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

Designation: D6729 – 20

Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography[1]

This standard is issued under the fixed designation D6729; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

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

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

1.3 The test method also determines 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 % mass to 30 % mass. However, the cooperative study data provided sufficient statistical data for MTBE only.

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 (for example, virgin naphthas), or both, constituents above *n*-octane may reflect significant errors in PONA type groupings. Based on the gasoline samples in the interlaboratory cooperative study, this procedure is applicable to samples containing less than 25 % mass of olefins. However, some interfering coelution with the olefins above C_7 is possible, particularly if blending components or their higher boiling cuts such as those derived from fluid catalytic cracking (FCC) are analyzed, and the total olefin content may not be accurate. Caution should also be exercised when analyzing olefin-free samples using this test method as some of the paraffins may be reported as olefins since analysis is based purely on retention times of the eluting components.

1.4.1 Total olefins in the samples may be obtained or confirmed, or both, if necessary, by Test Method D1319 (percent volume) or other test methods, such as those based on multidimensional PONA type of instruments (Test Method D6839).

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

1.6 Annex A1 of this test method compares results of the test procedure with other test methods for selected components, including olefins, and several group types for several interlaboratory cooperative study samples. Although benzene, toluene, and several oxygenates are determined, when doubtful as to the analytical results of these components, confirmatory analyses can be obtained by using specific test methods.

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

1.8 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

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

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

D1744 Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent (Withdrawn 2016)[3]

D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography

D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

D5623 Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection

D6839 Test Method for Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

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

4. Summary of Test Method

4.1 Representative samples of the petroleum liquid are introduced into a gas chromatograph equipped with an open tubular (capillary) column coated with the specified stationary phase. 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 that established by analyzing reference standards or samples under identical conditions. The concentration of each component in mass percent is determined by normalization of the peak areas after correction of selected components with detector response factors. The unknown components are reported individually and as a summary total.

5. Significance and Use

5.1 Knowledge of the specified 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.

6. Apparatus

6.1 *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 8.1 and 8.2.

6.2 *Inlet*—a capillary split/splitless inlet system operated in the split mode is recommended. It must be operated in its linear range. Refer to 8.4 to determine the proper split ratio.

6.2.1 *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.

6.2.2 *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.

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

6.3 *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 8.3. Columns from two different commercial sources were used in the interlaboratory cooperative study.

6.4 *Data System,* a computer based chromatography data system capable of accurately and repeatedly measuring the retention time and areas of eluting peaks. The system shall 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 8.3.

6.4.1 *Electronic Integrators,* shall be capable of storing up to 400 components in the peak table and shall be able to acquire the data at 10 Hz or faster speeds. They shall be capable of integrating peaks having peak widths at half height which are 1.0s wide. The integrator must be capable of

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

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

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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.

6.5 *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.

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

7. Reagents and Materials

7.1 *Calibrating Standard Mixture*—A spark ignition engine fuel standard of known composition and concentration by mass can be used. In order to corroborate the identification of the sample, a typical chromatogram (Fig. 1) was obtained from reference sample ARC96OX.[4]

7.2 *Gas Chromatograph Gases*—All of the following gases shall have a purity of 99.999 % (V/V) or greater.

NOTE 1—**Warning:** Gases are compressed. Some are flammable and all gases are under high pressure.

7.2.1 *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.

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

8. Instrument Check Out Prior to Analysis

8.1 *Setting:*

8.1.1 *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 cm/s methane or natural gas at 35 °C. Ensure that the retention time is 7.00 min ± 0.05 min. This corresponds to a linear velocity of 25 cm/s to 26 cm/s. This is equivalent to retention times of methane at 0 °C ranging from 6.5 min to 6.8 min.

8.1.2 If the gas chromatograph is not equipped with an electronic flow readout device, calculate the linear gas velocity in cm/s using Eq 1.

$$\text{linear gas velocity} = V = \frac{\text{column length (cm)}}{\text{retention time of methane(s)}} \quad (1)$$

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

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

8.2 *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 Eq 2 and 3.

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

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 atm,
T = temperature of the column oven,
T_{ref} = temperature at the column outlet, and
μ = linear velocity, cm/s.

$$\text{split ratio} = S = \frac{\text{split vent flow} + F}{F} \quad (3)$$

8.2.1 The column flow rate is calculated by the use of Eq 2. Use the results obtained from Eq 3 to adjust the split flow until a split flow of approximately 200:1 is achieved.

8.3 *Evaluation of Column Performance:*

8.3.1 Prior to using the column described in Table 1, measure the resolution of the column under the conditions of Table 2. Check that the resolution for the following pairs of components is obtained using Eq 4 to calculate the resolution of a pair of components:

$$R = \frac{2(t_{R2} - t_{R1})}{1.699\,(W_{h1} + W_{h2})} \quad (4)$$

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.

8.3.1.1 Column resolution should be checked frequently by examining the resolution of these compounds.

8.3.2 *Evaluation of the Baseline*—Carry out a blank baseline run utilizing no solvent injection, by setting the GC in accordance with the conditions of Table 1.

8.3.3 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 %.

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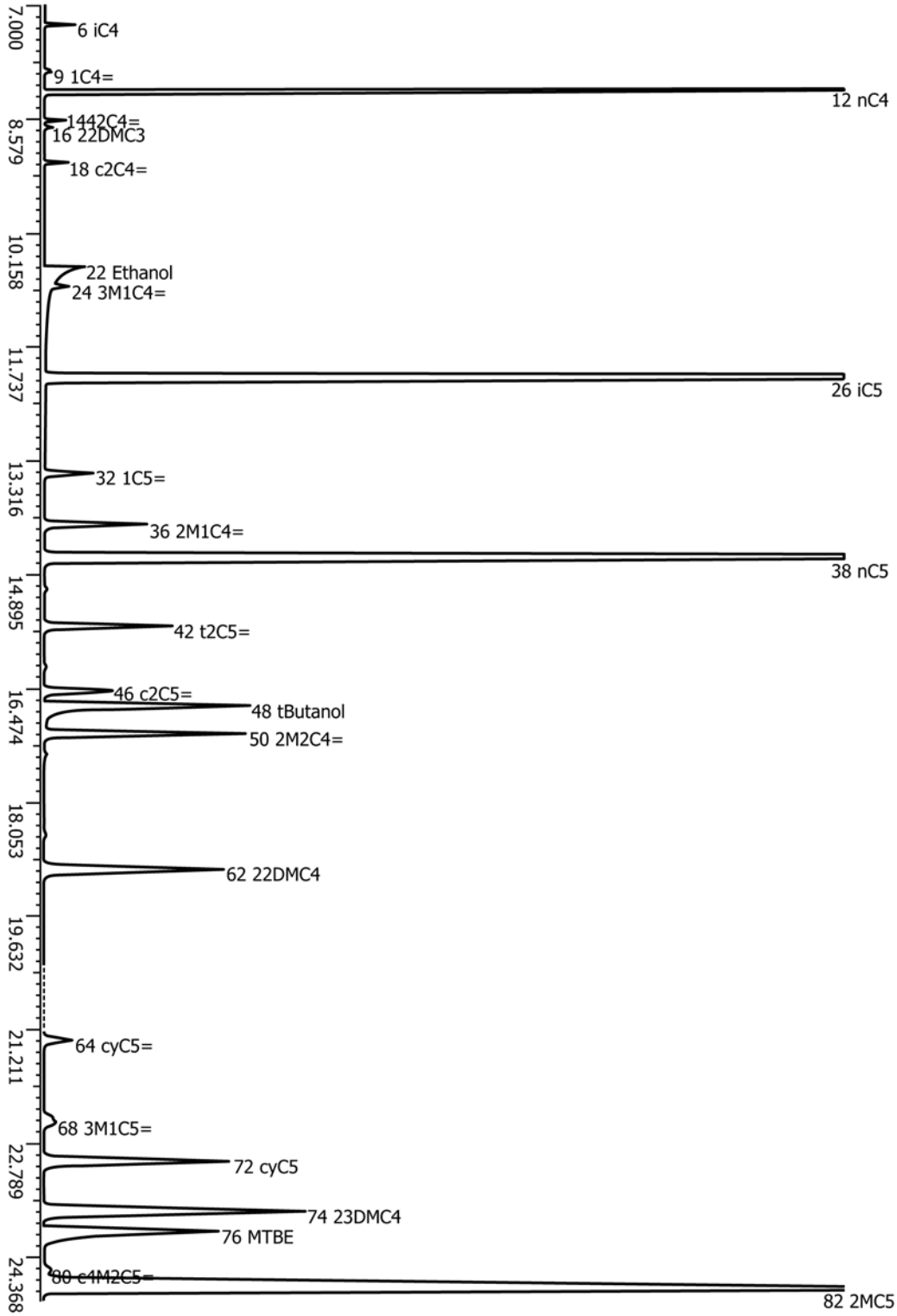

FIG. 1 Chromatogram for Reference Spiked Gasoline

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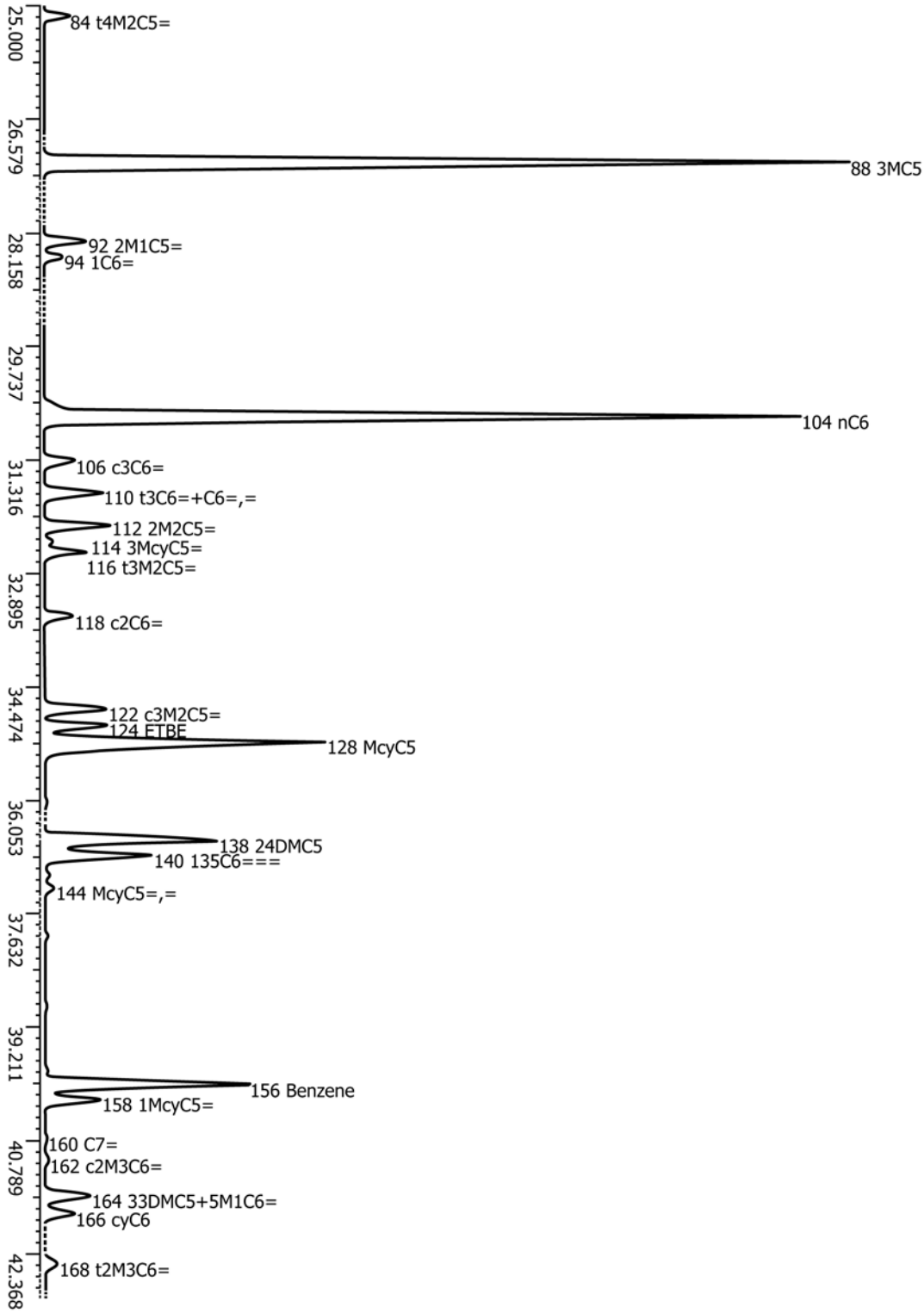

FIG. 1 Chromatogram for Reference Spiked Gasoline *(continued)*

8.4 *Evaluation of Splitter Linearity*—Using the reference gasoline sample, inject this sample according to the schedule listed in Table 3.

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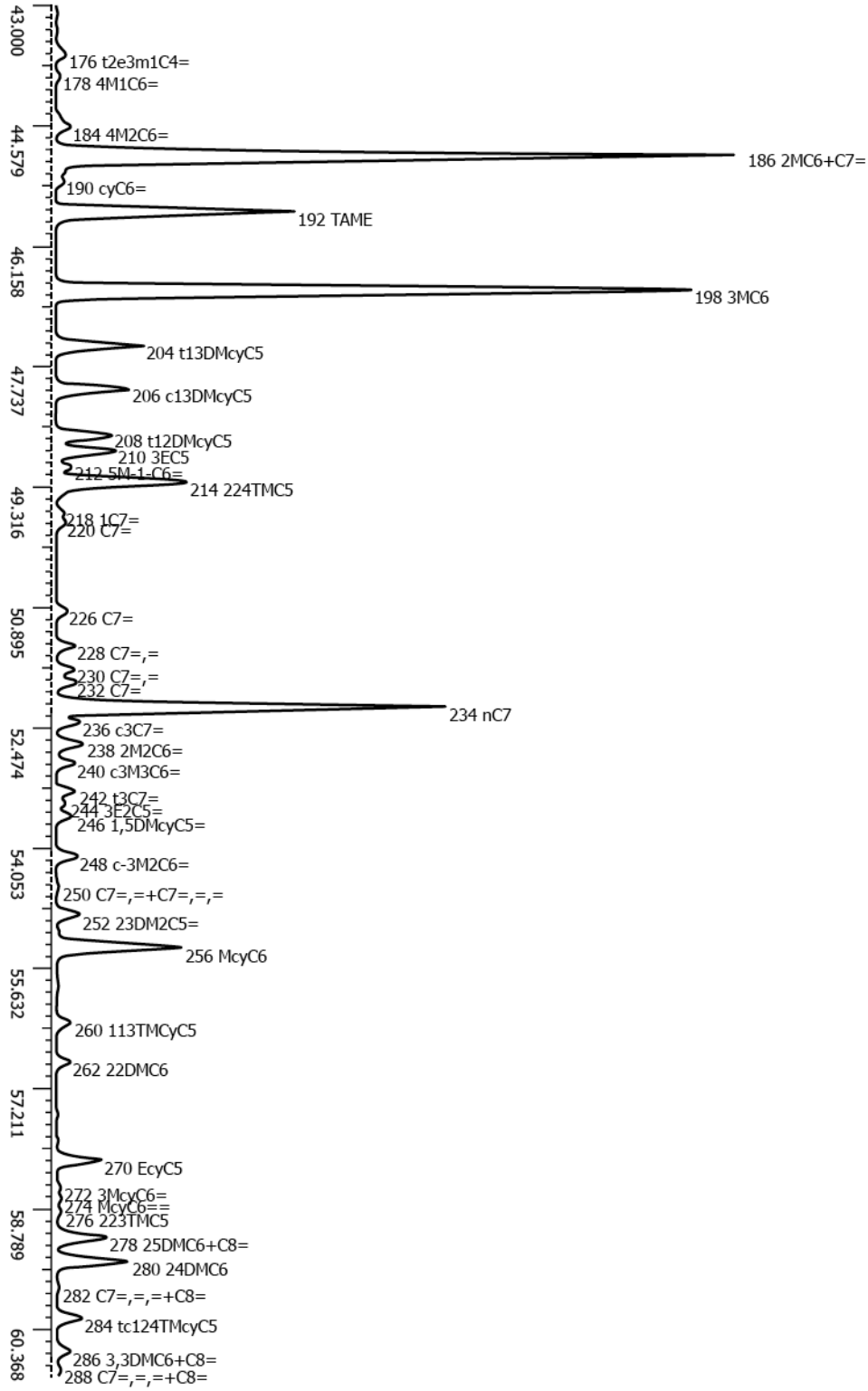

FIG. 1 Chromatogram for Reference Spiked Gasoline *(continued)*

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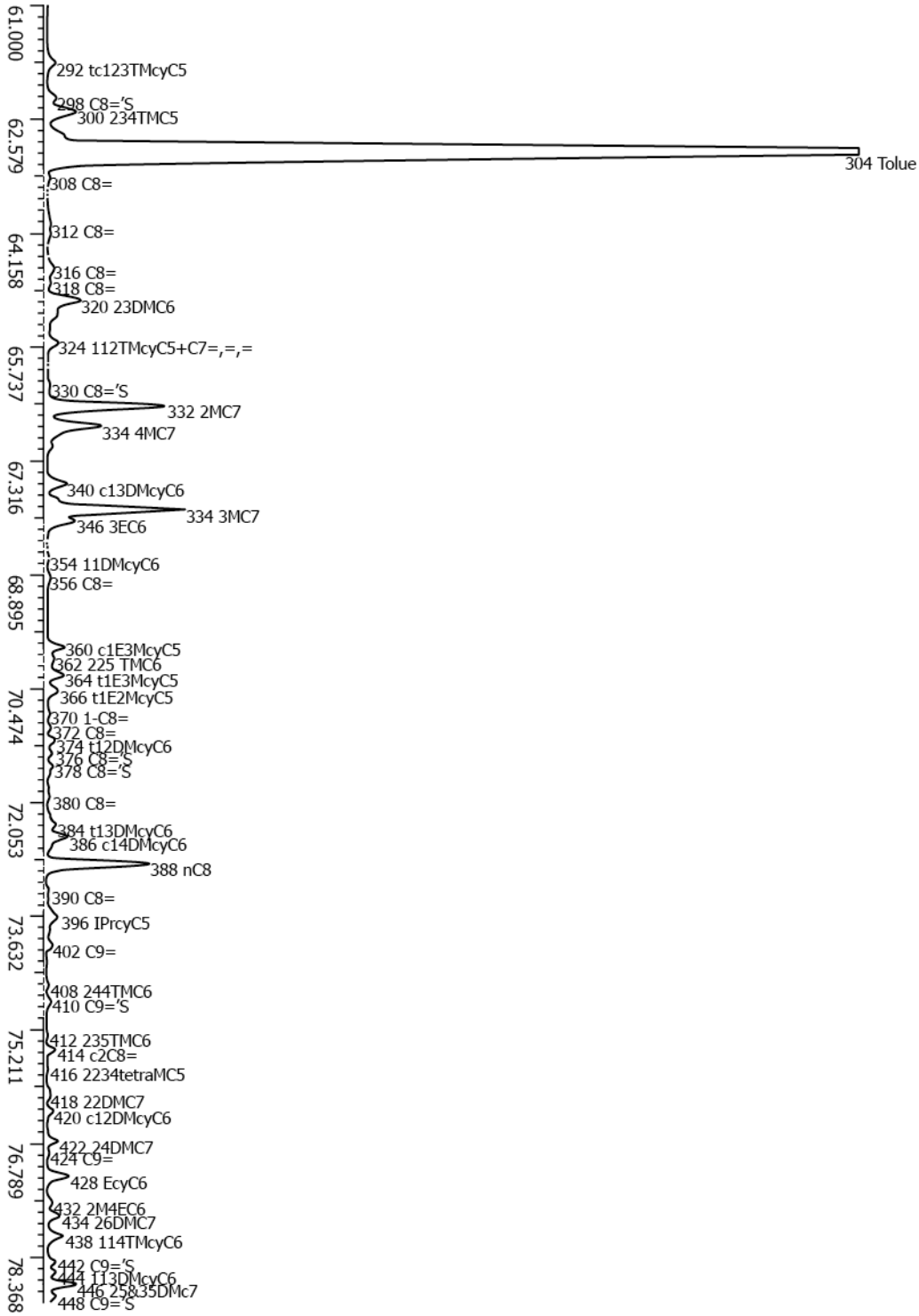

FIG. 1 Chromatogram for Reference Spiked Gasoline *(continued)*

8.4.1 Select from the chromatogram about 10 to 15 components, which have concentrations in the range of 0.01 % mass to 30 % mass. Tabulate for each split ratio the concentrations of the 10 to 15 components. Verify that for each component selected, its concentration does not vary by more than 3 %.

9. Procedure

9.1 Set the operating conditions of the gas chromatograph as shown in Table 1. These conditions will elute all components up to and including pentadecane (nC_{15}).

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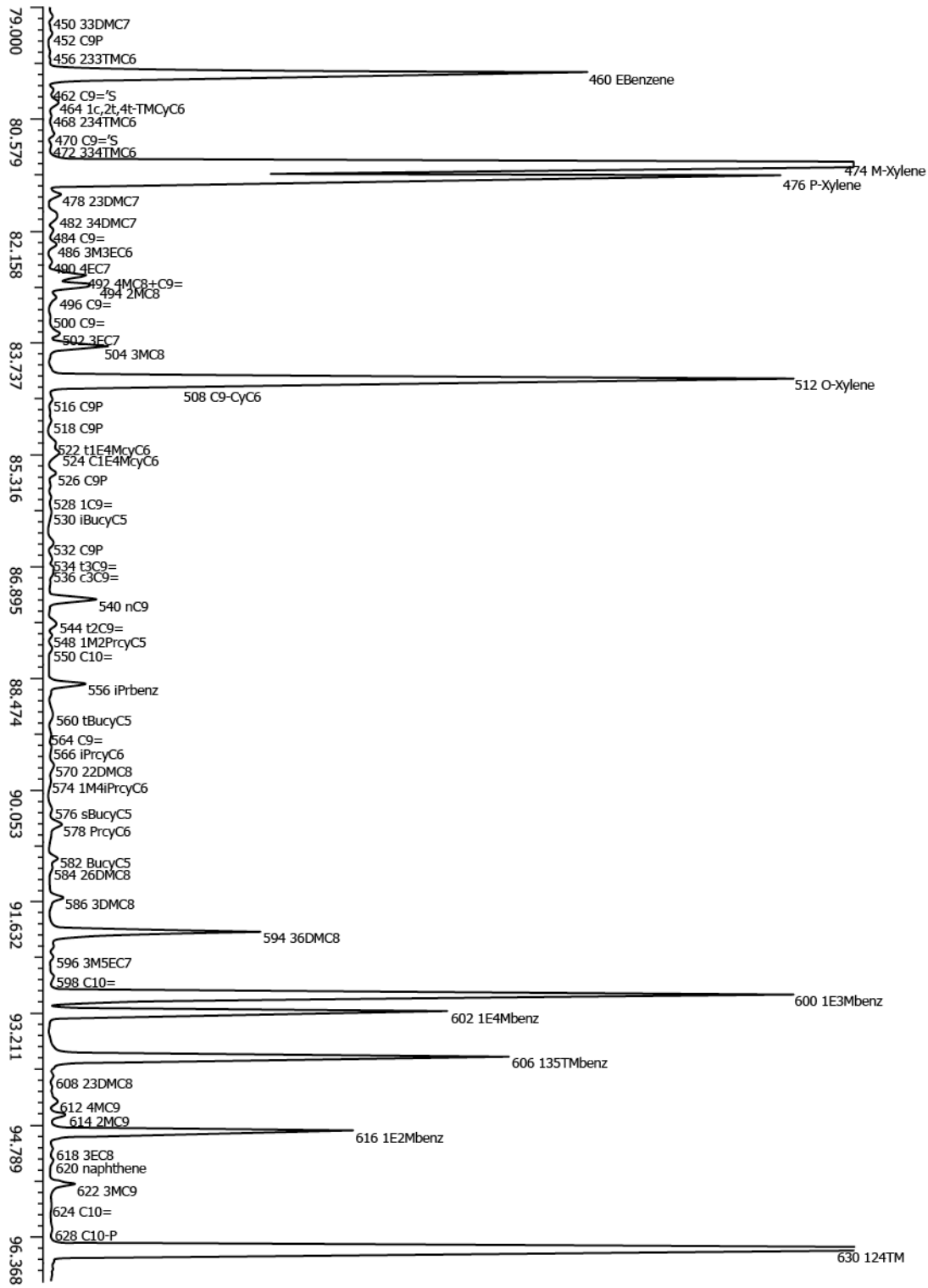

FIG. 1 Chromatogram for Reference Spiked Gasoline *(continued)*

9.2 All of the parameters in Table 1 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 nC_{15} and the column resolution (R) performance requirements listed in Table 2 should not be compromised.

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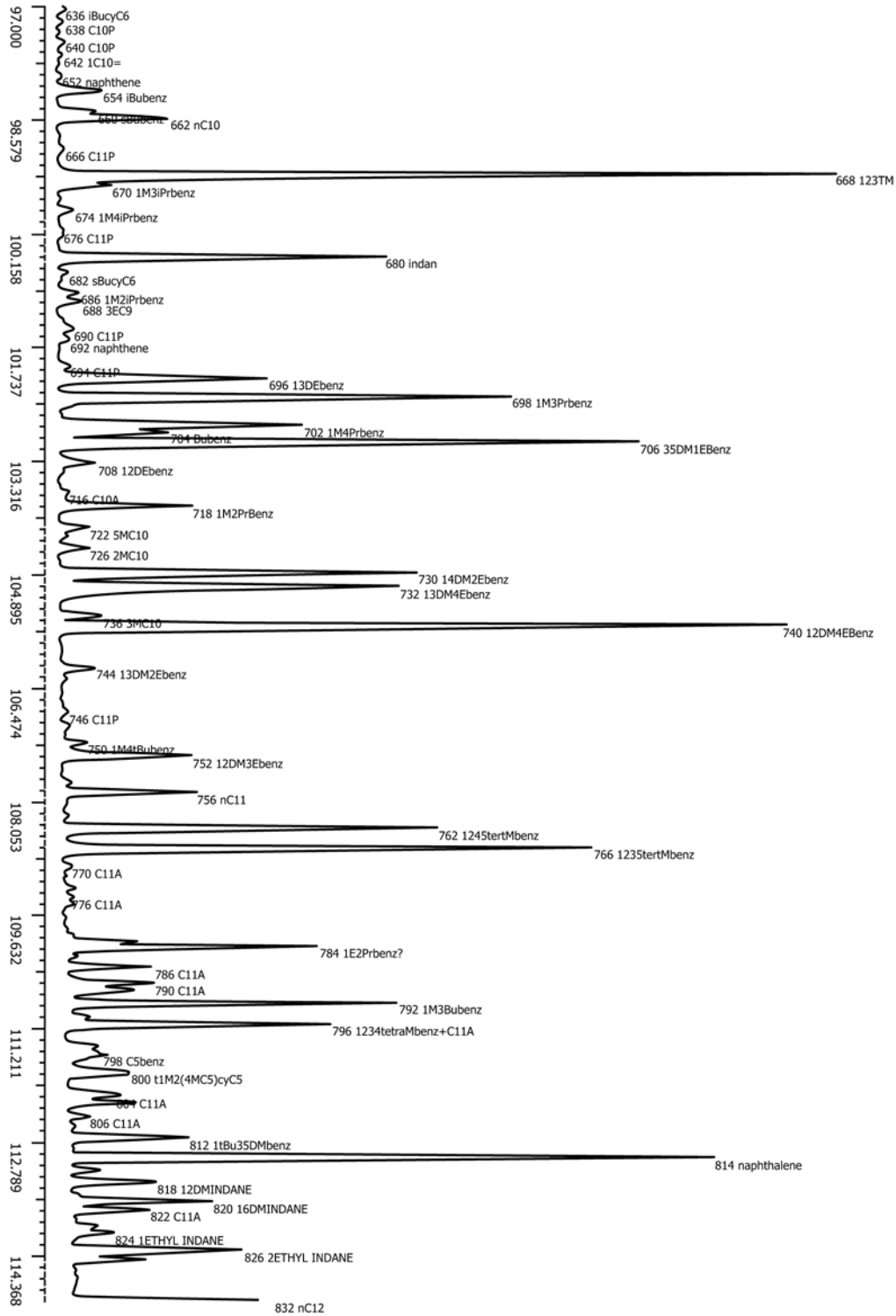

FIG. 1 Chromatogram for Reference Spiked Gasoline *(continued)*

9.3 Obtain a representative sample following the guidelines of Practice D4057 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.

9.4 *Preparation/Storage:*

9.4.1 *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.

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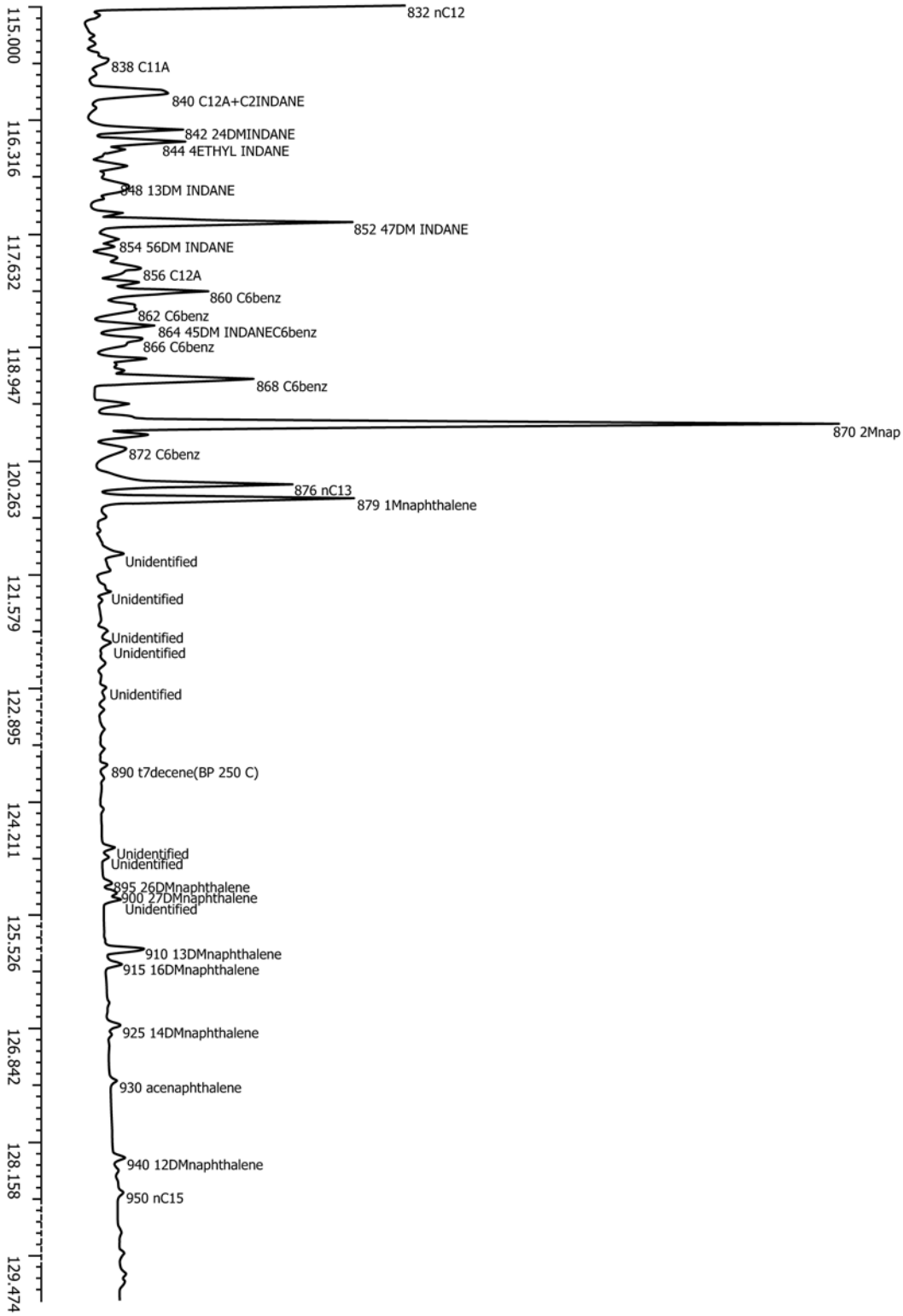

FIG. 1 Chromatogram for Reference Spiked Gasoline *(continued)*

9.4.2 *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 °C. Store pressure containers in accordance with the manufacturer's instructions.

9.5 It is recommended that a quality assurance (QA) sample similar to the reference material gasoline sample be run at regular intervals (see Fig. 1). An interval of once per 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

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TABLE 1 Chromatographic Operating Conditions, Column Requirements and Data Acquisition Requirements

Chromatographic Conditions	Requirements
Injector settings	
Injector temperature, °C	250
Split ratio	175:1 - 275:1
Liner	deactivated glass
Injection volume, µL	0.2–0.5
Detector settings	
FID detector temperature, °C[A]	300–350
Gas flows	
Hydrogen, mL/min[B]	30–40
Air, mL/min	300–450
Nitrogen make up, mL/min	30
Column oven settings	
Initial temperature, °C	0
Initial time, min	15
1st ramp rate, °C/min	1
Final temperature, °C	50
Final time, min	0
2nd ramp rate, °C/min	2
Final temperature, °C	130
Final time, min	0
3rd ramp rate, °C/min	4
Final temperature, °C	270
Final time, min[C]	0
Column Requirements	
Length, m	100
Inside diameter, mm	0.25
Liquid phase	100 % dimethylpolysiloxane
Film thickness, µ	0.5
Pressure, psig	40–50
Flow, mL/min	1.7–2.0
Linear gas velocity, cm/s	24.5
Data acquisition, Hz	10–20
Total analysis time, min	140–150

[A] Set to 25 °C to 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 2 Resolution Performance Requirements

Component Pair	Minimum Resolution	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 %

TABLE 3 Injection Schedule

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

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.

10. Data Analysis

10.1 *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.

10.2 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.

$$(R1)_i = 100n + 100\left[\frac{log(T_i) - log(T_n)}{log(TN) - log(T_n)}\right] \quad (5)$$

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,
T_i = adjusted retention time of component *i* (retention time of component *i* minus the retention time of methane),
T_n = adjusted retention time of *N*-paraffin n, and
TN = retention time of *N*-paraffin N.

10.3 Determine the hydrocarbon response factors by using the following equation.[5]

$$RRF_{CH4} = \frac{MW_i}{N_c} \times \frac{1}{MW_{CH4}} \quad (6)$$

[5] Sevcik, J., *Detectors in Gas Chromatography*, Elsevier, NY, 1976, p. 94.

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TABLE 4 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 (from Annex A1)	Predominant Compound	Coeluting Compound(s)
164	3,3-dimethylpentane	5-methyl-1-hexene
186	2-methylhexane	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	1,1,2-trimethylcyclopentane	C_7-triolefin
326	C_8-diolefin	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 5 Response Factors of Oxygenated Compounds

Analytes	Relative Response Factors	
	RRF C_7 = 1.000	RRF CH_4 = 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

where:

RRF_{CH4} = relative response factor of each component with respect to methane (RRF_{CH4} =1.000),
MW_i = molecular weight of the component, i,
N_c = number of carbon atoms in the molecule, and
MW_{CH4} = molecular weight of methane (16.04276).

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

$$A_{c_i} = (A)_I (RRF)_I \quad (7)$$

where:

$(A_c)_i$ = corrected area,
A_i = acquired area for an individual component, and
RRF = relative response factor (weight basis).

10.4.1 The percent mass (% W) is calculated as follows:

$$\% W_i = \frac{(A_C)_i}{\sum_{i=1}^{i=n} A_{c_i}} \times 100 \quad (8)$$

where:

$\% W$ = percent mass of the component i in the mixture, and
$\sum_{i=1}^{i=n} A_{c_i}$ = summation of all the corrected areas for the components analyzed.

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

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

11. Oxygenates

11.1 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 concentration ranges from 1.0 % mass up to 30 % mass (Annex A2). The average relative response factors for the oxygenates were calculated from the study and are listed in Table A2.1. 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 RR:D02-1007. Therefore the statistical data for MTBE should be taken from Table A1.2.

12. Expression of Results

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

12.2 The data for individual components may by 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 the calculation of other properties of petroleum liquids.

13. Precision and Bias[6]

13.1 The repeatability and reproducibility precision estimates are quoted in Annex A1.

[6] Supporting data describing the interlaboratory cooperative study to determine precision and bias has been filed at ASTM International Headquarters and may be obtained by requesting RR: RR:D02-1519. Contact ASTM Customer Service at service@astm.org.

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13.2 *Precision Statement Outline*—(> Analyte Qualification Process):

13.2.1 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 RR:D02-1007[7] requirements.

13.2.2 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 standard, is what CS94 is recommending.

13.3 A brief explanation of headers in Table A1.2 follows:

13.3.1 ID: self explanatory,

13.3.2 r_{min}: lower 95 % confidence limit of r_{est},

13.3.3 r_{est}: repeatability estimate in percentage of concentration,

13.3.4 r_{max}: upper 95 % confidence limit of r_{est},

13.3.5 R_{min}, R_{est}, R_{max}: same as above except for reproducibility,

13.3.6 C_{min}: lower concentration limit that rest, R_{est} is applicable, and

13.3.7 C_{max}: upper concentration limit that rest, R_{est} is applicable.

13.4 The summaries for the paraffins, isoparaffins, C_2 benzene, and oxygenates follow the same procedure that was used for the analytes and are listed in Table A1.3.

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

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1007. Contact ASTM Customer Service at service@astm.org.

14. Keywords

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

ANNEXES

(Mandatory Information)

A1. HYDROCARBON DATA

A1.1 Table A1.1 presents the component retention times and properties.

A1.2 Table A1.2 represents the repeatability and reproducibility precision estimates prepared by statisticians of CS94 in accordance with RR:D02-1519. The analyte qualification process for precision statements is outlined as follows:

A1.2.1 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 RR:D02-1007 requirements.

A1.2.2 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 standard, is what CS94 is recommending.

A1.3 *Summary for Oxygenates:* **Warning—**The statistical data could be done on the oxygenates but there was not an equal number of all oxygenates in the round robin. MTBE was the largest contributor to the statistical results. The number of samples that contained each oxygenate is as follows:

Oxygenate Type	No. of Samples	Approximate Concentration Range
Ethanol	2	1 %, and 12 %
t-butanol	2	0.20 %, and 1.0 %
MTBE	6	1, 2, 4, 4, 8 and 16 %
ETBE	1	0.50 %
TAME	1	15.00 %

A1.4 The precision statement for the olefins and cycloparaffins is determined by taking the square root of the value determined in the summary; multiply by the coefficient (r_{coef}) for repeatability and the coefficient (R_{coef}) for the reproducibility.

Name	r_{min}	r_{coef}	r_{max}	R_{min}	R_{coef}	R_{max}	C_{min}	C_{max}
Cyclo-paraffins	0.0726	0.08	0.098	0.286	0.384	0.586	2	10
Olefins	0.1555	0.18	0.21	0.382	0.555	1.012	2	25

A1.5 The precision for the aromatics does not depend on level and is stated below in mass percent.

Name	r_{min}	r %	r_{max}	R_{min}	R %	R_{max}	C_{min}	C_{max}
Aromatics	0.8549	0.98	1.155	2.151	2.706	3.651	15	50

A1.6 The summaries for the paraffins, isoparaffins, C_2benzene and oxygenates follow the same procedure that was used for the analytes. The statistics for the grouping are shown in Table A1.3 as an indication of reproducibility and repeatability of reporting the results as a group summary. However, there is a possibility that significant error could occur due to co-elution of peaks, the presence of significant amounts of olefinic or naphthenic constituents, or both, above octane and the percent unknown in the sample. If more accurate summary results are needed that are not covered by the above precision statement, for some or all of the above families of components, please consider another ASTM test method.

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TABLE A1.1 Component Retention Times and Properties

NOTE 1—The names used are from several other tables and changes have been made where the GCMS did not agree with the peak name or its retention time.

NOTE 2—*n*-propanol will coelute with 3M-1-C5=.

NOTE 3—MTBE will coelute with 23DN-1C4=.

NOTE 4—MSBE will coelute with 1-hexene.

NOTE 5—ETBE will coelute with 23DM-13C4= =.

NOTE 6—isobutanol will coelute with 44DM-1-c5=.

NOTE 7—233TM pentane will coelute with toluene when the ratio with toluene is greater than 5.0:1.

NOTE 8—The coeluting olefins in Notes 2-6 will usually be below 1000 ppm.

NOTE 9—In some instances the chemical group is known, but the chemical structure is not known (for example, C_6-olefin; the position of the double bond is not known).

NOTE 10—Relative response factors for six of the major oxygenated compounds have been determined by using the average results from seven laboratories analyzing six samples in duplicate. These same samples were used to determine linearity of methanol, ethanol, t-butanol, MTBE, ETBE and TAME from a concentration level ranging from 1 % mass up to 30 % mass.

Peak No.	Compound Name	Retention Time	Molecular Mass, MWt	Theoretical Mass, Rf, (C1)
1	Methane	6.74	16.04	1.000
2	Ethene	7.10	28.05	0.874
3	Ethane	7.21	30.07	0.937
4	Propene	7.41	42.05	0.874
5	Propane	7.87	44.11	0.916
6	Isobutane	8.26	58.12	0.906
7	Methanol	8.64	32.03	2.672
8	Isobutene	8.95	56.11	0.874
9	1-butene	8.99	56.11	0.874
10	1,3-butadiene	9.17	54.09	0.843
12	*N*-butane	9.28	58.12	0.906
14	Trans-2-butene	9.70	56.11	0.874
16	2,2-dimethylpropane	9.82	72.15	0.899
18	Cis-2-butene	10.33	56.11	0.874
20	1,2-butadiene	10.88	54.09	0.843
22	Ethanol	11.39	46.07	1.862
24	3-methyl-1-butene	12.21	70.13	0.874
26	Isopentane	13.57	72.15	0.899
28	1,4-pentadiene	14.25	68.12	0.849
30	2-Butyne (dimethylacetylene)	14.57	54.09	0.843
32	1-pentene	15.03	70.13	0.874
34	Isopropanol	15.28	60.11	1.950
36	2-methyl-1-butene	15.76	70.13	0.874
38	*N*-pentane	16.24	72.15	0.899
40	2-methyl-1,3-butadiene	16.73	68.12	0.849
42	Trans-2-pentene	17.23	70.13	0.874
44	3,3-dimethyl-1-butene	17.86	84.16	0.874
46	Cis-2-pentene	18.17	70.13	0.874
48	Tert-butanol (TBA)	18.51	74.12	1.161
50	2-methyl-2-butene	18.76	70.13	0.874
52	Trans-1,3-pentadiene	19.12	68.12	0.849
54	3-methyl-1,2-butadiene	19.48	68.12	0.849
56	Cyclopentadiene	19.76	66.10	0.824
58	Cis-1,3-pentadiene	20.25	68.12	0.849
60	1,2-pentadiene	20.51	68.12	0.849
62	2,2-dimethylbutane	20.69	86.18	0.895
64	Cyclopentene	23.16	68.12	0.849
66	4-methyl-1-pentene	24.30	84.16	0.874
68	3-methyl-1-pentene	24.38	84.16	0.874
70	*n*-propanol	24.68	60.11	1.770
72	Cyclopentane	24.86	70.13	0.874
74	2,3-dimethylbutane	25.57	86.18	0.895
76	2,3-dimethyl-1-butene	25.99	84.16	0.874
78	Methyl tert-butyl ether (MTBE)	26.18	88.09	1.407
80	Cis-4-methyl-2-pentene	26.48	84.16	0.874
82	2-methylpentane	26.66	86.18	0.895
84	Trans-4-methyl-2-pentene	27.09	84.16	0.874
86	Methyl ethyl ketone (MEK)	28.00	72.06	1.570
88	3-methylpentane	29.15	86.18	0.895
90	C_6-olefin	29.61	84.16	0.874
92	2-methyl-1-pentene	30.29	84.16	0.874
94	1-hexene	30.52	84.16	0.874
96	Methyl sec-butyl ether (MSBE)	30.66	88.09	1.550

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TABLE A1.1 *Continued*

Peak No.	Compound Name	Retention Time	Molecular Mass, MWt	Theoretical Mass, Rf, (C1)
98	C_6-olefin	30.94	84.16	0.874
100	2-butanol	31.56	74.12	1.600
102	2ethyl-1-butene	32.47	84.16	0.874
104	*N*-hexane	32.75	86.18	0.895
106	Cis-3-hexene	33.41	84.16	0.874
108	Di-isopropyl ether (DIPE)	33.58	102.00	1.600
110	Trans-3-hexene+hexadiene	33.86	84.16	0.874
112	2-methyl-2-pentene	34.33	84.16	0.874
114	3-methylcyclopentene	34.57	82.10	0.853
116	Trans-3-methyl-2-pentene	34.71	84.16	0.874
118	Cis-2-hexene	35.62	84.16	0.874
120	3,3-dimethyl-1-pentene	36.04	98.19	0.874
122	Cis-3-methyl-2-pentene	36.92	84.16	0.874
124	Ethyl tert-butyl ether (ETBE)	37.07	102.18	1.255
126	2,3-dimethyl-1,3-butadiene	37.19	82.10	0.853
128	Methylcyclopentane	37.40	84.16	0.874
130	2,2-dimethylpentane	37.60	100.21	0.892
132	4,4-dimethyl-1-pentene	37.91	98.19	0.874
134	Isobutanol	38.06	74.12	1.500
136	2,3-dimethyl-2-butene	38.30	84.16	0.874
138	2,4-dimethylpentane	38.99	100.21	0.892
140	1,3,5-hexatriene	39.31	80.06	0.832
142	2,2,3-trimethylbutane	39.48	100.21	0.892
144	Methylcyclopentadiene	40.17	80.06	0.832
146	C_7-olefin	40.30	98.19	0.874
148	C_7-olefin	40.68	98.19	0.874
150	C_7-diolefin	41.20	96.18	0.856
152	4-methylcyclopentene	41.44	82.10	0.853
154	Methylenecyclopentane	42.08	82.10	0.853
156	Benzene	42.30	78.05	0.812
158	1-methyl-1-cyclopentene	42.46	82.10	0.853
160	C_7-olefin	43.06	98.19	0.874
162	Cis-2-methyl-3-hexene	43.37	98.19	0.874
164	3,3-dimethylpentane+5-methyl-1-hexene	43.81	100.21	0.892
166	Cyclohexane	44.07	84.16	0.874
168	Trans-2-methyl-3-hexene	44.82	98.19	0.874
170	3,3-dimethyl-1,4-pentadiene	45.44	96.18	0.856
172	*N*-butanol	45.58	74.12	1.500
174	Dimethylcyclopentadiene	45.69	94.17	0.838
176	t,2-ethyl-3-methyl-1-butene	45.97	98.19	0.874
178	4-methyl-1-hexene	46.27	98.19	0.874
180	C_7-olefin	46.55	98.19	0.874
182	3-methyl-1-hexene	46.78	98.19	0.874
184	4-methyl-2-hexene	46.92	98.19	0.874
186	2-methylhexane+C_7-olefin	47.29	100.21	0.892
188	2,3-dimethylpentane	47.51	100.21	0.892
190	Cyclohexene	47.65	82.10	0.853
192	Tert-amyl methyl ether (TAME)	48.10	102.18	1.210
194	C_7-olefin	48.46	98.19	0.874
196	C_7-olefin	48.64	98.19	0.874
198	3-methylhexane	49.05	100.21	0.892
200	C_7-olefin	49.47	98.19	0.874
202	C_7-olefin	49.62	98.19	0.874
204	Trans-1,3-dimethylcyclopentane	49.83	98.19	0.874
206	Cis-1,3-dimethylcyclopentane	50.40	98.19	0.874
208	Trans-1,2-dimethylcyclopentane	51.01	98.19	0.874
210	3-ethylpentane	51.21	100.10	0.892
212	C_7-olefin	51.43	98.19	0.874
214	2,2,4-trimethylpentane	51.61	114.23	0.890
216	C_7-olefin	51.75	98.19	0.874
218	1-heptene	52.05	98.19	0.874
220	C_7-olefin	52.18	98.19	0.874
222	2,3-dimethyl-1,3-pentadiene	52.69	96.18	0.856
224	C_7-diolefin	53.00	96.18	0.856
226	C_7-olefin	53.36	98.19	0.874
228	C_7-diolefin	53.81	96.18	0.856
230	C_7-diolefin	54.13	96.18	0.856
232	C_7-olefin	54.28	98.19	0.874
234	*N*-heptane	54.59	100.21	0.892
236	Cis-3-heptene	54.81	98.19	0.874
238	2-methyl-2-hexene	55.10	98.19	0.874
240	Cis-3-methyl-3-hexene	55.35	98.19	0.874
242	Trans-3-heptene	55.72	98.19	0.874
244	3-ethyl-2-pentene	55.88	96.19	0.874

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TABLE A1.1 *Continued*

Peak No.	Compound Name	Retention Time	Molecular Mass, MWt	Theoretical Mass, Rf, (C1)
246	1,5-dimethylcyclopentene	56.06	96.18	0.856
248	Cis-3-methyl-2-hexene	56.58	98.19	0.874
250	C_7-diolefin+C_7-triolefin	57.01	96.18	0.856
252	2,3-dimethyl-2-pentene	57.35	98.19	0.874
254	3-ethylpentene	57.57	98.19	0.874
256	Methylcyclohexane	57.79	98.19	0.874
258	C_7-olefin	58.28	98.19	0.874
260	1,1,3-trimethylcyclopentane	58.79	112.22	0.874
262	2,2-dimethylhexane	59.29	114.10	0.890
264	2,3,4-trimethyl-1,4-pentadiene	59.45	110.21	0.859
266	3,3-dimethyl-1,5-hexadiene	59.79	110.21	0.859
268	C_8-olefin	60.12	112.22	0.874
270	Ethylcyclopentane	60.60	98.19	0.874
272	3-methylcyclohexene	60.99	96.18	0.856
274	Methylcyclohexadiene	61.14	94.17	0.838
276	2,2,3-trimethylpentane	61.22	114.10	0.890
278	2,5-dimethylhexane+C_8-olefin	61.59	114.23	0.890
280	2,4-dimethylhexane	61.91	114.23	0.890
282	C_7-triolefin+C_8-olefin	62.28	112.24	0.856
284	Trans,cis-1,2,4-trimethylcyclopentane	62.68	112.22	0.874
286	3,3-dimethylhexane+C_8-olefin	63.13	114.23	0.890
288	C_7-triolefin+C_8-olefin	63.39	112.24	0.856
290	C_8-olefin	63.69	112.22	0.874
292	Trans,cis-1,2,3-trimethylcyclopentane	64.27	112.22	0.874
294	C_8-olefin	64.52	112.22	0.874
296	C_8-olefin	64.73	112.22	0.874
298	C_8-olefin	64.82	112.22	0.874
300	2,3,4-trimethylpentane	64.94	114.23	0.890
302	C_7-diolefin	65.25	96.18	0.856
304	Toluene	65.50	92.06	0.821
306	2,3,3-trimethylpentane	65.76	114.23	0.890
308	C_8-olefin	65.90	112.22	0.874
310	C_8-diolefin	66.12	110.21	0.859
312	C_8-olefin	66.48	112.22	0.874
314	C_8-olefin	66.65	112.22	0.874
316	C_8-olefin	67.08	112.22	0.874
318	C_8-olefin	67.30	112.22	0.874
320	2,3-dimethylhexane	67.47	114.23	0.890
322	2-methyl-3-ethylpentane	67.71	114.23	0.890
324	1,1,2-trimethylcyclopentane+C_7-triolefin	68.04	112.22	0.874
326	C_8-diolefin+C_8-paraffin	68.31	114.23	0.859
328	C_8-olefin	68.41	112.22	0.874
330	C_8-olefin	68.64	112.22	0.874
332	2-methylheptane	68.86	114.23	0.890
334	4-methylheptane	69.11	114.23	0.890
336	C_8-diolefin+C_7-olefin	69.41	112.22	0.874
338	C_8-olefin	69.70	112.22	0.874
340	Cis-1,3-dimethylcyclohexane	69.91	112.22	0.874
342	Trans-1,4-dimethylcyclohexane	70.01	112.22	0.874
344	3-methylheptane	70.23	114.23	0.890
346	3-ethylhexane	70.38	114.23	0.890
348	C_8-diolefin	70.51	110.21	0.874
350	C_8-olefin	70.72	112.22	0.874
352	C_8-olefin	70.92	112.22	0.874
354	1,1-dimethylcyclohexane	71.18	112.22	0.874
356	C_8-olefin	71.43	112.22	0.874
358	C_8-olefin	71.70	112.22	0.874
360	Cis-1-ethyl-3-methylcyclopentane	72.10	112.22	0.874
362	2,2,5-trimethylhexane	72.23	128.26	0.888
364	Trans-1-ethyl-3-methylcyclopentane	72.46	112.22	0.874
366	Trans-1-ethyl-2-methylcyclopentane	72.68	112.22	0.874
368	1-methyl-1-ethylcyclopentane	72.96	112.22	0.874
370	1-octene	73.16	112.22	0.874
372	C_8-olefin	73.26	112.22	0.874
374	Trans-1,2-dimethylcyclohexane	73.36	112.22	0.874
376	C_8-olefin	73.48	112.22	0.874
378	C_8-olefin	73.68	112.22	0.874
380	C_8-olefin	74.08	112.11	0.874
382	C_8-olefins	74.45	112.22	0.874

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