3-ethylpentane	0.20 %	naphthalene	0.50 %
1,2t-dimethylcyclopentane	0.50 %	<i>N</i> -dodecane	0.25 %
<i>N</i> -heptane	2.00 %	1-methylnaphthalene	0.25 %
2,3,3-trimethylpentane	0.50 %	<i>N</i> -tridecane	0.25 %
toluene	7.00 %		

TABLE 2 Gas Chromatograph 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
⁴ 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

⁴ Use manufacturer's recommended detector gas flows or:

7.5.3 *Ethanol*—Only absolute ethanol of 99.5 minimum % 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. (**Warning**—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 (Test Methods D 4057 and D 4177). If the sample as received does not meet the upper boiling range requirements of 1.1.1, 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.

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 pre-cooled 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 100m column and, if required, a precolumn in accordance with 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.

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

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):

where:

P = (head pressure (psig) + ambient pressure)/ambient pressure,

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

u_o = u_{ave}/j = column outlet velocity,

A_c = $\pi(r)^2$ = column cross-sectional area (cm²),

where:

r = column internal radius (cm), and
flow rate (cm³/min) = $u_o \times A_c \times 60$.

9.5.2 Injection Split Ratio—(split flow rate + column flow rate)/column flow rate (Section 7).

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

where:

u_{ave} = $100 \times 100/6.98 \times 60 = 23.88$ cm/s,

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

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

u_o = $23.88/0.33 = 71.96$ cm/s,

A_c = $\pi(0.025/2)^2 = 4.9 \times 10^{-4}$ cm²,

flow rate = $71.96 \times 4.9 \times 10^{-4} \times 60 = 2.12$ cm³/min., and

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.

10.2 Set the injector temperature and split ratio to the values in Fig. 2 and for each set of conditions inject the listed quantities of the System and Column Evaluation Mixture (see 7.5.5), using the operating conditions listed in Table 2 or as determined in Section 12.

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

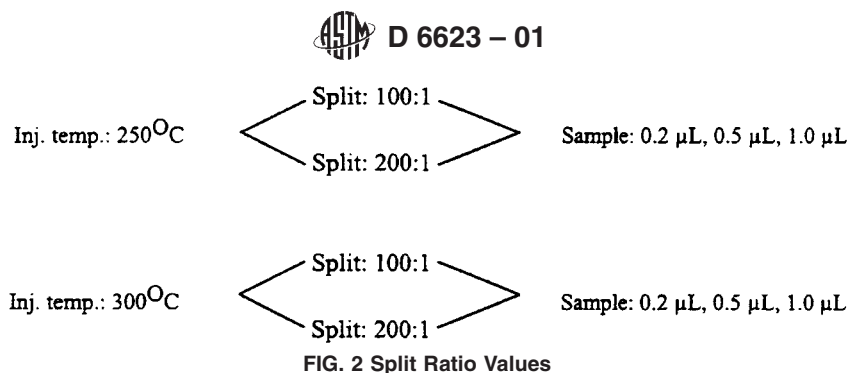
% relative error = 100

$\times (\text{concentration determined} - \text{concentration known}) / \text{concentration known}$



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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, Figure 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.

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:

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

where:

n = column efficiency (theoretical plates),

t_R = retention time of pentane, and

$w_{1/2}$ = peak width at half height.

h

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:

$$R = 2(t_{R2-M-Butene-2} - t_{R_{TBA}})/1.699(w_{1/2}^1_{h2-M-Butene-2} + w_{1/2}^1_{TBA}) \quad (5)$$

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.

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

This test 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-methyl-butene-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. See Fig. 3.

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. See Fig. 4.

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.

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-DMC₄, use a 9 min initial hold. If too close to the 2-MC₅, use an 11 min hold. See Fig. 5.

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. See Fig. 6.

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. See Fig. 7.

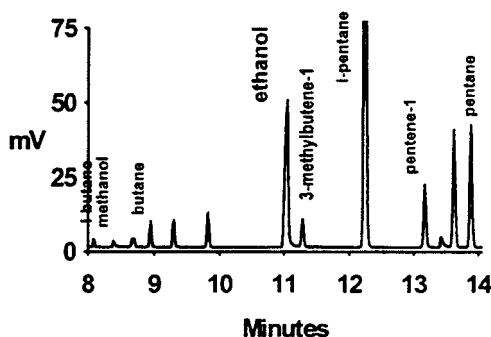


FIG. 3 Separation of *i*-butane/methanol and ethanol/3-methyl-butene-1

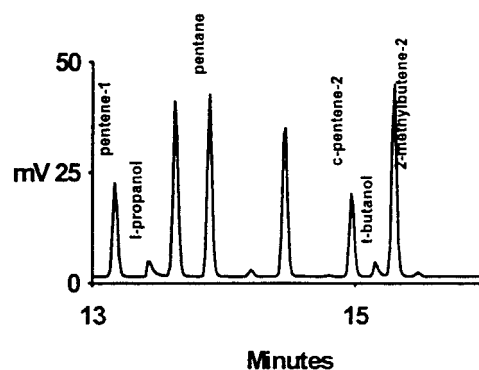


FIG. 4 Separation of *i*-propanol/2-methylbutene-1 and *t*-butanol/2-methylbutene-2

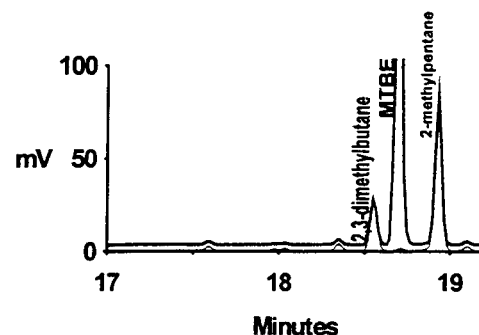


FIG. 5 Separation Between 2,3-dimethylbutane and methyl-*t*-butylether

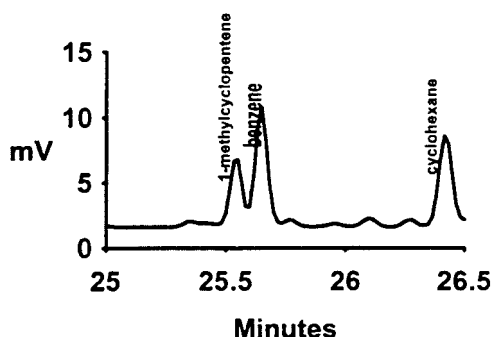


FIG. 6 Separation Between 1-methylcyclopentene and benzene

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. See Fig. 8.

12.3.7 I17 (unknown)/1,2-methylethylbenzene—The unknown isoparaffin (I17) 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. See Fig. 9.

12.3.8 1-methylnaphthalene/tridecane—The recommended final column temperature program rate of 1.5°/min. should be used.

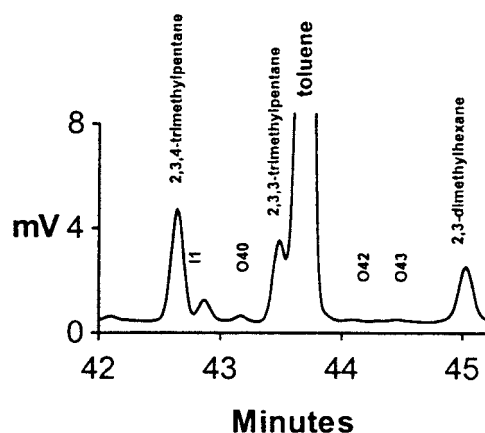


FIG. 7 Separation Between 2, 3, 3-trimethylpentane and toluene

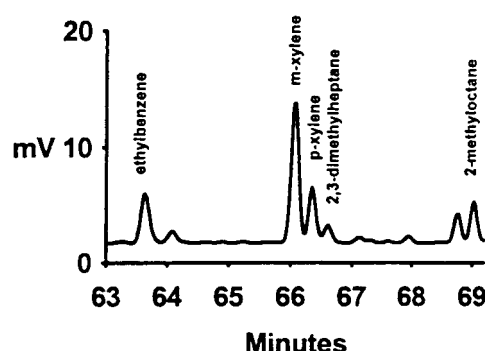


FIG. 8 Separation Between p-xylene and 2,3-dimethylheptane

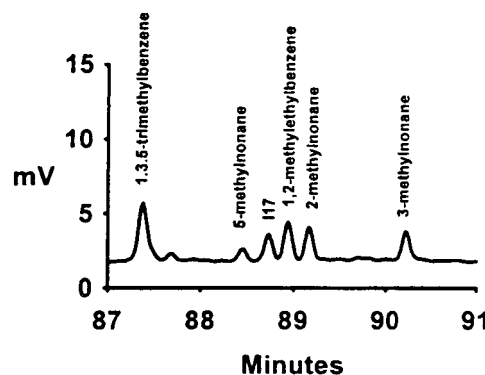


FIG. 9 Separation Between Unknown isoparaffin (I17) and 1,2-methylethylbenzene

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. See Fig. 10.

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

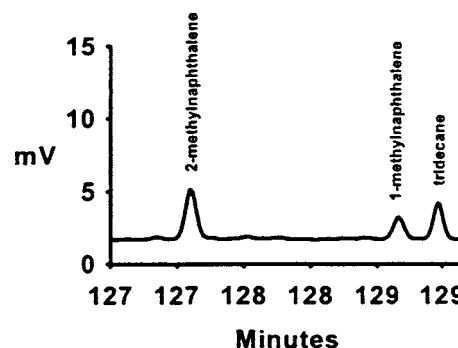


FIG. 10 Separation Between 1-methylnaphthalene and tridecane

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:

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

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 = the correction factor with heptane as unity (1.0000), and
- 0.7487 = 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

TABLE 3 Theoretical FID Relative Response Factors

Carbon Number	Saturated Aromatics Paraffins	Unsaturated Paraffins	Saturated Naphthenes	Unsaturated Naphthenes
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
7	1.0000	0.9799	0.9799	0.9598
8	0.9975	0.9799	0.9799	0.9623
9	0.9955	0.9799	0.9799	0.9642
10	0.9940	0.9799	0.9799	0.9658
11	0.9927	0.9799	0.9799	0.9671
12	0.9916	0.9799	0.9799	0.9681
13	0.9907	0.9799	0.9799	0.9690
14	0.9899	0.9799	0.9799	0.9698
15	0.9893	0.9799	0.9799	0.9705

conditions of this test method (see Fig. 11). Each individual apparatus must be calibrated using gravimetrically prepared standards, covering the sample concentration ranges expected and the scope of this method. Standards used must comply with the requirements in Section 7. Fig. 11 and Fig. 12 presents 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 2 or as determined in Section 12.

14.2 Set the recorder and/or integration device 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 of Results

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 retention index (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 3 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.

component % (m/m) = corrected peak area × (100 - % undetected)/total corrected peak area

16. Expression of Results

16.1 Report the concentration of each component as mass percent, % (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 warning 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 5 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 5 for the gasoline components.

17.3 *Bias*—No information can be presented on the bias of the procedure in Test Method D 6623 for measuring hydrocarbon concentrations because no material having an accepted reference value is available.

18. Keywords

18.1 detailed hydrocarbon analysis; DHA; DHC; gas chromatography; hydrocarbons; IHA; open tubular column; oxygenates; PIANO; PONA

⁹ Supporting data describing the interlaboratory cooperative study to determine precision has been filed at ASTM headquarters and may be obtained by requesting research report RR:D02-1505.

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	340.9089	717.4781	1046.1427		
	0.3599	33.8017	179.9043	353.4087	717.1507	980.1586		
ave.	0.3818	34.2830	177.3953	347.1578	717.3144	1013.1486		
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	967.7886	1526.2755		
	0.4065	46.7438	242.3003	500.4514	1007.0434	1537.3776		
ave.	0.3489	48.6314	240.0113	498.2116	987.4161	1531.8265		
RF	0.0267	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	406.5989	757.2307	1546.4197	2241.0530		
	1.1869	72.7872	392.8649	775.5192	1550.7498	2346.4085		
ave.	1.1116	75.1548	400.7309	786.3749	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	66.0965	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	19.8724	29.5727		
	0.4527	69.3251	374.3939	732.8740	1537.9748	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	762.9670	1488.8626	2346.1907		
	0.0072	75.1503	380.0280	763.6254	1420.3514	2230.3657		
ave.	0.1887	75.2480	371.8868	763.3112	1454.6070	2288.2782		
RF	0.0630	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	841.6063	802.3011		
ave.	869.0574	848.8858	838.7089	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	852.9184	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	865.4804	854.5747		
ave.	864.4997	850.9298	869.9455	861.5765	862.8718	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	849.0989	854.1742	881.9661	889.9074	860.0512		
ave.	856.2982	846.1489	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. 11 Determination of Oxygenate Response - DHA Speciation Analysis

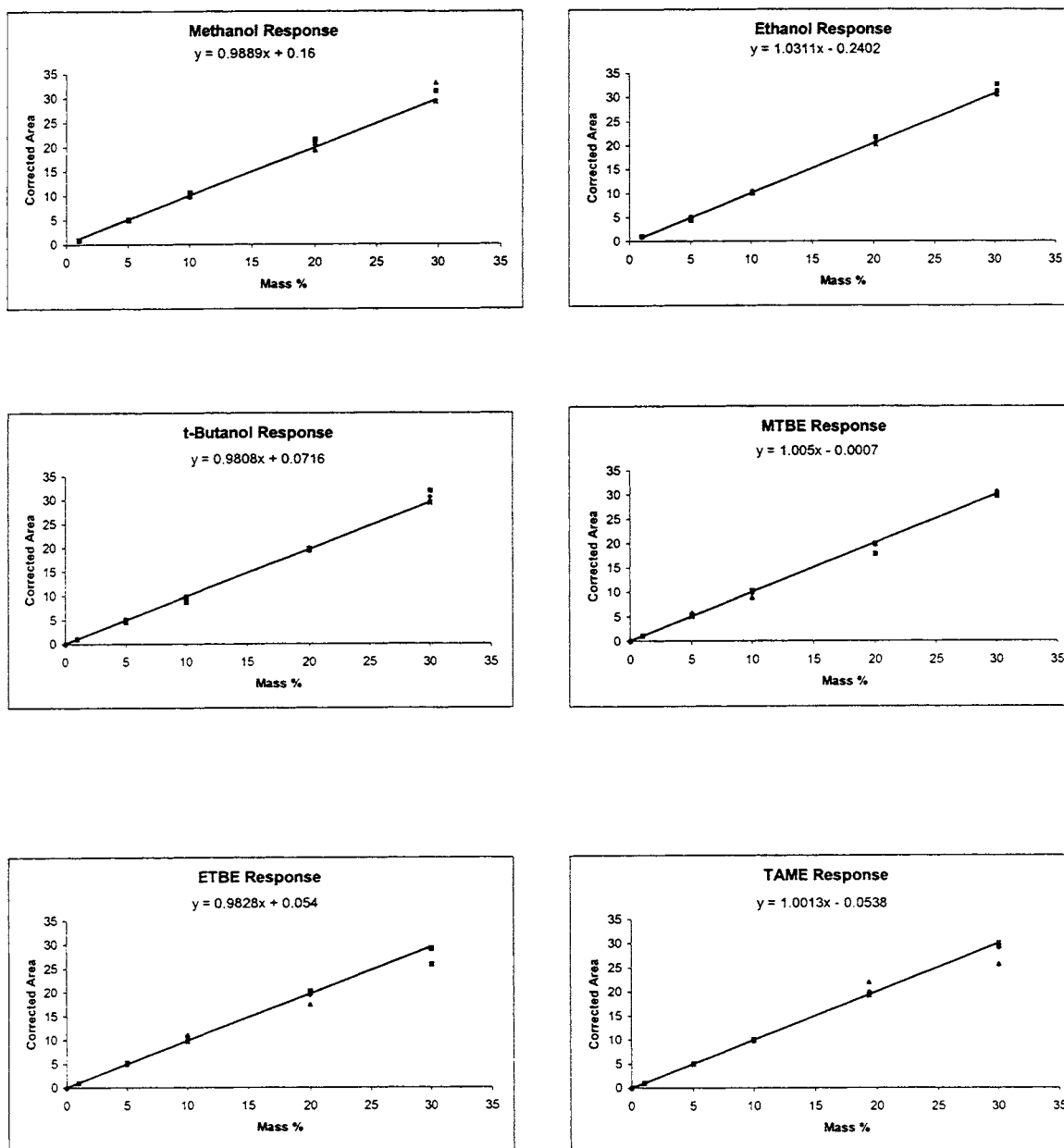


FIG. 12 Determination of Oxygenate Response for Procedure A — Speciation Analysis



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TABLE 4 Repeatability and Reproducibility of DHA Determinations

NOTE 1—The following is a partial list of precision data which has been prepared by statisticians of CS94 in accordance with research report RR:D02-1007, 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 labs, at least once. The (repeatability standard deviation)/mean value for each analyte/sample combination must be less than or equal to 0.1 in accordance with LOQ requirements which, while not a standard, is what CS94 is recommending.

- $r_{\min}$ – 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
- $C_{\max}$ – upper concentration limit that r_{est} , R_{est} is applicable

Component	Ave. 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



D 6623 – 01

TABLE 5 Repeatability and Reproducibility of DHA Determinations

NOTE 1—The following data has been prepared by statisticians of CS94 in accordance with RR:D02-1007, and represents their best estimate of the cooperative study data. Not all of the data qualified for this evaluation since:

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

$r_{\min}$ – 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
 $C_{\max}$ – upper concentration limit that r_{est} , R_{est} is applicable

Component	Ave. RI	$r_{\min}$	r_{est}	$r_{\max}$	$R_{\min}$	R_{est}	$R_{\max}$	$C_{\min}$	$C_{\max}$
i-butane	366.15	5.6	10.1	16.4	22.8	46.1	81.5	0.06	0.38
butene-1	390.72	6.4	11.1	17.6	31.2	64.5	115.8	0.01	0.14
n-butane	400.00	6.8	9.9	13.9	15.3	32.4	59.1	1.02	3.75
2,2-dimethylpropane	415.10	3.3	8.8	18.6	32.1	50.1	73.7	0.01	0.02
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	0.06	0.43
2-methylbutene-1	496.66	4.9	6.9	9.4	8.3	12.9	19.0	0.14	0.86
n-pentane	500.00	5.2	6.5	8.1	7.1	10.4	14.8	1.06	3.49
t-pentene-2	510.56	4.5	6.5	9.0	7.2	10.3	14.4	0.28	1.16
c-pentene-2	519.53	4.7	6.3	8.1	7.6	13.2	20.9	0.16	0.63
2-methylbutene-2	524.92	4.3	6.0	8.1	7.8	11.4	15.9	0.50	1.85
1,3-pentadiene	527.97	6.7	14.0	25.3	17.0	25.3	35.9	0.01	0.06
2,2-dimethylbutane	540.54	3.1	4.7	6.8	6.4	9.9	14.6	0.08	2.18
cyclopentene	557.21	4.0	5.8	8.1	7.6	10.5	13.9	0.07	0.27
4-methylpentene-1	562.02	2.7	4.2	6.1	8.9	11.3	14.0	0.02	0.09
3-methylpentene-1	562.81	3.5	5.0	6.9	6.1	8.8	12.0	0.03	0.12
cyclopentane	566.84	3.8	4.9	6.2	7.0	10.1	14.0	0.07	0.59
2,3-dimethylbutane	569.24	2.9	3.2	3.5	5.1	8.5	13.1	0.70	1.91
2-methylpentane	573.70	2.5	2.9	3.4	5.1	6.6	8.4	1.06	5.80
4-methyl-t-pentene-2	575.47	6.5	8.7	11.3	18.1	28.0	41.1	0.08	0.28
3-methylpentane	585.52	2.6	2.9	3.2	4.0	5.6	7.5	0.60	2.50
2-methylpentene-1	590.19	2.3	2.7	3.2	3.8	5.4	7.4	0.11	0.45
hexene-1	591.06	3.1	4.2	5.5	5.9	8.2	10.9	0.06	0.26
n-hexane	600.00	2.0	2.4	2.9	3.6	5.1	6.9	0.33	2.52
t-hexene-3	602.83	1.9	3.2	4.9	7.4	11.8	17.7	0.08	0.35
t-hexene-2	605.44	2.5	2.8	3.2	4.5	6.4	8.9	0.16	0.71
2-methylpentene-2	607.86	2.4	3.0	3.8	6.1	13.1	24.1	0.22	0.97
3-methyl-c-pentene-2	610.54	2.1	2.5	2.9	5.3	6.9	8.7	0.11	0.48
3-methylcyclopentene	611.61	3.0	4.6	6.8	10.1	12.8	15.9	0.02	0.10
c-hexene-2	614.67	2.6	3.3	4.1	4.8	5.4	6.1	0.09	0.40
3,3-dimethylpentene-1	620.91	1.9	2.5	3.1	4.3	5.7	7.5	0.17	0.75
2,2-dimethylpentane	624.17	3.3	4.3	5.5	4.4	8.2	13.7	0.01	0.09
methylcyclopentane	625.86	2.2	2.6	3.1	4.5	6.4	8.7	0.37	2.35



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TABLE 5 Continued

Component	Ave. RI	T_{min}	T_{est}	T_{max}	R_{min}	R_{est}	R_{max}	C_{min}	C_{max}
2,4-dimethylpentane	630.60	1.6	2.5	3.8	4.2	5.3	6.6	0.20	1.94
2,2,3-trimethylbutane	634.86	3.2	7.1	13.1	12.5	20.4	31.1	0.02	0.08
3,4-dimethylpentene-1	642.87	5.5	14.7	30.6	9.7	22.3	43.0	0.01	0.03
4,4-dimethyl-c-pentene-2	646.65	3.8	5.6	8.0	6.1	11.0	17.9	0.01	0.11
2,4-dimethylpentene-1	647.67	3.8	6.7	10.8	11.9	13.5	15.3	0.01	0.04
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	9.0	13.7	0.17	1.58
5-methylhexene-1	655.56	5.3	7.5	10.1	18.0	30.4	47.6	0.01	0.22
cyclohexane	657.81	2.7	3.7	4.9	8.2	14.8	24.3	0.07	0.90
2-methyl-t-hexene-3	661.03	3.2	6.3	11.0	16.8	23.4	31.6	0.03	0.14
2-ethyl-3-methylbutene-1	662.60	4.1	8.9	16.5	89.5	117.0	149.7	0.01	0.04
4-methylhexene-1	663.81	2.5	4.5	7.2	11.7	14.7	18.3	0.02	0.09
4-methyl-t-c-hexene-2	666.23	2.1	3.2	4.7	5.4	7.3	9.5	0.05	0.28
2-methylhexane	667.61	1.6	2.2	2.9	5.1	6.1	7.2	0.39	1.09
2,3-dimethylpentane	668.84	1.6	2.3	3.2	5.4	6.4	7.5	0.33	3.16
3-methylhexane	675.89	1.9	2.8	4.0	4.7	5.6	6.7	0.37	1.08
3,4-dimethyl-c-pentene-2	679.46	3.6	5.9	9.1	11.6	23.4	41.2	0.02	0.14
1c,3-dimethylcyclopentane	681.68	1.7	2.7	4.0	5.4	7.5	10.1	0.11	0.56
1t,3-dimethylcyclopentane	684.37	1.7	2.8	4.4	5.4	7.7	10.5	0.08	0.48
3-ethylpentane	685.98	3.1	3.7	4.3	5.6	8.3	11.9	0.08	0.26
2,2,4-trimethylpentane	688.48	2.4	3.2	4.1	7.4	11.4	16.7	0.10	11.26
3-methyl-c-hexene-3	694.82	3.2	6.5	11.6	7.3	12.9	20.8	0.03	0.17
t-heptene-3	698.39	2.6	3.2	3.8	5.0	8.1	12.3	0.11	0.67
n-heptane	700.00	2.5	3.4	4.5	7.7	10.8	14.7	0.21	1.06
3-methyl-c-hexene-2	702.30	1.5	2.5	4.0	4.6	7.2	10.6	0.13	0.75
3-methyl-t-hexene-3	702.99	2.2	4.1	6.7	8.1	10.1	12.3	0.05	0.26
t-heptene-2	704.58	2.6	4.2	6.4	5.9	7.1	8.4	0.06	0.34
3-ethylpentene-2	705.96	4.7	8.3	13.4	14.5	17.9	21.8	0.03	0.16
c-heptene-2	708.82	1.9	3.2	5.0	7.0	7.8	8.7	0.12	0.63
2,3-dimethylpentene-2	712.07	2.4	3.7	5.5	7.8	9.1	10.5	0.06	0.57
O29	715.67	6.8	11.5	18.0	15.7	22.6	31.3	0.01	0.08
1c,2-dimethylcyclopentane	717.13	2.4	3.7	5.3	9.5	11.6	13.9	0.05	0.20
methylcyclohexane	717.89	2.8	3.4	4.0	4.1	5.9	8.2	0.11	1.20
2,2-dimethylhexane	720.70	4.2	7.2	11.3	10.2	15.4	22.3	0.02	0.10
2,5-dimethylhexane	730.05	2.5	3.0	3.5	4.9	6.2	7.7	0.16	1.12
2,4-dimethylhexane	731.84	3.5	4.3	5.2	6.5	9.0	12.1	0.29	1.39
1c,2t,4-trimethylcyclopentane	737.11	3.0	4.2	5.6	6.9	7.9	9.0	0.03	0.17
2,3,4-trimethylpentane	746.83	2.3	3.8	6.0	5.8	7.8	10.3	0.08	4.26
11	747.91	2.2	6.2	13.4	10.1	21.1	38.1	0.09	0.59
toluene	751.77	1.9	2.7	3.8	10.8	13.5	16.5	1.99	10.34
2,3-dimethylhexane	757.87	2.2	3.7	5.7	5.0	6.9	9.2	0.22	1.23
1,1,2-trimethylcyclopentane	760.33	7.6	13.5	21.8	13.6	25.7	43.4	0.02	0.26
O44	761.73	4.2	9.4	17.7	12.7	20.5	30.8	0.03	0.24
2-methylheptane	764.14	3.5	4.9	6.6	4.8	6.1	7.5	0.15	0.63
4-methylheptane	765.62	4.1	6.2	9.1	7.1	9.1	11.5	0.05	0.29
3-methyl-3-ethylpentane	766.62	5.4	7.1	9.3	11.0	15.8	21.8	0.05	0.10
3-methylheptane	771.78	2.1	3.4	5.3	4.4	5.1	5.9	0.13	0.71
1c,2t,3-trimethylcyclopentane	772.98	3.4	4.4	5.7	5.9	7.4	9.1	0.06	0.29
3-ethylhexane	773.76	6.9	10.8	15.9	13.1	23.8	39.1	0.01	0.07
1t,4-dimethylcyclohexane	774.89	9.8	18.0	29.8	22.2	49.5	93.1	0.01	0.11
2,2,5-trimethylhexane	782.93	3.1	4.3	5.7	5.7	8.0	10.8	0.14	2.21
3c-ethylmethylcyclopentane	784.35	5.7	12.1	22.1	9.7	22.2	42.5	0.05	0.21
3t-ethylmethylcyclopentane	786.55	7.4	9.7	12.4	8.4	22.1	46.0	0.02	0.11
2t-ethylmethylcyclopentane	787.86	8.9	11.4	14.2	12.6	26.7	48.7	0.02	0.12



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TABLE 5 Continued

Component	Ave. RI	r_{min}	r_{est}	r_{max}	R_{min}	R_{est}	R_{max}	C_{min}	C_{max}
1,2-dimethylcyclohexane	792.77	3.7	6.7	11.0	7.0	10.1	14.0	0.04	0.29
t-octene-4	794.21	12.7	14.5	16.6	16.7	21.9	28.1	0.02	0.18
1c,2c,3-trimethylcyclopentane	797.25	3.5	6.0	9.4	6.3	9.2	12.9	0.07	0.51
1t,3-dimethylcyclohexane	798.80	6.8	9.3	12.4	11.9	16.3	21.7	0.02	0.10
n-octane	800.00	2.2	3.6	5.5	6.5	15.7	30.9	0.14	0.75
octene-2	804.40	4.9	8.2	12.7	11.1	20.1	32.9	0.03	0.23
I2	806.39	4.7	10.9	20.9	8.7	19.7	37.4	0.05	0.36
i-propylcyclopentane	808.06	4.1	10.7	22.0	8.4	19.8	38.4	0.03	0.18
2,3,4-trimethylhexane	818.10	2.5	5.0	8.9	5.1	7.2	9.8	0.05	0.37
N2	819.93	7.7	11.5	16.4	6.8	17.4	35.7	0.01	0.06
N3	822.29	8.0	13.3	20.7	11.3	23.2	41.5	0.01	0.09
2,3,5-trimethylhexane	827.51	3.9	5.4	7.1	7.5	31.4	82.4	0.07	0.12
1,1,4-trimethylcyclohexane	832.56	8.6	17.1	29.9	21.7	36.0	55.6	0.03	0.26
2,2,3-trimethylhexane	834.96	8.4	13.1	19.2	14.8	20.3	27.0	0.05	0.09
2,5-dimethylheptane	842.63	6.8	8.8	11.1	7.8	12.3	18.2	0.11	0.18
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
1,4-dimethylbenzene	865.20	3.6	4.2	5.0	10.4	14.1	18.5	0.62	2.97
I5	870.95	6.6	11.5	18.3	13.8	28.4	50.9	0.02	0.13
4-methyloctane	873.81	4.4	7.6	12.0	5.9	11.2	18.9	0.05	0.20
2-methyloctane	874.76	4.6	8.2	13.3	6.0	10.4	16.6	0.07	0.35
3-ethylheptane	879.11	8.5	13.4	20.1	27.7	38.7	52.5	0.02	0.09
3-methyloctane	880.24	5.1	8.5	13.0	8.7	15.5	24.9	0.07	0.29
1,2-dimethylbenzene	883.47	2.1	3.2	4.7	8.8	11.5	14.8	0.83	3.85
I6	885.34	10.2	17.0	26.4	23.3	44.5	75.8	0.02	0.06
I7	886.38	6.5	9.0	12.0	7.8	21.1	44.7	0.05	0.32
N22	895.99	7.9	16.5	29.6	16.7	29.4	47.2	0.03	0.22
N23/c-nonene-2	897.24	5.7	15.9	34.2	26.1	48.7	81.6	0.02	0.15
I10	898.70	4.5	12.3	26.0	9.3	31.1	73.3	0.04	0.44
n-nonane	900.20	3.9	6.4	9.8	8.6	10.3	12.2	0.06	0.34
i-propylbenzene	912.28	3.2	5.0	7.3	8.3	15.1	24.9	0.04	0.33
N27	914.45	3.6	12.3	29.2	9.0	21.1	40.8	0.02	0.14
I12	921.30	4.4	11.0	22.2	8.7	21.2	42.2	0.03	0.34
2,4-dimethyloctane	924.39	6.1	12.1	21.3	16.8	26.0	38.1	0.03	0.11
2,6-dimethyloctane	930.83	7.0	14.6	26.4	15.4	27.7	45.3	0.02	0.10
2,5-dimethyloctane	932.66	5.6	11.2	19.6	15.3	22.0	30.4	0.04	0.13
3,3-dimethyloctane	942.30	4.3	10.4	20.6	7.5	17.5	34.0	0.03	0.11
n-propylbenzene	946.33	2.8	5.0	8.1	7.6	11.9	17.7	0.21	0.77
3,6-dimethyloctane	948.31	7.6	14.9	25.7	18.1	38.9	71.4	0.01	0.04
1,3-methylethylbenzene	954.42	3.7	5.2	7.2	7.6	10.2	13.3	0.81	2.61
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
3-methylnonane	977.26	7.5	13.5	22.1	23.5	41.0	65.5	0.03	0.16
I18	980.12	7.3	15.7	28.8	14.9	30.0	52.9	0.04	0.82
1,2,4-trimethylbenzene	983.40	4.2	5.7	7.5	7.8	10.6	13.9	1.19	4.32
I21	987.40	6.9	18.6	39.3	16.9	49.6	109.2	0.03	0.27
I24	994.53	6.9	12.2	19.6	18.9	31.1	47.7	0.04	0.36
n-decane	1000.20	7.5	9.2	11.1	12.1	17.9	25.3	0.03	0.25
N38	1003.39	9.7	19.8	35.2	25.8	47.6	79.3	0.01	0.12
1,2,3-trimethylbenzene	1006.88	3.8	5.8	8.5	7.2	8.5	10.0	0.28	0.96
2-3-dihydroindene	1019.44	5.2	7.8	11.3	8.8	10.8	13.0	0.18	0.37
I30	1024.82	7.5	13.9	23.3	20.4	61.8	138.4	0.01	0.15
1,2-methyl-i-propylbenzene	1027.73	17.3	19.5	22.0	66.4	99.4	141.9	0.02	0.08

TABLE 5 Continued

Component	Ave. RI	r_{min}	r_{ref}	r_{max}	R_{min}	R_{ref}	R_{max}	C_{min}	C_{max}
?	1038.53	6.8	16.0	31.1	16.8	37.4	70.2	0.02	0.16
1,3-diethylbenzene	1039.97	5.0	7.3	10.1	9.9	13.7	18.5	0.08	0.22
1,3-methyl-n-propylbenzene	1042.60	4.0	6.4	9.5	6.7	13.5	23.6	0.30	0.68
1,4-methyl-n-propylbenzene	1046.40	4.6	8.7	14.7	7.8	12.7	19.4	0.16	0.32
1,3-dimethyl-5-ethylbenzene	1049.78	3.4	6.0	9.8	7.6	10.6	14.3	0.22	0.51
1,2-methyl-n-propylbenzene	1057.87	6.3	9.3	13.2	20.9	30.3	42.1	0.11	0.20
		4.5	11.4	23.2	14.4	36.1	73.1	0.06	0.56
138	1065.53	7.9	16.6	30.0	28.4	37.4	48.2	0.02	0.09
1,4-dimethyl-2-ethylbenzene	1068.05	4.1	6.7	10.3	15.3	27.8	45.7	0.15	0.38
1,2-dimethyl-4-ethylbenzene	1075.25	5.1	7.0	9.3	13.8	18.7	24.6	0.29	0.71
undecene-1	1090.45	8.2	17.8	32.9	20.5	35.4	56.1	0.01	0.09
1,2-dimethyl-3-ethylbenzene	1093.12	6.8	10.3	14.8	15.2	18.4	22.1	0.09	0.19
1,2-ethyl-i-propylbenzene	1097.22	14.3	31.3	58.2	51.7	74.6	103.4	0.02	0.06
n-undecane	1100.00	8.6	13.9	21.0	24.4	40.0	61.2	0.03	0.18
1,2,4,5-tetramethylbenzene	1104.83	6.1	8.3	11.1	12.5	16.0	20.1	0.15	0.36
1,2,3,5-tetramethylbenzene	1108.79	6.4	7.8	9.3	10.2	13.9	18.3	0.21	0.51
5-methylindan	1127.35	6.6	9.2	12.4	7.5	9.3	11.4	0.06	0.34
143	1131.42	9.1	15.0	23.0	18.8	30.8	47.1	0.02	0.35
4-methylindan	1133.70	8.0	13.8	21.9	15.3	20.9	27.6	0.02	0.10
1,2-ethyl-n-propylbenzene	1136.52	7.4	12.0	18.3	25.3	39.6	58.4	0.02	0.11
2-methylindan	1138.11	5.6	7.7	10.2	6.4	8.9	12.0	0.08	0.34
1,3-di-i-propylbenzene	1142.70	7.9	9.5	11.2	16.2	17.9	19.7	0.06	0.18
1,2-di-i-propylbenzene	1153.16	13.9	22.4	34.0	21.3	36.0	56.2	0.01	0.06
?	1157.64	12.8	20.7	31.4	24.5	44.1	71.9	0.02	0.06
1,4-di-i-propylbenzene	1159.52	11.1	18.6	28.8	18.6	35.6	60.8	0.01	0.09
naphthalene	1168.01	6.1	8.5	11.3	12.9	16.9	21.5	0.13	0.40
1,4-ethyl-t-butylbenzene	1173.72	9.8	12.0	14.5	18.0	28.1	41.3	0.04	0.30
148	1187.14	9.1	14.3	21.1	16.8	30.7	50.8	0.01	0.09
1,3-di-n-propylbenzene	1188.64	9.9	14.4	19.9	18.9	24.2	30.4	0.02	0.08
A5	1190.24	11.5	19.2	29.8	26.7	30.3	34.2	0.02	0.06
A6	1198.52	13.7	23.3	36.7	28.1	39.5	53.5	0.01	0.05
n-dodecane	1200.00	12.2	16.7	22.1	20.2	32.9	50.0	0.01	0.11
1,4-methyl-n-pentylbenzene	1241.71	8.2	14.1	22.3	16.5	31.2	52.7	0.01	0.14
1,2,3,4,5-pentamethylbenzene	1274.04	11.4	13.9	16.7	23.1	29.7	37.5	0.01	0.11
2-methylnaphthalene	1282.57	7.6	11.1	15.4	17.5	22.3	28.0	0.05	0.50
1-methylnaphthalene	1297.72	7.3	11.0	15.8	14.0	21.0	30.1	0.02	0.22

PROCEDURE B – INDIVIDUAL HYDROCARBON ANALYSIS

19. Apparatus

19.1 *Gas Chromatograph*—A gas chromatograph equipped with cryogenic column oven cooling and capable of producing repeatable oven ramps from 0°C to at least 300°C is required. The following features are useful during the sample analysis phase; electronic flow readout, electronic sample split-ratio readout, and electronic pneumatic control of flow. Though their use is not required, careful review of this test method will demonstrate the usefulness of a gas chromatograph equipped with these features. These features will replace the need to carry out the manual calculations that must be performed as listed in 21.1 and 21.2.

19.2 *Inlet*—A capillary split/splitless inlet system operated in the split mode is recommended. It must be operated in its linear range. Refer to 21.4 to determine the proper split ratio.

19.2.1 *Carrier Gas Pneumatic Control*—Constant carrier gas pressure control was used by all cooperative study participants. This may be either direct pressure to the inlet (injector) or by using a total flow/back pressure system.

19.2.2 *Pneumatic Operation of the Chromatograph*—The use of constant pressure was the mode of operating the gas chromatography used by the participants in the interlaboratory cooperative study. Other carrier gas control methods such as constant flow (pressure programming) may be used, but this may change the chromatography elution pattern unless the temperature programming profile is also adjusted to compensate for the flow differences.

19.2.3 *Temperature Control*—The injector operated in the split mode must be heated by a separate heating zone and heated to temperatures of 200° to 275°C.

19.3 *Column*—A fused silica capillary column, 100 m in length by 0.25 mm inside diameter, coated with a 0.5 µm film of bonded dimethylpolysiloxane. The column must meet the

resolution requirements expressed in 21.3. Columns from two different commercial sources were used in the interlaboratory cooperative study.

19.4 *Data System*—A computer based chromatography data system capable of accurately and repeatedly measuring the retention time and areas of eluting peaks. The system must be able to acquire data at a rate of at least 10 Hz. Although it is not mandatory, a data system which calculates column resolution (R) is extremely useful as it will replace the need to carry out the manual calculations which must be performed as listed in 21.3.

19.4.1 *Electronic Integrators*—Must be capable of storing up to 400 components in the peak table. Must be able to acquire the data at 10 Hz or faster speeds. They must be capable of integrating peaks having peak width at half height which are 1.0 s wide. The integrator must be capable of displaying the integration mode of partially resolved peaks. In addition, these integrators should be able to download a commonly readable format of data (that is, ASCII) to a computer in order to facilitate data processing.

19.5 *Sample Introduction*—Sample introduction by way of a valve, automatic injection device, robotic arm, or other automatic means is highly recommended. An automatic sample introduction device is essential to the reproducibility of the analysis. Manual injections are not recommended. All of the reproducibility data reported by this test method for the samples analyzed were gathered using automatic injection devices.

19.6 *Flame Ionization Detector (FID)*—The gas chromatograph possess a FID having a sensitivity of 0.005 coulombs/gr for *N*-butane. The linear dynamic range of the detector should be 10^6 or better. The detector is heated to 300°C.

20. Reagents and Materials

20.1 *Calibrating Standard Mixture*—A spark ignition engine fuel standard of known composition and concentration by mass may be used. In order to corroborate the identification of the sample, a typical chromatogram (Fig. 13), was obtained from reference sample ARC960X¹⁰

20.2 *Gas Chromatograph Gases*—All of the following gases shall have a purity of 99.999 % (V/V) or greater. (**Warning**—Gases are compressed. Some are flammable and all gases are under high pressure.)

20.2.1 *Helium*—The test data was developed with helium as the carrier gas. It is possible that other carrier gases may be used for this test method. At this time, no data is available from this test method with other carrier gases.

20.2.2 *Air, Hydrogen, and Make-up Gas (Helium or Nitrogen)*—Shall have a purity of 99.999 % (V/V) or greater.

21. Instrument Check Out Prior to Analysis

21.1 *Setting, Linear Gas Velocity*—If the gas chromatograph is equipped with an electronic flow readout device, set the flow to 1.8 mL/min. This is achieved by setting the carrier

gas flow rate by injection of methane or natural gas at 35°C. Ensure that the retention time is 7.00 min. $\pm$ 0.05. This corresponds to a linear velocity of 25 to 26 cm/s. This is equivalent to retention times of methane at 0°C ranging from 6.5 to 6.8 min.

21.1.1 If the gas chromatograph is not equipped with an electronic flow readout device, calculate the linear gas velocity in cm/s using Eq 9.

$$\text{linear gas velocity} = V = \frac{\text{column length (cm)}}{\text{Retention time of methane (s)}} \quad (9)$$

The typical retention times for methane and linear gas velocity for helium are 6.5 to 6.8 and 24 to 26 cm/s respectively.

21.2 *Setting the Split Ratio*—If the gas chromatograph is equipped with an electronic split-ratio readout device, set the split ratio to a sample split of 200:1. If the gas chromatograph is not equipped with an electronic split-ratio readout device, one must first calculate column flow rate and then proceed to calculating split ratio using the equations below.

$$\text{column flow rate} = F = \frac{(60 \pi r^2) L (T_{ref}) 2(P_i - P_o)}{(T) 3(P_{ref})(P_i^2 - P_o^2) \mu} \quad (10)$$

where:

- F = flow rate as calculated by using the equation,
- r = column radius (cm),
- L = column length, (cm),
- P_i = inlet pressure,
- P_o = outlet pressure,
- P_{ref} = reference pressure, 1 atmosphere,
- T = temperature of the column oven,
- T_{ref} = temperature at the column outlet, and
- μ = linear velocity in cm/s.

$$\text{split ratio} = S = \frac{\text{split vent flow} + F}{F} \quad (11)$$

The column flow rate is calculated by the use of Eq 10. Use the results obtained from Eq 11 to adjust the split flow until a split flow of approximately 200:1 is achieved.

21.3 *Evaluation of Column Performance:*

21.3.1 Prior to using the column described in Table 6, measure the resolution of the column under the conditions of Table 7. Check that the resolution for the following pairs of components is obtained as follows. Use the following equation to calculate the resolution of a pair of components.

$$R = \frac{(t_{R2} - t_{R1})^2}{1.699 (W_{h1} + W_{h2})} \quad (12)$$

where:

- R = resolution,
- t_{R2} = retention time of the first member of the pair,
- t_{R1} = retention time of the second member of the pair,
- W_{h1} = peak width at half height of the first member of the pair, and
- W_{h2} = peak width at half height of the second member of the pair.

Column resolution should be checked frequently by examining the resolution of these compounds. (See Table 8 for an example.)

¹⁰ Reference spark ignition sample No. ARC 960X was obtained from the Alberta Research Council, Edmonton, Alberta, Canada. Other samples are available from suppliers.

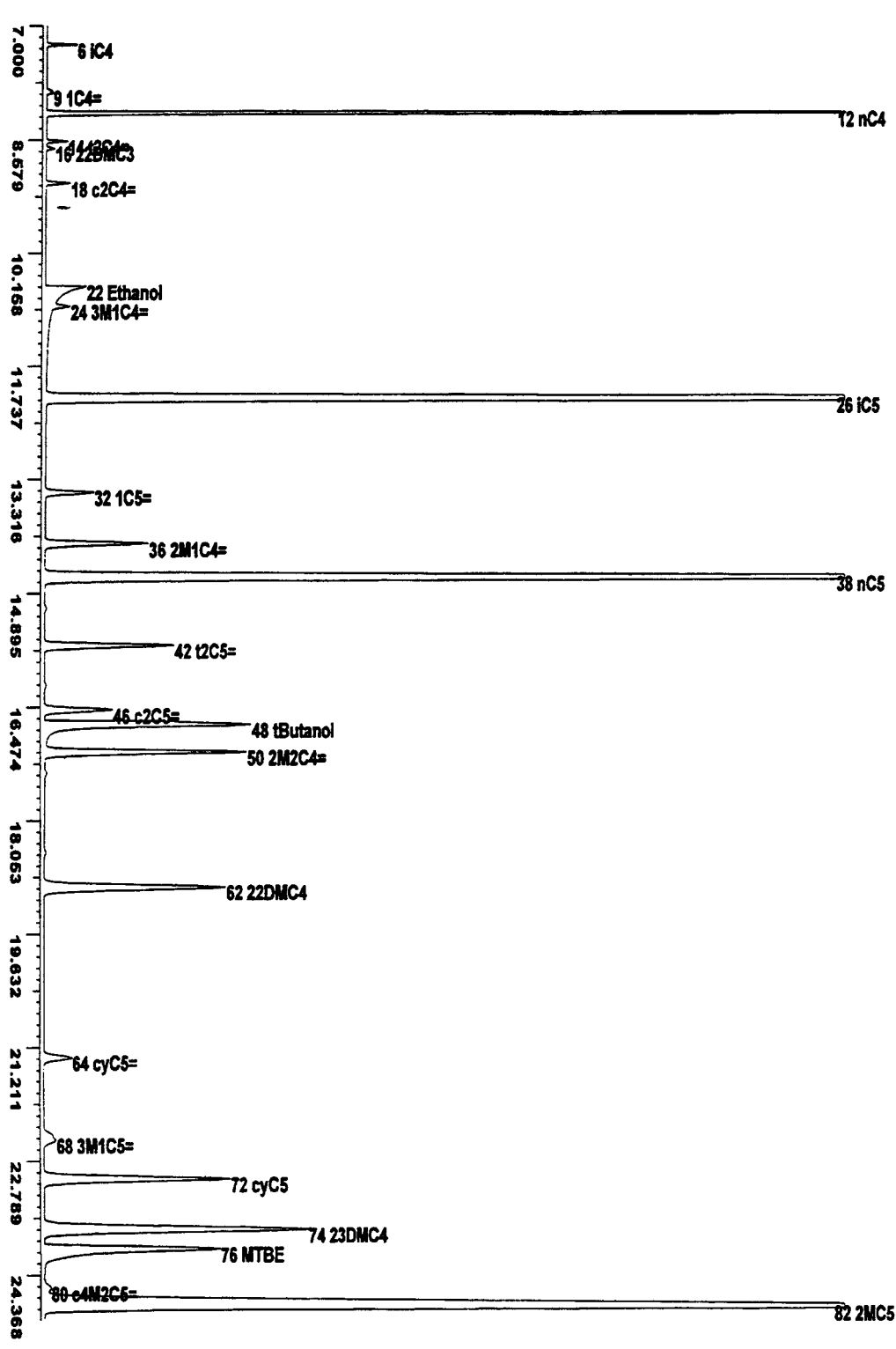


FIG. 13 Chromatogram for Reference Spiked Gasoline

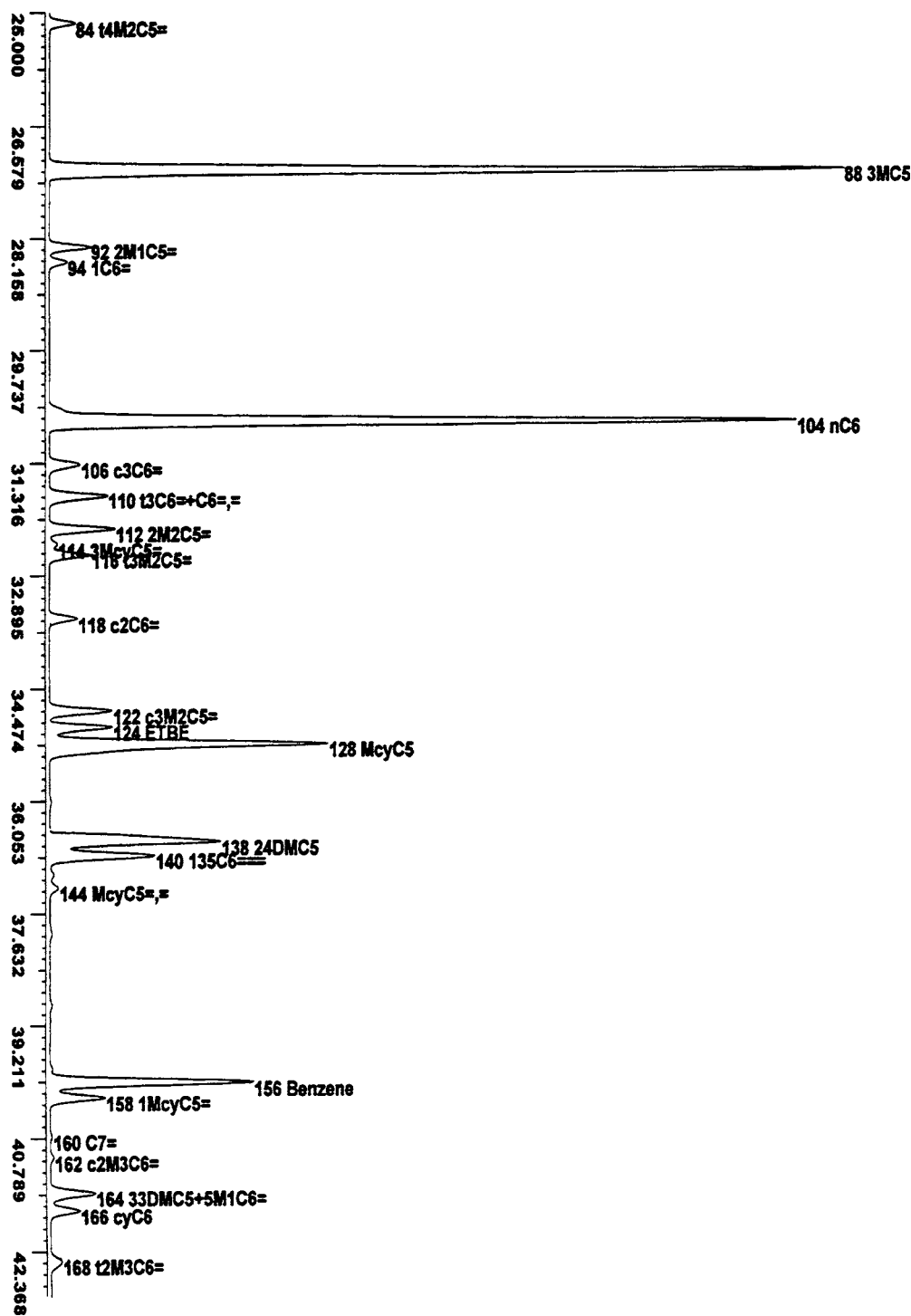


FIG. 13 Chromatogram for Reference Spiked Gasoline (continued)

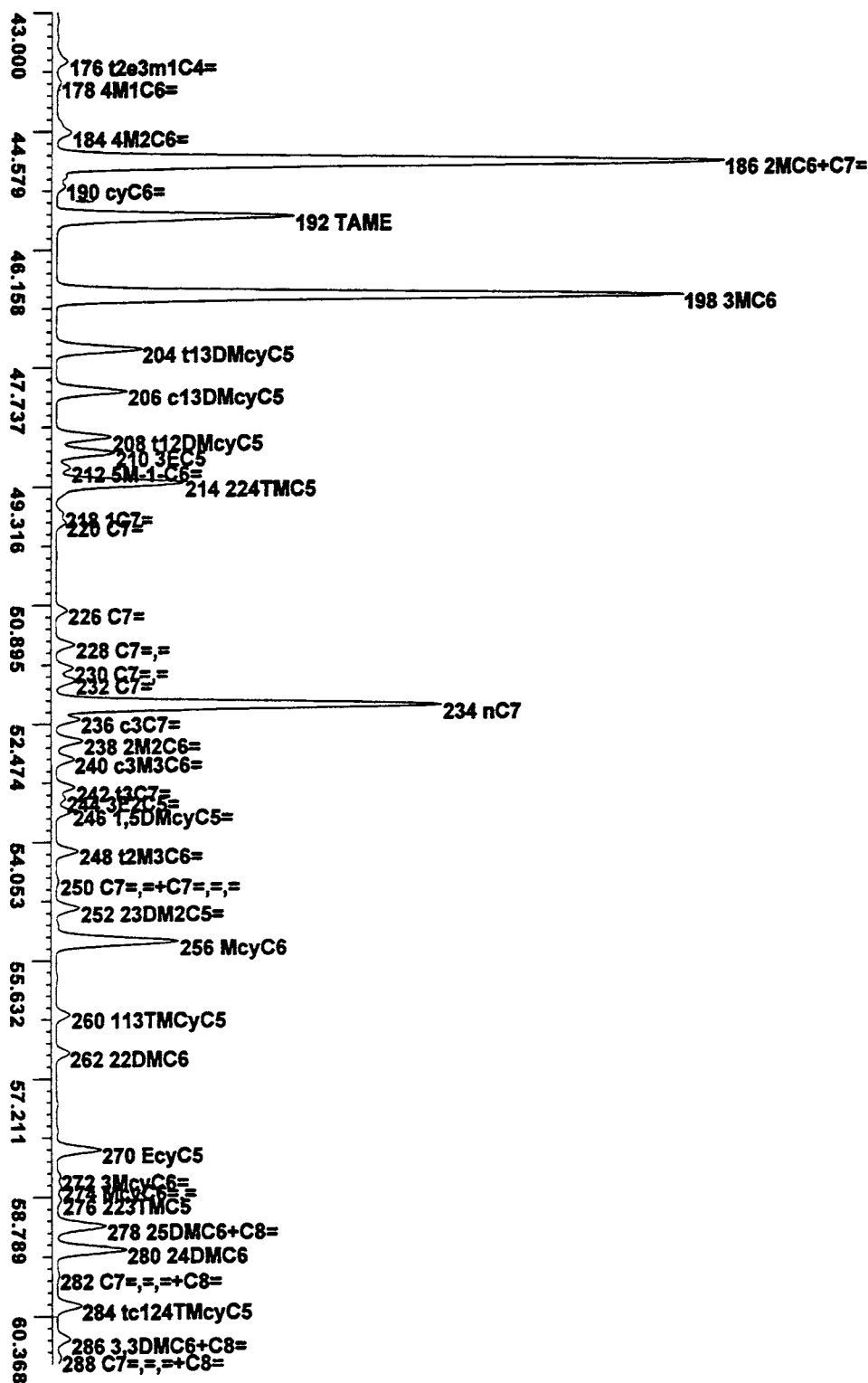


FIG. 13 Chromatogram for Reference Spiked Gasoline (continued)



FIG. 13 Chromatogram for Reference Spiked Gasoline (continued)

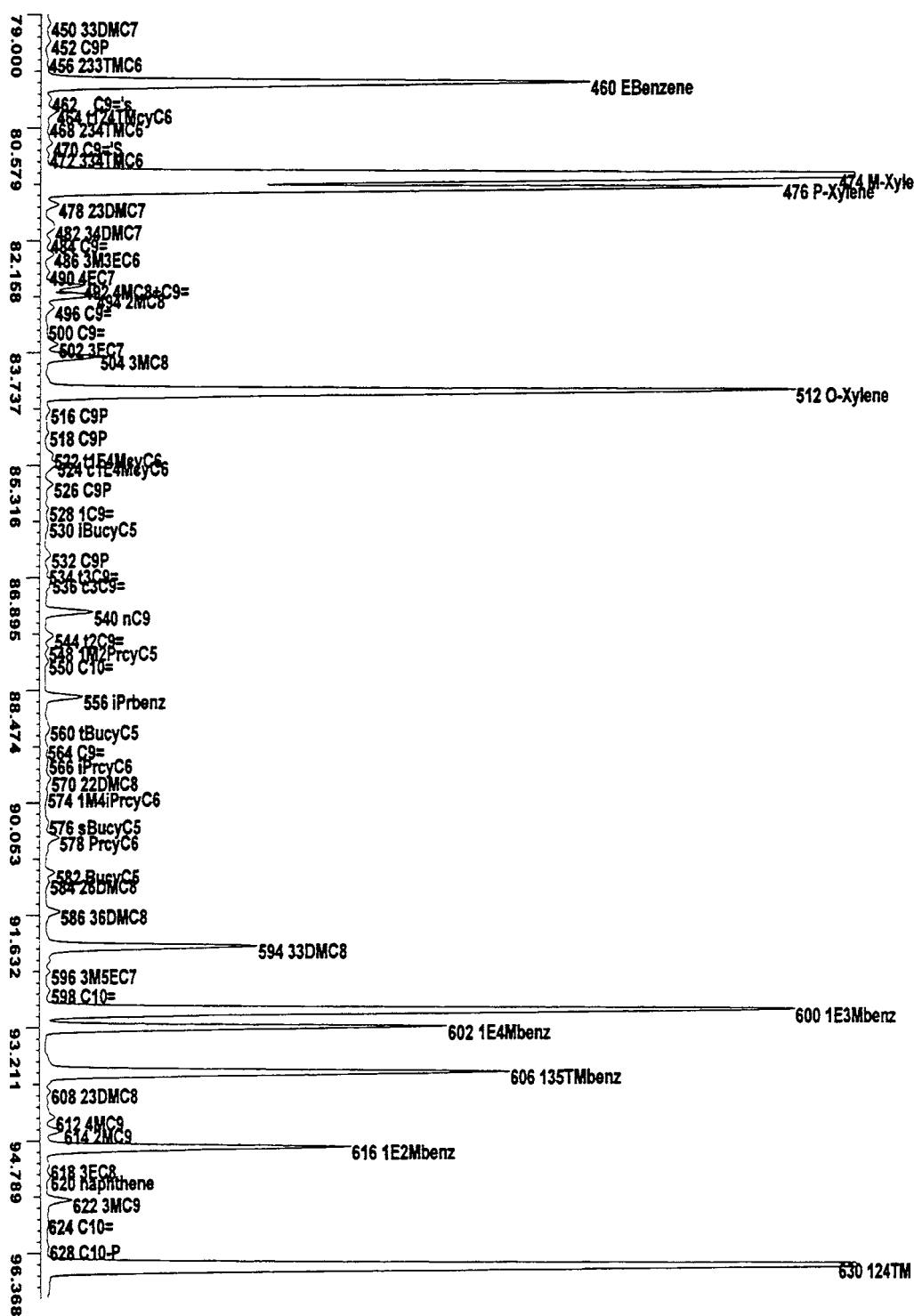


FIG. 13 Chromatogram for Reference Spiked Gasoline (continued)

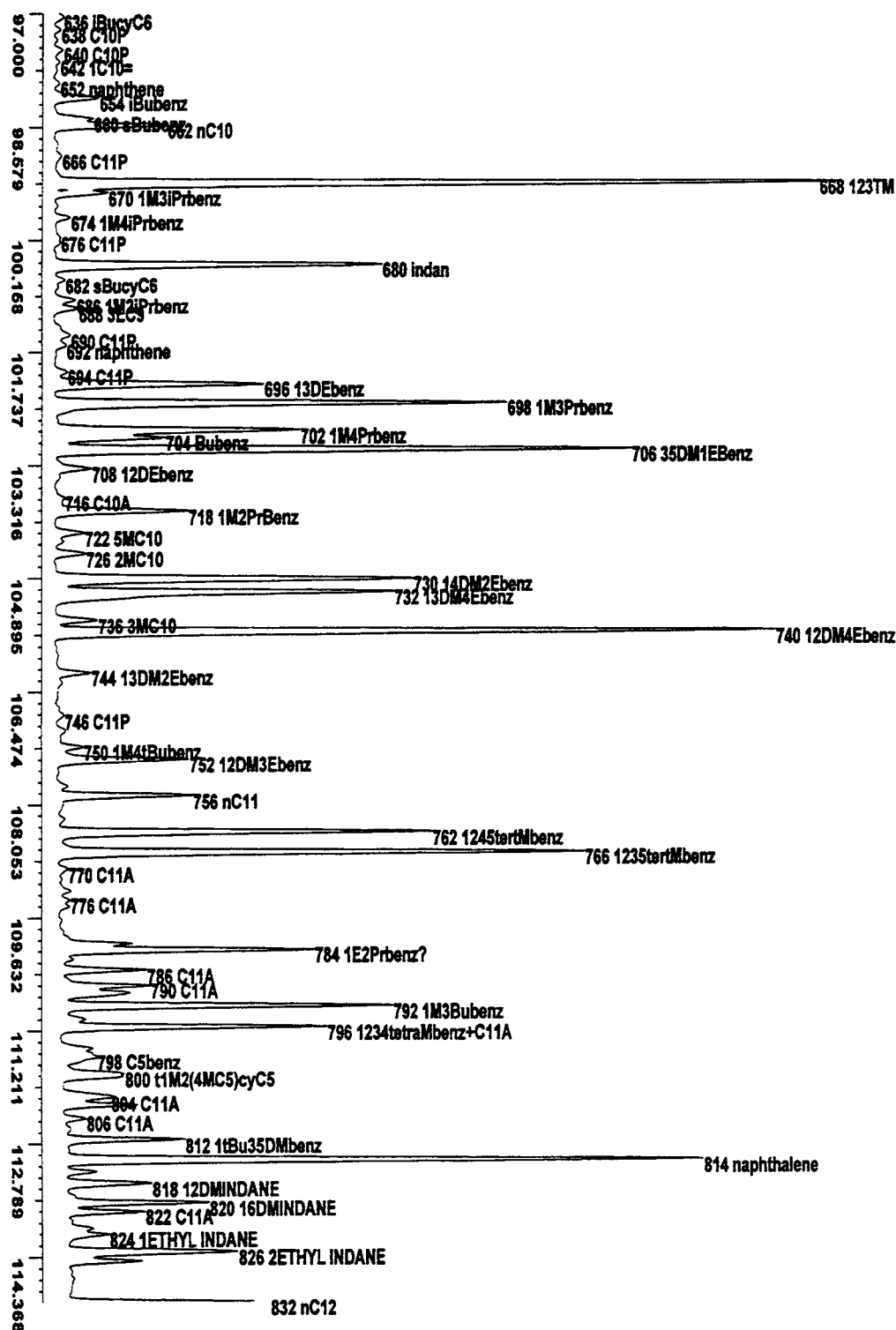


FIG. 13 Chromatogram for Reference Spiked Gasoline (continued)

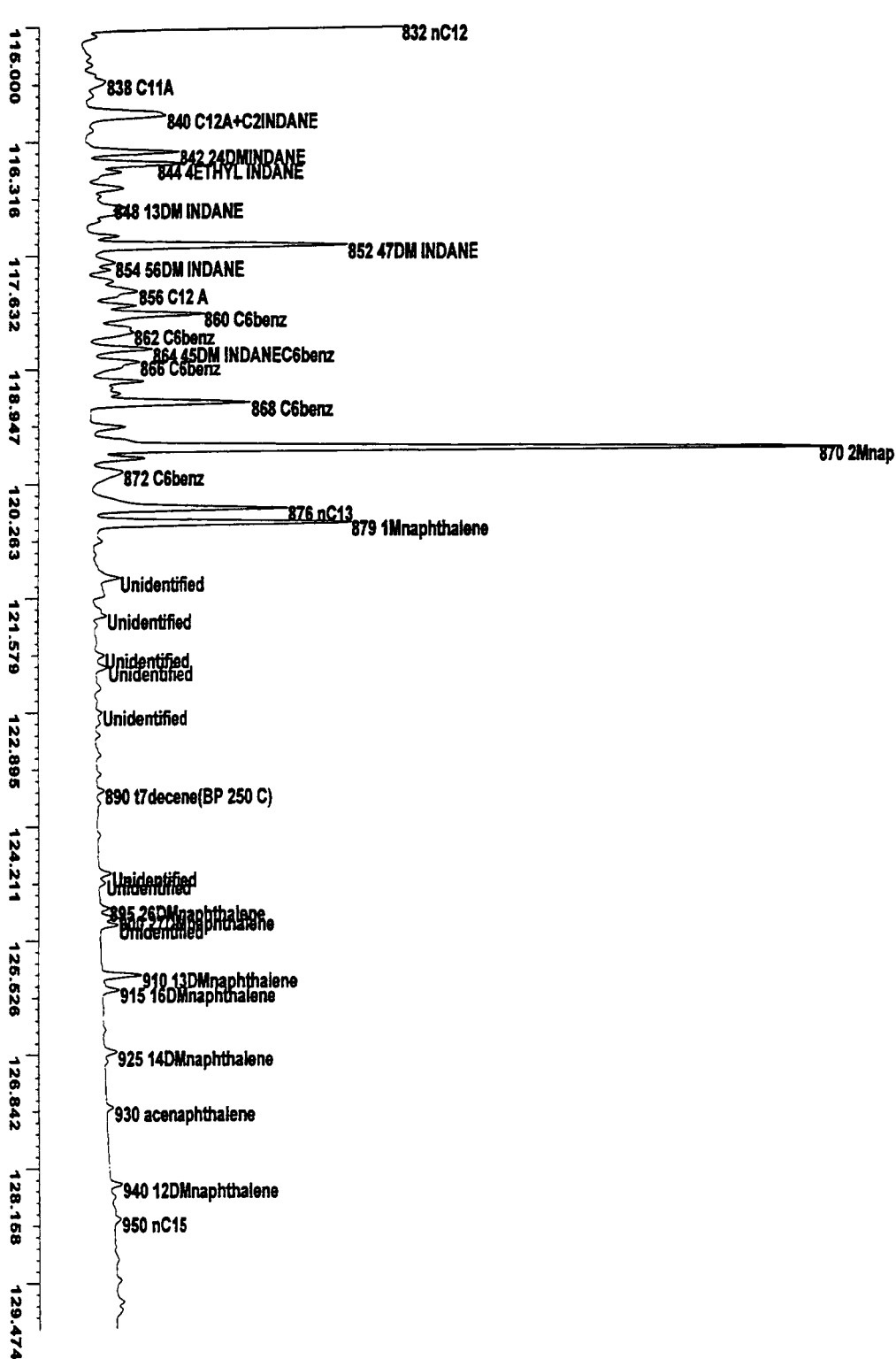


FIG. 13 Chromatogram for Reference Spiked Gasoline (continued)

TABLE 6 Chromatographic Operating Conditions, Column Requirements, and Data Acquisition Requirements

Chromatographic Conditions	Requirements
Injector settings	
Injector temperature	250°C
Split ratio	175:1 - 275:1
Liner	deactivated glass
Injection volume	0.2 - 0.5 µl
Detector settings	
FID detector temperature ^A	300° - 350°C
Gas flows	
Hydrogen ^B	30 - 40 mL/min
Air	300 - 450 mL/min
Nitrogen make up	30 mL/min
Column oven settings	
Initial temperature	0°C
Initial time	15 min
First ramp rate	1°C/min
Final temperature	50°C
Final time	0 min.
Second ramp rate	2°C/min
Final temperature	130°C
Final time	0 min
Third ramp rate	4.0°C/min
Final temperature	270°C
Final time ^C	0 min
Column requirements	
Length	100 m
Inside diameter	0.25 mm
Liquid phase	100 % dimethylpolysiloxane
Film thickness	0.5 µ
Pressure	40 - 50 psig
Flow	1.7-2.0 mL/min
Linear gas velocity	24.5 cm/s
Data acquisition	10 -20 Hz
Total analysis time	140-150 min

^A Set to 25 – 50°C above the highest column temperature.

^B Values to be set as recommended by instrument manufacturer.

^C Final temperature or time may be adjusted to ensure complete elution of the sample components.

TABLE 7 Column Resolution

Component Pair	Resolution, min	Concentration of each Component, W/W, %
benzene 1-methyl-Cyclopentene	1.0	0.5 - 0.5
m-xylene p-xylene	0.4	2.0 - 2.0
N-tridecane 1-methylnaphthalene	1.0	0.5 - 0.5

21.3.2 *Evaluation of the Baseline*—Carry out a blank baseline utilizing no solvent injection, by setting the GC in accordance with conditions of [Table 5](#).

21.3.3 Subtract the baseline from a sample chromatogram and verify that the residual signal at the beginning of the chromatogram does not differ from the end of the chromatogram by more than 2 %.

21.4 *Evaluation of Splitter Linearity*—Using the reference gasoline sample, inject this sample according to the schedule listed in [Table 9](#). Select from the chromatogram about 10 to 15 components, which have concentrations in the range of .01 to 30-wt. %. Tabulate for each split ratio the concentrations of the

TABLE 8 Operating Conditions

Temperatures	Method 1	Method 2
Column initial isotherme	35°C	10°C
Initial hold time	10 min.	15 min.
Rate 1	1.1°C/min.	1.3°C/min
Final temperature 1	114°C	70°C
Hold time 2	0 min.	0 min.
Rate 2	1.7°C/min.	1.7°C/min
Final temperature 2	250°C	250°C
Final hold time 2	5 min.	20 minutes
Injector	250°C	250°C
Detector	280°C	280°C
Carrier gas helium		
Pressure	207kPa (30psi)	190 kP(27 psi)
Flow rate (initial isotherme)	0.9 mL/min.	0.7 mL/min.
Average linear velocity	22 cm/s	21.5 cm/s
Injection		
Sample size	0.5µL	0.3µL
Splitter vent - flow out	250 mL/min.	200 mL/min.

TABLE 9 Schedule of Splitter Linearity Injections

Split Ratio	Injection Volume	Injection Temperature
100:1	0.1 µL	250°C
200:1	0.5 µL	250°C
300:1	1.0 µL	250°C

10 to 15 components. Verify that for each component selected, its concentration does not vary by more than 3 %.

22. Procedure

22.1 Set the operating conditions of the gas chromatograph as shown in [Table 5](#). These conditions will elute all components up to and including pentadecane (nC15).

22.2 All of the parameters in [Table 5](#) can be marginally changed to optimize for sample types and optimize for characteristics of each gas chromatographic system. The final boiling point of samples should not exceed nC15 and the column resolution (*R*) performance requirements listed in [Table 6](#) should not be compromised.

22.3 Obtain a representative sample following the guidelines of Practice [D 4057](#) and any other applicable guidelines. Take precautions to minimize the loss of light ends from volatile samples. The sample container may be cooled prior to transfer of sample into it. Cool the sample to less than 4°C, maintain at that approximate temperature until the autosampler is loaded and analysis begins.

22.4 Preparation/Storage:

22.4.1 *Samples Stored in Vials*—Cool the original sample to less than 4°C prior to taking a sample aliquot or prior to filling the sample vials. The sample aliquot container, or the vial, or both, can also be cooled prior to the transfer of the original sample. Syringes may also be cooled along with the sample for manual injections.

22.4.2 *Samples Stored in Pressurized Containers*—It is recommended that they be kept away from direct heat or light. No other sample preparations are necessary for samples stored in pressurized containers. Avoid storage at temperatures greater than 25°. Store pressure containers in accordance with manufacturer's instructions.

22.5 It is recommended that a quality assurance (QA) sample similar to the reference material gasoline sample be used.

at regular intervals (See Fig. 13). An interval of once a week or after every 15 samples is recommended. The quantitation results use statistical quality control charts can track benzene. Other components of interest in the reference sample can be tracked in a similar manner. By monitoring these components over an extended period of time, the performance of the column and the chromatographic system can be determined.

23. Data Analysis

23.1 *Compound Identification*—Prepare a table listing all of the retention times of the components in the sample. Compare the retention time of each peak with that of the reference gasoline. Pay particular attention to the fact that columns can be overloaded, and peaks can shift in retention time. Observe the peak pattern so that proper identification is made by comparison with the reference material.

23.2 Consistency in peak identification can be achieved by using software (data handling software, spreadsheet software, and so forth). Alternatively, a retention index system can be used.

$$(R1)_i = n100 + 100 \left(\frac{\log(Ti) - \log(Tn)}{\log(TN) - \log(Tn)} \right) \quad (13)$$

where:

$(R1)_i$ = retention index of component i bracketed by the N -paraffin, n in its lower boundary and N -paraffin N in its upper boundary,

Ti = adjusted retention time of component i , (Retention time of component i minus the retention time of methane),

Tn = adjusted retention time of N -paraffin n , and

TN = retention time of N -paraffin N .

23.3 Determine the hydrocarbon response factors by using the following equation.¹¹

$$RRF_{CH4} = \frac{MW_i}{N_c} \times \frac{1}{MW_{CH4}} \quad (14)$$

where:

RRF_{CH4} = relative response factor of each component with respect to methane ($RRF_{CH4} = 1.000$),

MW_i = the molecular weight of the component, i

N_c = the number of carbon atoms in the molecule, and

MW_{CH4} = the molecular weight of methane (16.04276).

23.4 Convert the acquired areas to corrected areas by multiplying each area by its corresponding relative response factor as indicated in the following equation.

$$A_{ci} = (A)_i (RRF)_i \quad (15)$$

where:

$(Ac)_i$ = the corrected area,

A_i = acquired area for an individual component, and

RRF = the relative response factor (weight basis).

The percent weight (% W) is calculated as follows:

$$\% Wi = \frac{(Ac)_i}{\sum_{i=1}^n A_{ci}} \times 100 \quad (16)$$

where:

% W_i = the % weight of the component i in the mixture, and

$\sum_{i=1}^n A_{ci}$ = the summation of all the corrected areas for the components analyzed.

The subscript i indicates that the operations are carried out for each individual component in the matrix.

23.5 In the case of unidentified components, utilize a relative response factor of 0.800 (relative to methane).

24. Oxygenates

24.1 A cooperative study for linearity was performed for methanol, ethanol, t-butanol, methyl-t-butyl ether (MTBE), ethyl-t-butyl ether (ETBE), and t-amyl methyl ether (TAME) in concentrations ranges from 1.0 up to 30 mass % (Annex A2 Oxygenate Linearity Study). The average relative response factors for the oxygenates were calculated from the study and are listed in Table 10. They have been incorporated into the IHA Method. The percent standard deviation of these relative response values was as high as 7 %. MTBE was the only oxygenate that was present in sufficient number of samples to meet the ASTM requirements for round robin testing in accordance with research report RR:D02-1007. Therefore the statistical data for MTBE should be taken from Table A2.2.

25. Expression of Results

25.1 Report the concentration of each components as mass percent % (m/m) to the nearest 0.001 %.

25.2 The data for individual components 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 warning in 5.2.

26. Precision and Bias⁸

26.1 The repeatability and reproducibility precision estimates are quoted in Table A2.2.

26.2 *Precision Statement Outline*—analyte qualification process:

26.2.1 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, in accordance with research report RR:D02-1007 requirement.

26.2.2 The (repeatability standard deviation)/mean value for each analyte/sample combination must be less than or equal to 0.1, in accordance with LOQ requirements which, while not a

TABLE 10 Response Factors of Oxygenated Compounds

Analytes	Relative Response Factors	
	RRF C7 = 1.000	RRF CH4 = 1.000
Methanol	2.996	2.672
Ethanol	2.087	1.862
t-Butanol (TBA)	1.302	1.161
Methyl-t-butyl ether (MTBE)	1.577	1.407
Ethyl-t-butyl ether (ETBE)	1.407	1.255
t-Amyl methyl ether (TAME)	1.356	1.210

¹¹ Sevcik, J., *Detectors in Gas Chromatography*, Elsevier, NY, 1976, p 94.

standard, is what CS94 is recommending. The summaries for the paraffins, isoparaffins, C₂ benzene, and oxygenates follow the same procedure that was used for the analytes and are at the end of analyte Table A2.2.

26.3 *Bias*—The bias of this test method cannot be determined since an appropriate standard reference material is not available.

27. Keywords

27.1 gas chromatograph; gasoline; individual hydrocarbon analysis; oxygenated fuels; spark-ignition engine fuels

PROCEDURE C – DETAIL HYDROCARBON CHARACTERIZATION (DHC)

28. Apparatus

28.1 *Instrumentation*—A gas chromatograph capable of operating under the conditions outlined in Table 11, equipped with a split injector, a carrier gas pressure control and a flame ionization detector are required.

28.2 *Sample Introduction System*—Manual or automatic liquid syringe sample injection may be employed.

28.3 *Data Acquisition System*—Any data system can be used with a requirement:

28.3.1 Sampling rate of 10 hz or more with a storage of sampling data for later processing.

28.3.2 Capacity for at least 400 peaks/analysis.

28.3.3 *Identification of Individual Components from Retention Time*—Software can be used to automatically identify the peaks with the index system determined from Table A3.1, or A3.2.

28.4 *Sampling*—2 mL or more crimp top vials and aluminum caps with polytetrafluoroethylene (PTFE)-lined septa are used to transfer the sample.

28.5 *Capillary Column*—A 50 m fused silica capillary column with an internal diameter of 0.2 mm, containing a 0.5µm film thickness of bonded dimethylpolysiloxane phase is used. The features must be respected to reproduce the separation of the reference chromatogram. The column must meet the criteria of efficiency, resolution and polarity defined in Section 32.

29.1 *Carrier Gas and Make-up*—Helium, 99.99 mol % pure (**Warning**—Compressed gas under high pressure).

29. Reagents and Materials

29.2 *Fuel Gas*—Hydrogen, hydrocarbon free, 99.99 mol % pure (**Warning**—Compressed gas under high pressure. Extremely flammable).

29.3 *Oxidizing Gas*—Air, 99 mol % (**Warning**—Compressed gas under high pressure).

29.4 *N-Pentane*—99 + mol % pure (**Warning**—Extremely Flammable. Harmful if inhaled).

29.5 *N-Hexane*, 99 + % mol % pure (**Warning**—Extremely Flammable. Harmful if inhaled).

29.6 *N-Heptane*—99 + mol % pure (**Warning**—Extremely Flammable. Harmful if inhaled).

29.7 *2-Methylheptane*—99+ mol % pure (**Warning**—Extremely Flammable. Harmful if inhaled).

29.8 *4-Methylheptane*—99+ mol % pure (**Warning**—Extremely Flammable. Harmful if inhaled).

29.9 *N-Octane*—99 + mol % pure (**Warning**—Extremely Flammable. Harmful if inhaled).

29.10 *N-Dodecane*—99 + mol % pure (**Warning**—Extremely Flammable. Harmful if inhaled).

29.11 *Toluene*—99 + mol % pure (**Warning**—Extremely Flammable. Harmful if inhaled).

29.12 *System Performance Mixture*—Weigh an equal amount of *N*-pentane, *N*-heptane, *N*-octane, *N*-dodecane, 2-methylheptane, 4-methylheptane and toluene. Dilute this mixture in *N*-hexane to obtain a concentration of 2 mass % for each compound.

30.1 *Container Sampling*—Samples shall be taken as described in Practice D 4057 for instructions on manual sampling into open container.

30.2 The sample and a 2 mL vial must be cooled at 4°C. Part of sample is transferred to the vial up to 80 % of its volume and aluminium cap with septum is crimped.

30. Sampling

31.1 *Installation*—Install and condition column in accordance with supplier's instruction.

31.2 *Operating Conditions*—Two sets of operating conditions are proposed in the Table 8, the first with an initial column temperature above the ambient temperature, the second with a subambient column temperature profile. Adjust the operating conditions of the gas chromatograph to conform to the first or second method.

31.3 *Carrier Gas Pressure*—Set a correct carrier gas pressure using the system performance mixture such that the retention time of *N*-Heptane, *N*-Octane and *N*-Dodecane are between the values given in Table 12.

31. Preparation of Apparatus

31.1 *Installation*—Install and condition column in accordance with supplier's instruction.

31.2 *Operating Conditions*—Two sets of operating conditions are proposed in the Table 8, the first with an initial column temperature above the ambient temperature, the second with a subambient column temperature profile. Adjust the operating conditions of the gas chromatograph to conform to the first or second method.

31.3 *Carrier Gas Pressure*—Set a correct carrier gas pressure using the system performance mixture such that the retention time of *N*-Heptane, *N*-Octane and *N*-Dodecane are between the values given in Table 12.

TABLE 11 Predominant Compounds and Identified Coeluting Compounds^A

NOTE 1—The response factor of the predominant compound will be used for the analyte and this analyte will be used for the calculations.

Peak Number	Predominant Compound	Coeluting Compound(s)
164 186	3,3-dimethylpentane 2-methylhexane	5-methyl-1-hexene C ₇ -olefin
278	2,5-dimethylhexane	C ₈ -olefin
286	3,3-dimethylhexane	C ₈ -olefin
304	toluene	2,3,3-trimethylpentane ^B
324 326	1,1,2-trimethylcyclopentane C ₈ -diolefin	C ₇ -triolefin C ₈ -paraffin
492	4-methyloctane	C ₉ -olefin
796	1,2,3,4-tetramethylbenzene	C ₁₁ -aromatic

^A This is not an exhaustive list. Due to the possibility of coeluting peaks in other areas, the user is cautioned in the interpretation of the data.

^B In most alkylated gasolines, a split may occur between toluene and 233 TMC₅.

TABLE 12 Reference Retention Times of Normal Paraffins (min. and one tenth of a minute)

	Method 1	Method 1	Method 1	Method 2	Method 2	Method 2
N-Paraffins	Lower Time	Reference Time	Upper Time	Lower Time	Reference Time	Upper Time
N-Heptane	18.5	19.4	20.3	39.5	40.7	42.0
N-Octane	32.0	33.0	34.0	57.0	57.8	59.0
N-Dodecane	92.8	94.0	95.2	106.4	107.6	108.8

32. System Performance Evaluation

32.1 Evaluation of the column and linearity of the split injection are carried out with a system performance mixture defined in 29.12 and with the column temperature conditions defined as follows:

initial temperature	35°C
hold time	50 min.
final temperature	220°C
hold time	20 min.
rate	3°C/min.

32.2 Column Evaluation— To perform the required separation, the column must meet three criteria of separation – efficiency, resolution, and polarity.

32.2.1 Efficiency— The number of theoretical plates is calculated with the normal octane peak using Eq.

$$n = 5.545(Rt/W_{0.5})^2 \quad (17)$$

where:

- n = number of theoretical plates,
- Rt = retention time of normal octane, and
- $W_{0.5}$ = mid-height peak width of normal octane in the same unit as retention time.

The number of theoretical plates must be greater than 200 000.

32.2.2 Resolution— Resolution is determined between the peaks of 2-methylheptane and 4-methylheptane using Eq 18.

$$R = \frac{2(Rt_{(a)} - Rt_{(b)})}{1.699(W_{0.5(a)} + W_{0.5(b)})} \quad (18)$$

where:

- $Rt_{(a)}$ = retention time of 4-methylheptane,
- $Rt_{(b)}$ = retention time of 2-methylheptane,
- $W_{0.5(a)}$ = mid-height peak width of 4-methylheptane in the same unit as retention time, and
- $W_{0.5(b)}$ = the mid-height peak width of 2-methylheptane in the same unit as retention time.

The resolution must be equal or greater than 1.20

32.2.3 Polarity—Polarity is defined by the Mc Reynolds constant of toluene, using Eq 19.

$$Rn_{tol} = Ki_{ana} - Ki_{squalane} \quad (19)$$

where:

- $Ki_{squalane}$ = toluene Kovats index on Squalane at 35°C = 742.6, and
- Ki_{ana} = toluene Kovats index on the analytical column at 35°C.

Toluene Kovats index is calculated using Eq 20.

$$Ki_{ana} = 700 + 100 \left(\frac{\log T'_{R(t)} - \log T'_{R(h)}}{\log T'_{R(o)} - \log T'_{R(h)}} \right) \quad (20)$$

where:

- $T'_{R(t)}$ = the adjusted retention time for toluene,
- $T'_{R(h)}$ = the adjusted retention time for *N*-heptane, and
- $T'_{R(o)}$ = the adjusted retention time for *N*-octane.

Adjusted retention time of a peak is determined by subtracting the retention time of an unretained compound (air or methane) from the retention time of the peak. The McReynolds constant must be less than 10.

32.2.4 Base Line Stability—Base line stability is calculated with the difference between area slices at the beginning and at the end of analysis, divided by the maximum area slice of *N*-octane obtained with the system performance mixture.

32.2.4.1 Measurement of the Stability—Carry out one temperature programming defined in 32.1 without injecting any sample. Subtract the area slices at the start of the analysis with those corresponding to 120 min. (average of three slices).

32.2.4.2 Stability Standardization—Standardization is carried out using the system performance mixture defined in 29.12 with the column temperature conditions defined in 32.1. The value obtained in 32.2.4.1 is divided by the maximum area slice of *N*-octane and multiplied by 100. The value obtained must be less than 2 %. If this is not the case, check for possible leaks, or recondition the column according to the manufacturer's recommendations.

32.3 Evaluation of the Linearity of the Split Injector— Evaluation is carried out using the system performance mixture defined in 29.12 with the column temperature conditions defined in 32.1. The % (m/m) of each compound is determined from the corrected area % using the response factors for each compound given in Annex CA Table C1A or CA2. The relative % error is determined from the known mixture concentrations according to Eq 21.

Relative Error

$$\text{relative \% error} = \frac{100(\text{calculated concentration} - \text{known concentration})}{\text{known concentration}} \quad (21)$$

The relative error must not exceed 3 %.

33. Response Factor

33.1 Theoretical response factors are used for correction of the detector response of hydrocarbons. The response factor for each compound is relative to that of benzene taken equal to unity and are listed in Tables 11 and 12. For peaks corresponding to the co-elution of compounds with benzene, toluene and oxygenates, the response factor is the one of the co-eluted compound of % (m/m). Co-eluted compounds are footnoted in A3.1 and A3.2.

34. Procedure

34.1 Preparation of Apparatus—After optimization of the carrier gas pressure (Section 31.3) and evaluation of apparatus (Section 32), set the temperature program corresponding to the selected method (Table 8).

34.2 Injection of Sample—Inject with a 5 or 10 µL syringe, manually or by autosampler, the size corresponding to the method (Table 8).

34.3 Integration of Chromatogram—Integration codes must be selected to obtain a horizontal baseline with the dependence

drop to the baseline for partially resolved peaks. An example of correct baseline is given in Figs. A3.1 and A3.2.

34.4 *Identification*— Each peak is identified by matching the retention time with that of compounds listed in Table 11 or Table 12 and standard chromatogram given in Fig. A3.1 or A3.2. A specific software using the data of Table 11 or Table 12 can be employed. If an oxygenate has been determined by Test Methods D 4815 or D 5599 and is not in the table, it is necessary to prepare a mixture of a weighed amount of this oxygenate in a known spark-ignition engine fuel to know its retention time and to determine its response factor and then add it to the table.

35. Calculation of Results

35.1 *Calculation of % (m/m) of Each Compound Without Co-elution and Not Corrected for Co-elutions*— % (m/m) of each component without co-elution and no corrected co-elutions is calculated according to the Eq 22.

$$C_{i'} = \frac{A_i B_i}{\sum_{i=0} (A_i B_i + A_{int} B_{int})} 100 \quad (22)$$

where:

$C_{i'}$ = % (m/m) of compound i without co-elution and no correction of co-elutions,

A_i = peak area of compound i without co-elution (benzene, toluene, and oxygenates),

A_{int} = peak area of compounds co-eluting (benzene, toluene and oxygenates),

B_i = response factor for component i (given in Tables A3.1 or A3.2), and

B_{int} = response factor for components co-eluted with benzene, toluene, and oxygenates.

35.2 *Calculation of Components Co-eluted with Benzene, Toluene, and Oxygenates*—Benzene, toluene contents are determined by Test Methods D 3606 or D 4420 or Test Method D 5580 oxygenates contents are determined by Test Methods D 4815 or D 5599. The % (m/m) of components coeluted with benzene, toluene and oxygenates is calculated according to the Eq 23.

$$C_{coeluted} = C_{int.} 0.01 \left[100 - \sum \left(C_{ext.} - C_{ext.} \times \frac{B_{int.}}{B_{ext.}} \right) \right] - C_{ext.} \times \frac{B_{int.}}{B_{ext.}} \quad (23)$$

where:

$C_{coeluted}$ = % (m/m) of component eluted with benzene, toluene, or oxygenates,

C_{int} = % (m/m) calculated with the Eq 22 for the peak with co-elution,

C_{ext} = % (m/m) of benzene, toluene, or oxygenates determined by other method, and

B_{ext} = response factor of benzene, toluene or oxygenates.

35.3 *Calculation of Other Components*—% (m/m) of other components is calculated using Eq 24.

$$C_i = C_{i'} \frac{100 - \sum C_{coeluted} - \sum C_{ext.}}{\sum C_{i'}} \quad (24)$$

36. Report

36.1 Report the content of each component as % (m/m) to the nearest 0.01 %.

37. Precision⁸

37.1 *Individual Components*—The precision of this test method was determined by a statistical analysis of interlaboratory test results. It applies only to a range of 0.1 to 15 % (m/m), for all components with a resolution greater than 1.0 and without co-elution with oxygenate components. When two components of the same hydrocarbon type have a resolution less than 1.0, the precision can be applied by adding the concentration of two components. The precision is the same for all:

37.1.1 Light components (saturates and olefins) with a carbon number of C₄ and C₅

37.1.2 Saturates and olefins with a range of carbon number of C₆ to C₁₂ aromatics.

37.1.3 This precision is as follows:

37.1.3.1 *Repeatability*— The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, in the normal and correct operation of the test method, would exceed the value given in the Table 12 in only one case in twenty.

37.1.3.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators in different laboratories on nominally identical test material, in the normal and correct operation of the test method, would exceed the values given in the Table 13 in only one case in twenty.

38. Keywords

38.1 detailed hydrocarbon analysis; DHA; gas chromatography; gasoline; hydrocarbons; open tubular; oxygenates; spark ignition engine fuels



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TABLE 13 Repeatability and Reproducibility for Individual Components

	Range of Carbon	Range % (m/m)	Repeatability X (% (m/m))	Reproducibility X (% (m/m))
Light components	C ₄ - C ₅	0.1 - 14	0.04 × X	0.16 × X
Paraffins	C ₆ - C ₁₂	0.1 - 11.5	0.01 + 0.03 × X	0.04 + 0.07 × X
Naphthenes	C ₆ - C ₈	0.1 - 3		
Olefins	C ₆ - C ₈	0.1 - 1		
Aromatics	C ₆ - C ₁₂	0.1 - 14	0.05 + 0.02 × X	0.1 + 0.06 × X

ANNEXES

(Mandatory Information)

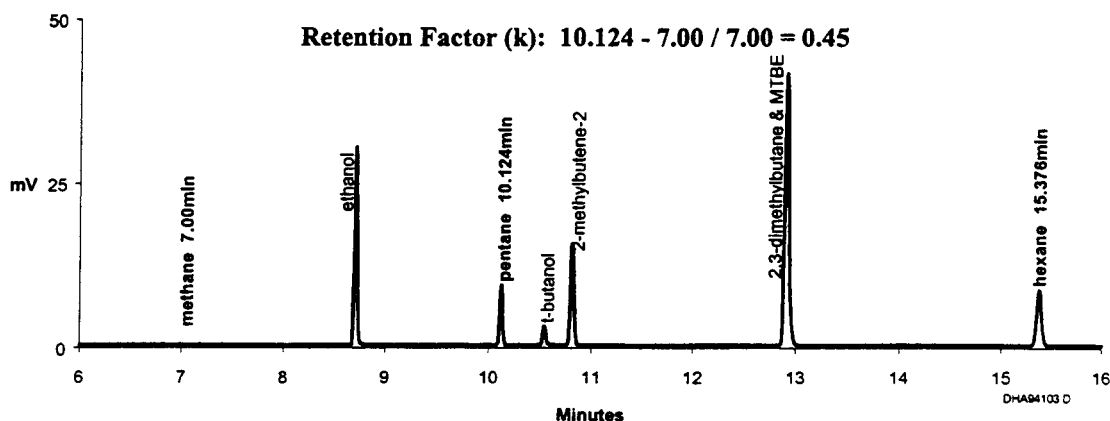
A1. PROCEDURE FOR ADJUSTING THE SELECTIVITY OF A DHA DIMETHYLPOLYSILOXANE OPEN TUBULAR COLUMN

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 100 % dimethylpolysiloxane 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 100 % dimethylpolysiloxane 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 100 % dimethylpolysiloxane capillary column, using a 35° isothermal analysis to determine the basic column characteristics of efficiency, reten-

tion 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 the result of an active injector liner or packing, or both, material 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 dimethylpolysiloxane. The film thickness is likely not critical, only the total amount of phase. Lengths ranging from one to more than 3 m have been necessary to provide sufficient selectivity, depending on the initial selectivity of the methyl



NOTE 1—Efficiency (n): $5.545 (10.124/0.032)^2 = 555$ 016
FIG. A1.1 Column Retention Factor Calculation (9.1)

$$\text{Efficiency (n): } 5.545 (10.124 / 0.032)^2 = 555,016$$

$$\text{Resolution (R): } 2(10.817 - 10.547) / 1.699(0.034+0.034) = 4.673$$

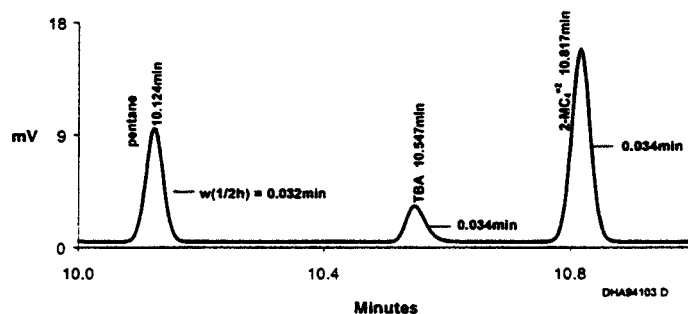


FIG. A1.2 Column Efficiency and Resolution Calculations (9.2 and 9.3)

$$\text{Skew: ratio of B / A} = 3.5 / 2.2 = 1.59$$

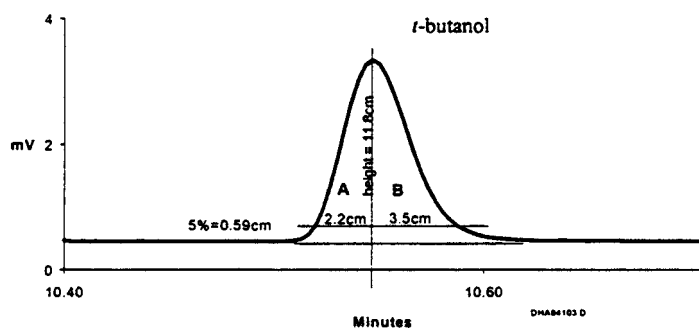


FIG. A1.3 Column Inertness – Peak Skewness Calculation (11.5)

silicone column used. One meter 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 1, 2, and 3 m 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.

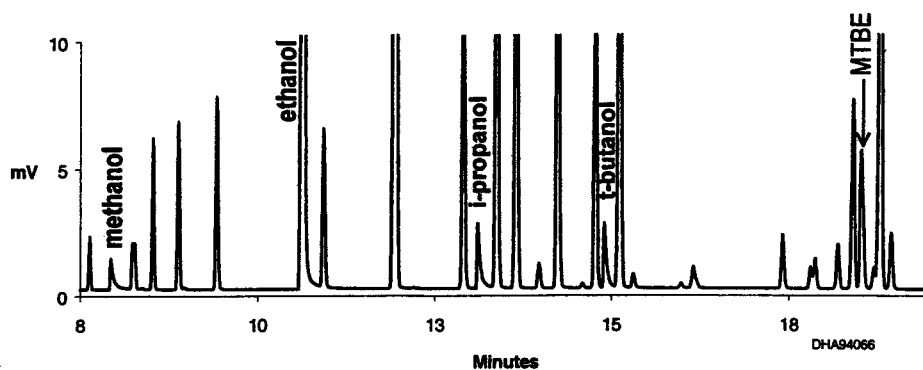
A1.7 Fig. A1.9 illustrates graphically the effect of different lengths of precolumn attached to the same 100 m column. The key component separations are shown. These analyses were made using the conditions given in Table 3. In this case, the use of the 1.25 m precolumn provides the best compromise for the three key separations.

A1.8 Fig. A1.10 illustrates the use of different lengths of precolumn to achieve the specified selectivity for three different 100 m columns. The final precolumn length will provide adequate resolution of all three of the key separations.

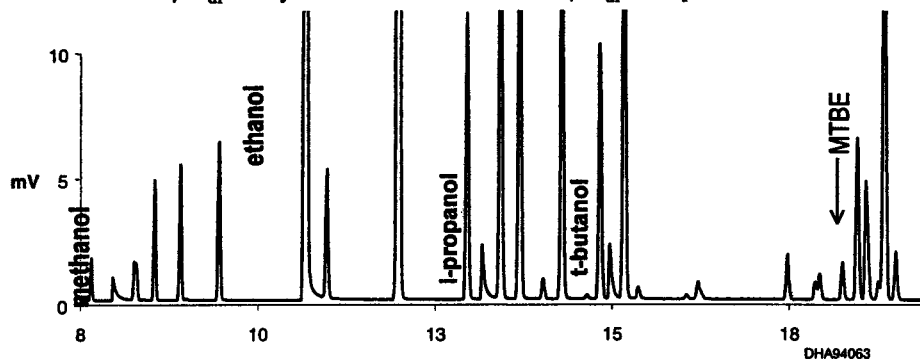
A1.9 Figs. A1.11-A1.17 illustrate typical chromatographic elution.

A1.10 Table A1.1 provides the data for the physical constants used in the cooperative study. Table A1.2 presents data on the analyses of various refinery samples.

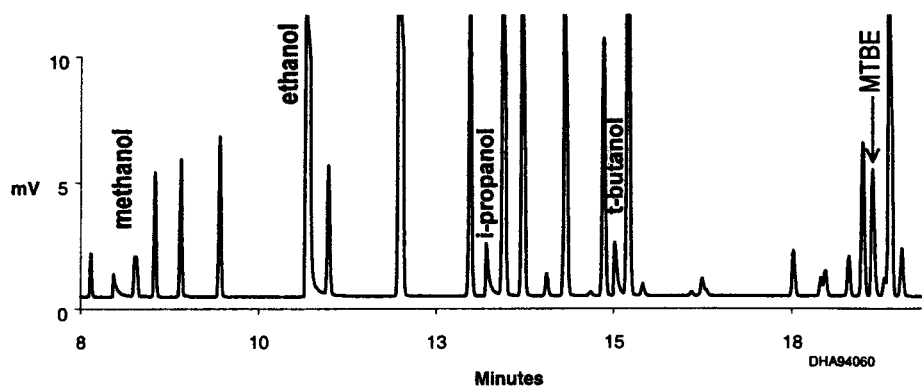
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Petrocol DH100 0.5 μm_{df} methylsilicone column + 1.25m 1 μm_{df} DB5 precolumn



Petrocol DH100 0.5 μm_{df} methylsilicone column + 1.5m 1 μm_{df} DB5 precolumn



Petrocol DH100 0.5 μm_{df} methylsilicone column + 2.0m 1 μm_{df} DB5 precolumn

FIG. A1.4 Oxygenates Separations – Effect of Different Precolumn Lengths



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$$R = 2(21.658 - 21.590) / 1.699(0.08 + 0.08) = 0.500$$

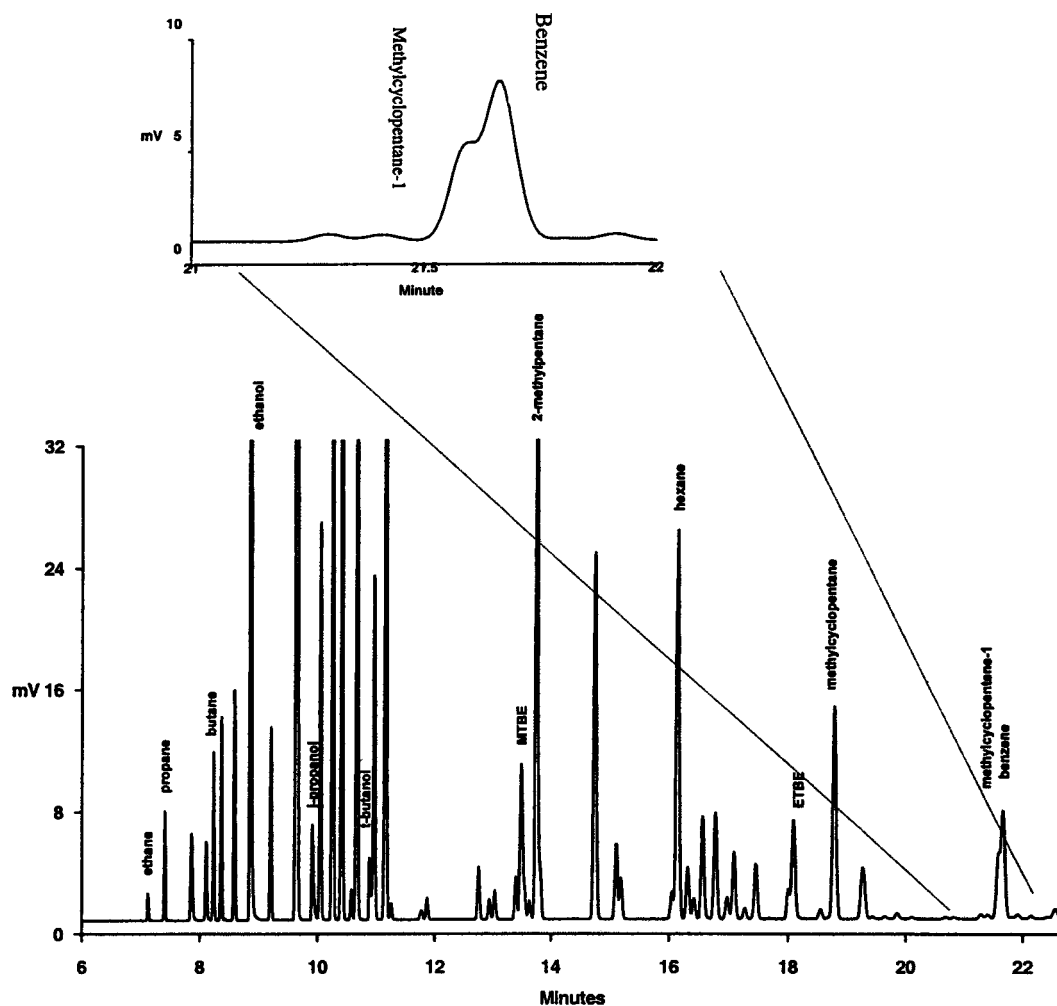


FIG. A1.5 PONA-V Standard – Analysis through Benzene (New DHA Column Analyzed at 35°C Isothermal)



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$$R = 2(21.025 - 20.925) / 1.699(0.076 + 0.081) = 0.750$$

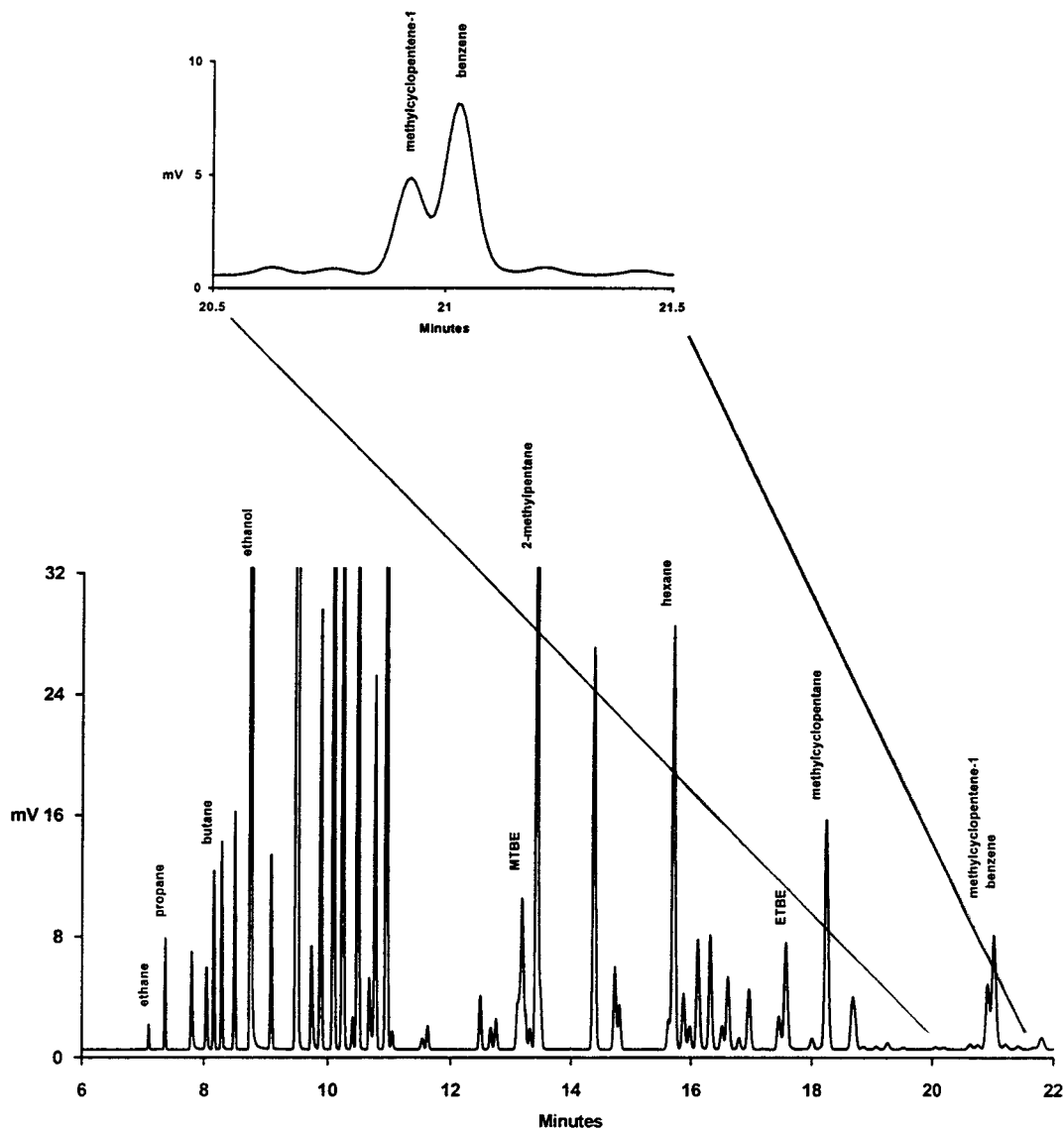


FIG. A1.6 PONA-V Standard – Analysis through Benzene (New DHA Column plus 1 m × 0.25 mm 1 μm DB5 Precolumn Analyzed at 35°C Isothermal)



$$R = 2(21.258 - 21.125) / 1.699(0.079 + 0.081) = 0.978$$

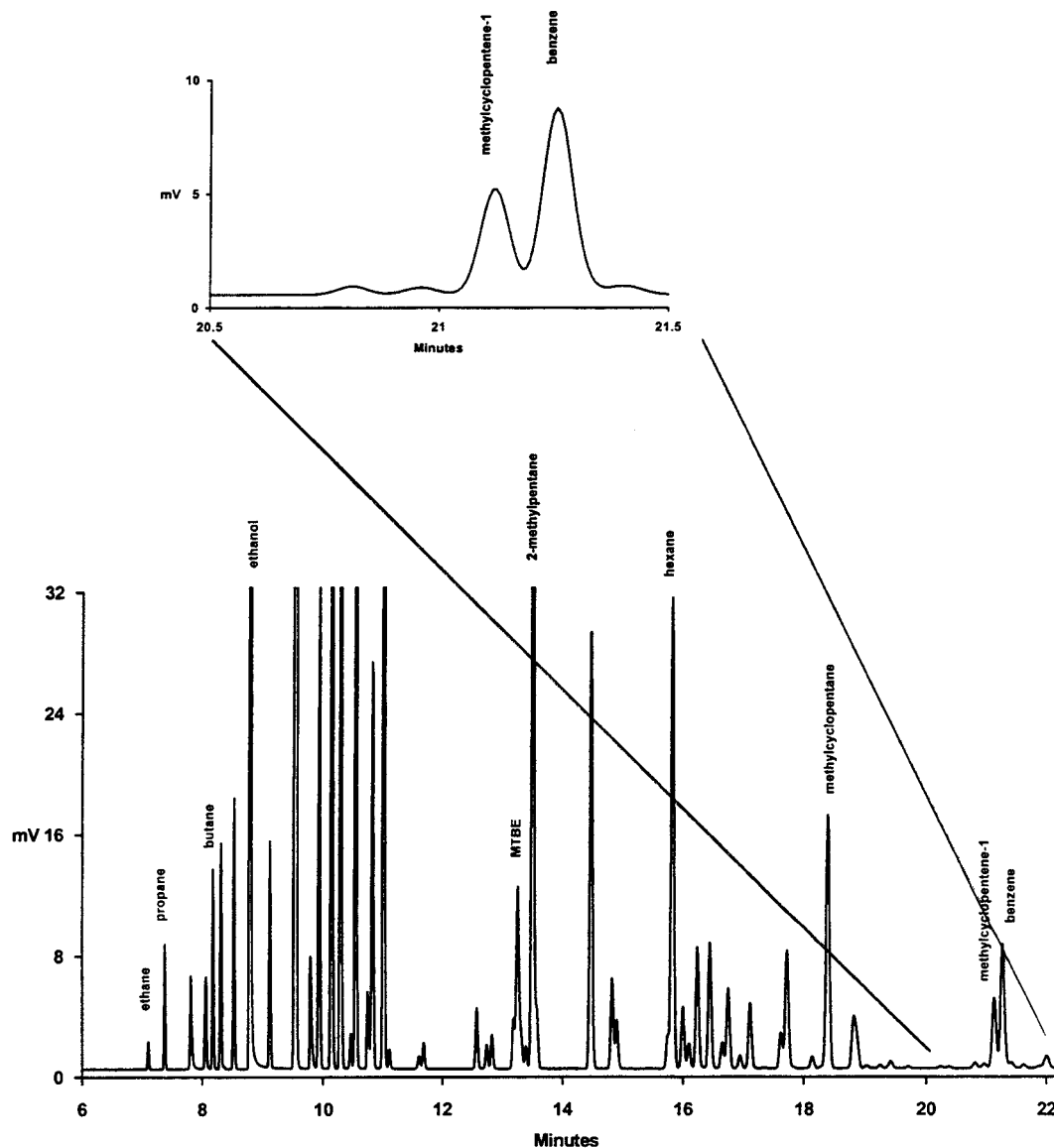


FIG. A1.7 PONA-V Standard – Analysis through Benzene (New DHA Column plus 2 m × 0.25 mm 1 μm DB5 Precolumn Analyzed at 35°C Isothermal)



$$R = 2(22.642 - 22.458) / 1.699(0.089 + 0.093) = 1.190$$

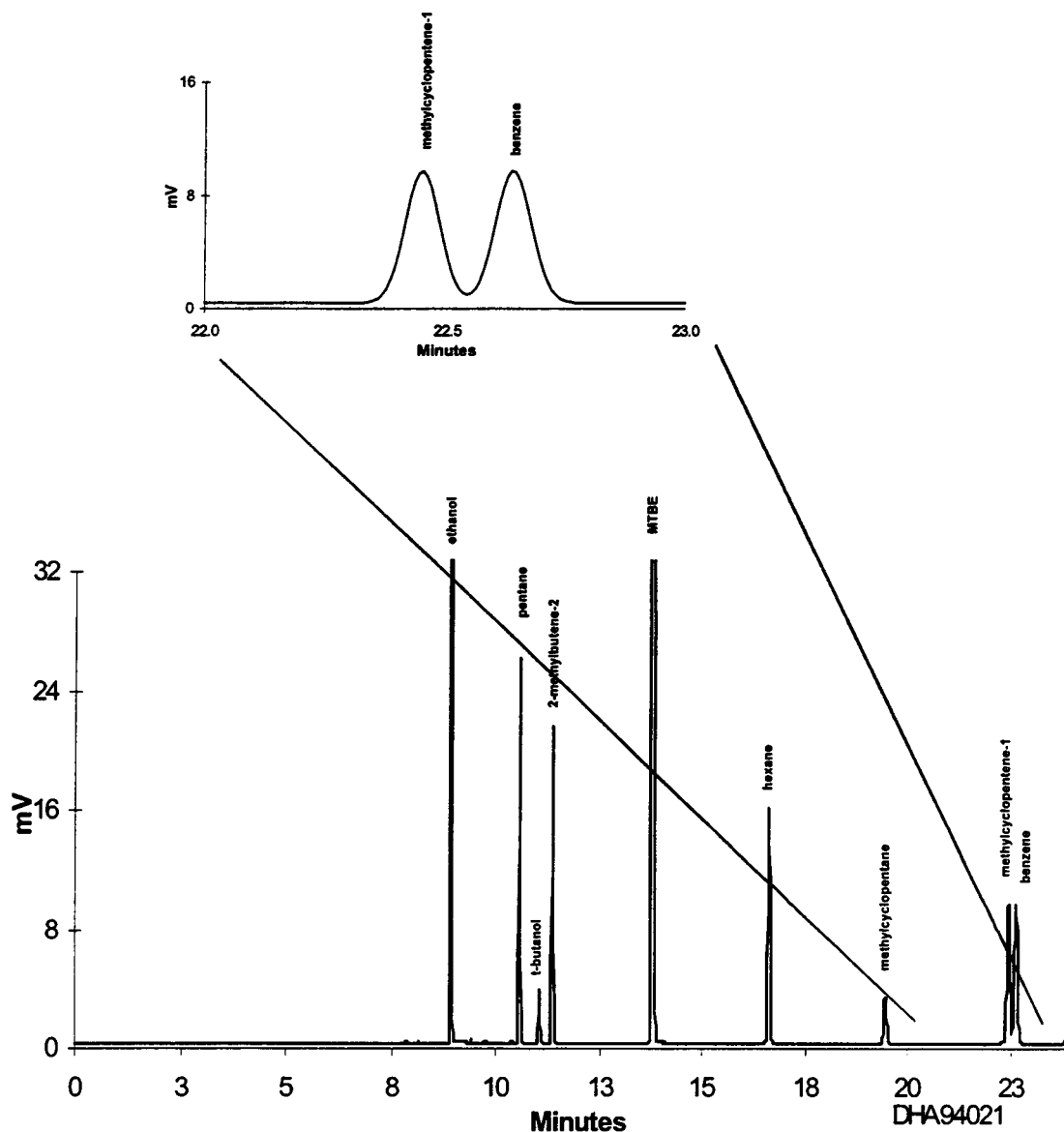


FIG. A1.8 DHA Calibration Standard – Analysis through Benzene (New DHA Column plus 3 m × 0.25 mm 1 µm DB5 Precolumn Analyzed at 35°C Isothermal)

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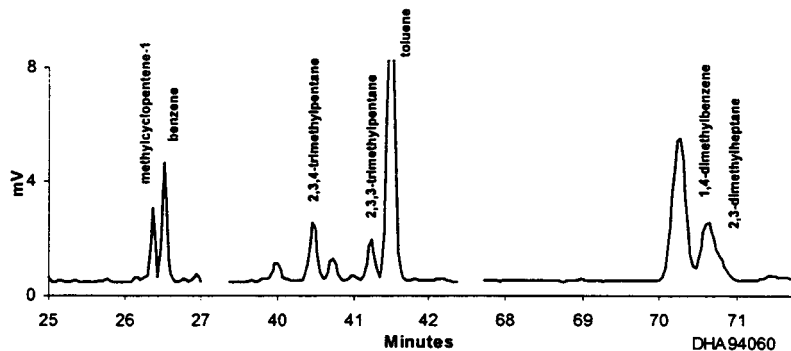
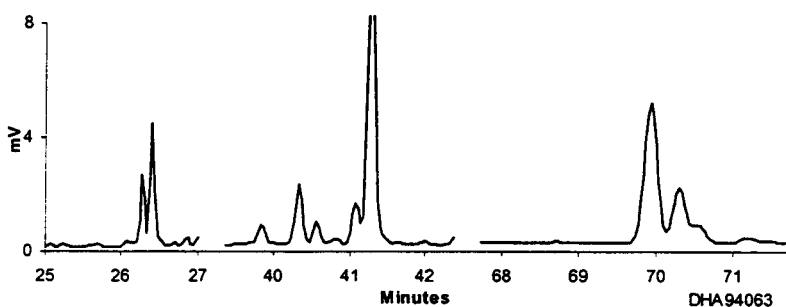
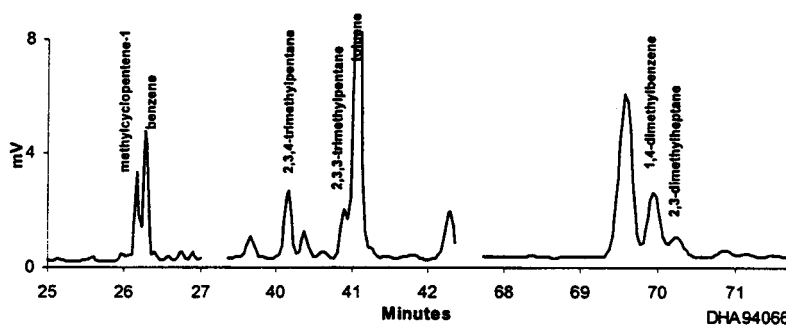
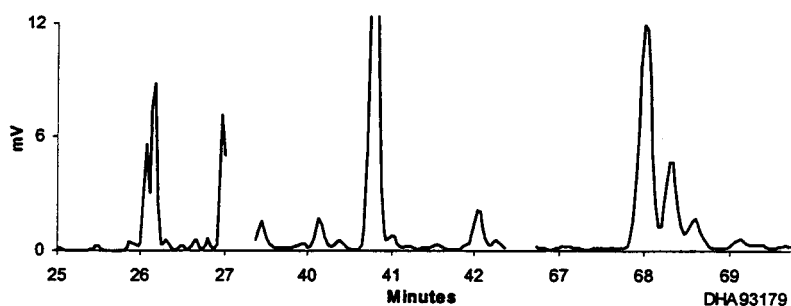


FIG. A1.9 Key Separations – Effect of Different Precolumn Lengths (Same Primary Column. Conditions according to Table 3 Top to Bottom - 1.00m, 1.25m, 1.50m, and 2.00m DB5 precolumn)