Designation: D7213 – 12$^{\varepsilon 1}$

StandardTest Method for
Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100 to 615°C by Gas Chromatography[1]

This standard is issued under the fixed designation D7213; 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.

ε^1 NOTE—Editorial changes made in April 2013.

1. Scope*

1.1 This test method covers the determination of the boiling range distribution of petroleum products. This test method is applicable to petroleum distillates having an initial boiling point greater than 100°C and a final boiling point less than 615°C at atmospheric pressure as measured by this test method.

1.2 The test method is not applicable for analysis of petroleum distillates containing low molecular weight components (for example, naphthas, reformates, gasolines, crude oils). Materials containing heterogeneous components (for example, alcohols, ethers, acids or esters) or residue are not to be analyzed by this test method. See Test Methods D3710, D2887, D6352, or D5307.

1.3 This test method uses the principles of simulated distillation methodology.

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

1.5 *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:*[2]
D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

D1160 Test Method for Distillation of Petroleum Products at Reduced Pressure

D2887 Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography

D2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)

D3710 Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D5307 Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography (Withdrawn 2011)[3]

D6352 Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 700°C by Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E355, E594, and E1510.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *area slice, n*—the area, resulting from the integration of the chromatographic detector signal, within a specified retention time interval. In area slice mode (see 6.4.2), peak detection parameters are bypassed and the detector signal integral is recorded as area slices of consecutive, fixed duration time intervals.

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

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3.2.2 *corrected area slice, n*—an area slice corrected for baseline offset, by subtraction of the exactly corresponding area slice in a previously recorded blank (non-sample) analysis.

3.2.3 *cumulative corrected area, n*—the accumulated sum of corrected area slices from the beginning of the analysis through a given retention time, ignoring any non-sample area (for example, solvent).

3.2.4 *final boiling point (FBP), n*—the temperature (corresponding to the retention time) at which a cumulative corrected area count equal to 99.5 % of the total sample area under the chromatogram is obtained.

3.2.5 *initial boiling point (IBP), n*—the temperature (corresponding to the retention time) at which a cumulative corrected area count equal to 0.5 % of the total sample area under the chromatogram is obtained.

3.2.6 *slice rate, n*—the time interval used to integrate the continuous (analog) chromatographic detector response during an analysis. The slice rate is expressed in Hz (for example, integrations or slices per second).

3.2.7 *slice time, n*—the cumulative slice rate (analysis time) associated with each area slice throughout the chromatographic analysis. The slice time is the time at the end of each contiguous area slice.

3.2.8 *total sample area, n*—the cumulative corrected area, from the initial point to the final area point.

3.3 *Abbreviations*—A common abbreviation of hydrocarbon compounds is to designate the number of carbon atoms in the compound. A prefix is used to indicate the carbon chain form, while a subscripted suffix denotes the number of carbon atoms (for example, normal decane n-C_{10}; iso-tetradecane = i-C_{14}).

4. Summary of Test Method

4.1 The boiling range distribution by distillation is simulated by the use of gas chromatography. The solvent should not interfere with measurement of the sample in the 100 to 615°C range, and it should be apolar. A non-polar open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point.

4.2 A sample aliquot is diluted with a viscosity reducing solvent and introduced into the chromatographic system. Sample vaporization is provided by separate heating of the point of injection or in conjunction with column oven heating.

4.3 The column oven temperature is raised at a reproducible linear rate to effect separation of the hydrocarbon components in order of increasing boiling point. The elution of sample components is quantitatively determined using a flame ionization detector. The detector signal integral is recorded as area slices for consecutive retention time intervals during the analysis.

4.4 Retention times of known normal paraffin hydrocarbons spanning the scope of this test method (C_5-C_{60}) are determined and correlated to their boiling point temperatures. The normalized cumulative corrected sample areas for each consecutive recorded time interval are used to calculate the boiling range distribution. The boiling point temperature at each reported percent off increment is calculated from the retention time calibration.

5. Significance and Use

5.1 The boiling range distribution of light and medium petroleum distillate fractions provides an insight into the composition of feed stocks and products related to petroleum refining process, This gas chromatographic determination of boiling range can be used to replace conventional distillation methods for control of refining operations. This test method can be used for product specification testing with the mutual agreement of interested parties.

5.2 This test method extends the scope of boiling range determination by gas chromatography to include light and medium petroleum distillate fractions beyond the scope of Test Method D2887 (538°C) and below Test Method D6352 (700°C).

5.3 Boiling range distributions obtained by this test method are theoretically equivalent to those obtained by true boiling point (TBP) distillation (see Test Method D2892). They are not equivalent to results from low efficiency distillation such as those obtained with Test Method D86 or D1160.

6. Apparatus

6.1 *Chromatograph*—The gas chromatographic system used shall have the following performance characteristics:

6.1.1 *Column Oven*—Capable of sustained and linear programmed temperature operation from near ambient (for example, 35 to 50°C) up to 400°C.

6.1.2 *Column Temperature Programmer*—The chromatograph shall be capable of linear programmed temperature operation up to 400°C at selectable linear rates up to 20°C/min. The programming rate shall be sufficiently reproducible to obtain the retention time repeatability of 0.1 min (6 s) for each component in the calibration mixture described in 7.5.

6.1.3 *Detector*—This test method requires a flame ionization detector (FID). The detector shall meet or exceed the following specifications as detailed in Practice E594. The flame jet should have an orifice of approximately 0.45 to 0.50 mm.

6.1.3.1 *Operating Temperature,* 400°C.

6.1.3.2 *Sensitivity,* >0.005 coulombs/g carbon.

6.1.3.3 *Minimum Detectability,* 1×10^{-11} g carbon/s.

6.1.3.4 *Linear Range,* >10^6.

6.1.3.5 Connection of the column to the detector shall be such that no temperature below the column temperature exists. Refer to Practice E1510 for proper installation and conditioning of the capillary column.

6.1.4 *Sample Inlet System*—Any sample inlet system capable of meeting the performance specification in 7.6 may be used. Programmed temperature vaporization (PTV) and programmable cool on-column injection systems have been used successfully.

6.1.5 *Carrier Gas Flow Control*—The chromatograph shall be equipped with carrier gas pressure or flow control capable of maintaining constant carrier gas flow control through the column throughout the column temperature program cycle.

6.2 *Microsyringe*—A microsyringe with a 23 gauge or smaller stainless steel needle is used for on-column sample introduction. Syringes of 0.1 to 10 µL capacity are available.

6.2.1 Automatic syringe injection is recommended to achieve best precision.

6.3 *Column*—This test method is limited to the use of non-polar wall coated open tubular (WCOT) columns of high thermal stability. Glass, fused silica, and stainless steel columns, with a 0.53 mm diameter have been successfully used. Cross-linked or bonded 100 % dimethyl-polysiloxane stationary phases with film thickness of 0.5 to 1.0 µm have been used. The column length and liquid phase film thickness shall allow the elution of at least C_{60} *n*-paraffin (BP = 615°C). The column and conditions shall provide separation of typical petroleum hydrocarbons in order of increasing boiling point and meet the column resolution requirements of 8.2.1. The column shall provide a resolution between one and ten using this test method's operating conditions.

6.4 *Data Acquisition System:*

6.4.1 *Recorder*—A 0 to 1 mV range recording potentiometer or equivalent, with a full-scale response time of 2 s or less may be used to provide a graphical display.

6.4.2 *Integrator*—Means shall be provided for determining the accumulated area under the chromatogram. This can be done by means of an electronic integrator or computer-based chromatography data system. The integrator/computer system shall have normal chromatographic software for measuring the retention time and areas of eluting peaks (peak detection mode). In addition, the system shall be capable of converting the continuously integrated detector signal into area slices of fixed duration (area slice mode). These contiguous area slices, collected for the entire analysis, are stored for later processing. The electronic range of the integrator/computer (for example, 1 V, 10 V) shall be operated within the linear range of the detector/electrometer system used.

NOTE 1—Some gas chromatographs have an algorithm built into their operating software that allows a mathematical model of the baseline profile to be stored in memory. This profile is automatically subtracted from the detector signal on subsequent sample runs to compensate for the column bleed. Some integration systems also store and automatically subtract a blank analysis from subsequent analytical determinations.

7. Reagents and Materials[4]

7.1 *Carrier Gas*—Helium or hydrogen of high purity. (**Warning**—Helium and hydrogen are compressed gases under high pressure; hydrogen is an extremely flammable gas under high pressure.) These gases may be used as the carrier gas and should not contain more than 5 mL/m^3 of oxygen. The total amount of impurities should not exceed 10 mL/m^3. Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available pressure shall be sufficient to ensure a constant carrier gas flow rate.

7.2 *Hydrogen*—Hydrogen of high purity (for example, hydrocarbon-free) is used as fuel for the flame ionization detector (FID). (**Warning**—Hydrogen is an extremely flammable gas under high pressure.)

7.3 *Air*—High purity (for example, hydrocarbon-free) compressed air is used as the oxidant for the flame ionization detector (FID). (**Warning**—Compressed air is a gas under high pressure and supports combustion.)

7.4 *Solvents*—Unless otherwise indicated, it is intended that all solvents conform to the specifications of the committee on analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used provided it is first ascertained that the solvent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.4.1 *Carbon Disulfide (CS_2)*—(99+ % pure) may be used as a viscosity reducing solvent and as a means of reducing mass of sample introduced onto the column to ensure linear detector response and reduced peak skewness. It is miscible with asphaltic hydrocarbons and provides a relatively small response with the FID. The quality (hydrocarbon content) should be determined by this test method prior to use as a sample diluent. (**Warning**— Carbon disulfide is extremely flammable and toxic.)

7.5 *Cyclohexane (C_6H_{12})*—(99+ % pure) may be used as a viscosity reducing solvent. It is miscible with asphaltic hydrocarbons, however, it responds well to the FID. The quality (hydrocarbon content) should be determined by this test method prior to use as a sample diluent. (**Warning**—Cyclohexane is flammable.)

7.6 *Calibration Mixture*—A qualitative mixture of *n*-paraffins (nominally C_5 to C_{60}) dissolved in a suitable solvent. The final concentration should be approximately one part of *n*-paraffin mixture to one hundred parts of solvent. At least one compound in the mixture shall have a boiling point lower than the initial boiling point of the sample being analyzed, as defined in the scope of this test method (1.1). The calibration mixture shall contain at least 13 known *n*-paraffins (for example, C_6, C_7, C_8, C_9, C_{10}, C_{12}, C_{16}, C_{20}, C_{30}, C_{40}, C_{50}, C_{52}, C_{60}). Boiling points of *n*-paraffins are listed in Table 1.

NOTE 2—A suitable calibration mixture can be obtained by dissolving a polyolefin wax (for example, Polywax 500[5]) in a volatile solvent (for example, carbon disulfide or cyclohexane). Solutions of one part Polywax to one hundred parts solvent can be prepared. Lower boiling point paraffins will have to be added to insure conformance with 7.6. Fig. 1 illustrates a typical calibration mixture chromatogram.

7.7 *Response Linearity Mixture*—Prepare a quantitatively weighed mixture of at least ten individual paraffins (>99 % purity), covering the boiling range of the test method. The highest boiling point component should be at least n-C_{60}. The mixture shall contain n-C_{40}. Use a suitable solvent to provide

[4] *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 *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[5] Polywax is a trademark of the Baker Petrolite Corporation, Barnsdall, OK.

TABLE 1 Boiling Points of *n*-Paraffins^{A,B}

Carbon Number	Boiling Point °C	Boiling Point °F
5	36	97
6	69	156
7	98	209
8	126	258
9	151	303
10	174	345
11	196	385
12	216	421
13	235	456
14	254	488
15	271	519
16	287	548
17	302	576
18	316	601
19	330	626
20	344	651
21	356	674
22	369	695
23	380	716
24	391	736
25	402	755
26	412	774
27	422	791
28	431	808
29	440	825
30	449	840
31	458	856
32	466	870
33	474	885
34	481	898
35	489	912
36	496	925
37	503	937
38	509	948
39	516	961
40	522	972
41	528	982
42	534	993
43	540	1004
44	545	1013
45	550	1022
46	556	1033
47	561	1042
48	566	1051
49	570	1058
50	575	1067
51	579	1074
52	584	1083
53	588	1090
54	592	1098
55	596	1105
56	600	1112
57	604	1119
58	608	1126
59	612	1134
60	615	1139

^{A} API Project 44, 72-10-31, is believed to have provided the original normal paraffin boiling point data that are listed in Table 1. However, over the years some of the data contained in both API Project 44 (Thermodynamics Research Center Hydrocarbon Project) and Test Method D7213 have changed, and they are no longer equivalent. Table 1 represents the current normal paraffin boiling point values accepted by Subcommittee D02.04 and found in all test methods under the jurisdiction of Section D02.04.H.
^{B} Test Method D7213 has traditionally used *n*-paraffin boiling points rounded to the nearest whole degree for calibration. The boiling points listed in Table 1 are correct to the nearest whole number in both degrees Celsius and degrees Fahrenheit. However, if a conversion is made from one unit to the other and then rounded to a whole number, the results will not agree with the table values for a few carbon numbers. For example, the boiling point of *n*-heptane is 98,425°C which is correctly rounded to 98°C in the table. However, converting 98.425°C gives 209.165°F, which rounds to 208°F, while converting 98°C gives 208.4°F, which rounds to 208°F. Carbon numbers 2, 4, 7, 8, 9, 13, 14, 15, 16, 25, 27, and 32 are affected by rounding.

a solution of each component at approximately 0.5 to 2.0 % by mass.

7.8 *Reference Material*—A reference sample that has been analyzed by laboratories participating in the test method
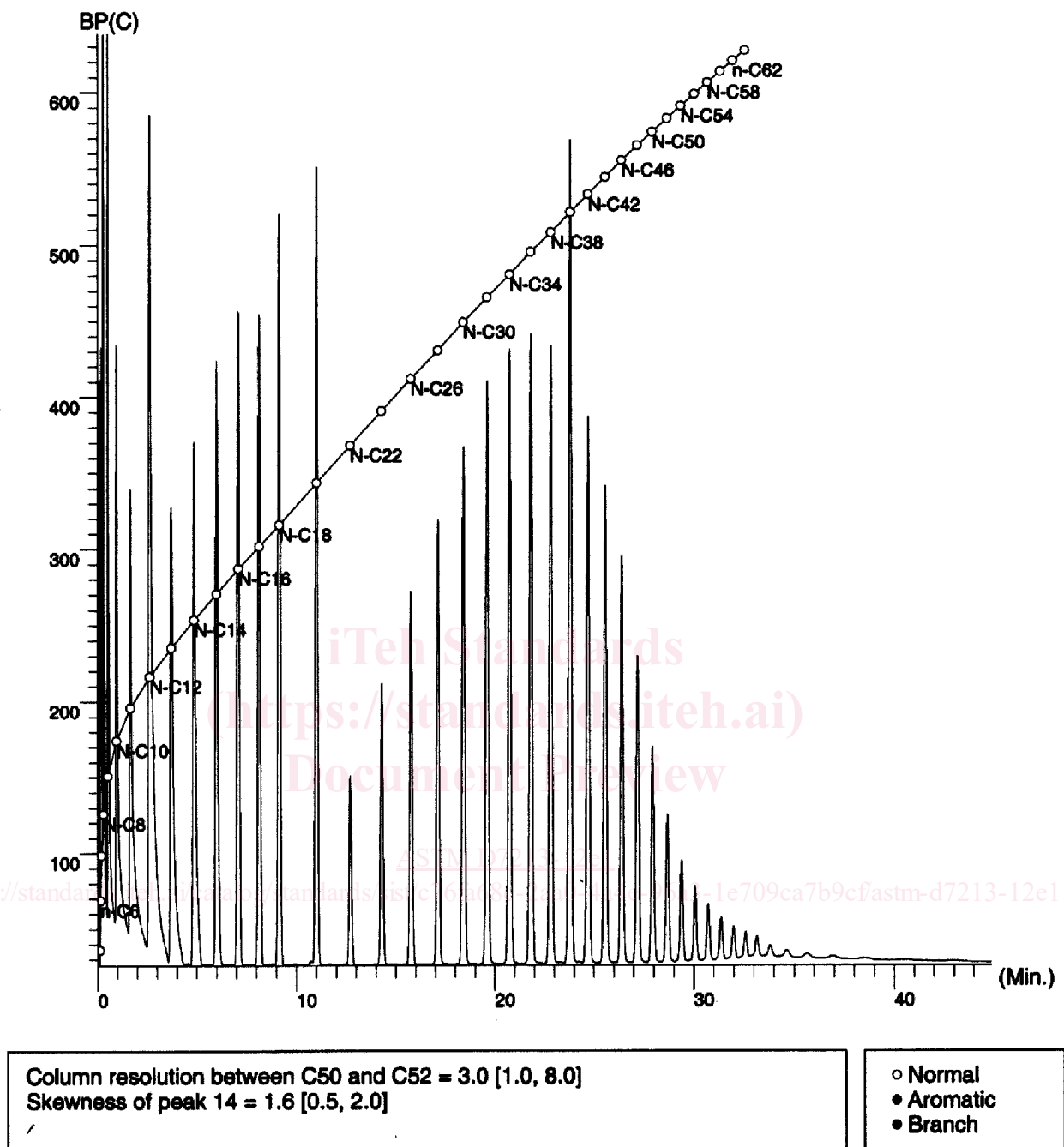
FIG. 1 Typical Calibration Curve with Plot

cooperative study. Consensus values for the boiling range distribution of this sample are being determined.

8. Preparation of Apparatus

8.1 *Gas Chromatograph Setup:*

8.1.1 Place the gas chromatograph and ancillary equipment into operation in accordance with the manufacturers instructions. Recommended operating conditions are shown in Table 2.

8.1.2 When attaching the column to the detector inlet, ensure that the end of the column terminates as close as possible to the FID jet. Follow the instructions in Practice E1510.

8.1.3 The FID should be periodically inspected and, if necessary, remove any foreign deposits formed in the detector from combustion of silicone liquid phase or other materials. Such deposits will change the response characteristics of the detector.

TABLE 2 Recommended Operating Conditions^{A}

Injector	Cool on-column. Temperature Programmable Inlet (no Split)
Injection temperature	Oven-track mode
Auto sampler	Required for best precision
Data collection	Data is collected as independent area slices
	(average data collection rate is 1.0 Hz or
	3.3 slices per second)
Column	Capillary, 5 m by 0.53 mm id
	film thickness; 0.1 to 1.0 µm (polymethylsiloxane) 0.8-1.0 µm was used
	in the ILS study
Flow conditions	UHP helium at 12 mL/min (constant flow)
Carrier: He and Hydrogen were used in the ILS Study	(make-up gas helium at 18 mL/min)
Detector	Flame Ionization;
	Temperature: 390°C
Oven program	Initial oven temperature 35 - 50°C,
	initial hold 0 min.,
	program rate 10 °C/min.,
	final oven temperature 380°C,
	final hold 12 min,
	equilibration time 2 min
Sample size	1 µL
Sample dilution	2 wt % in carbon disulfide
Calibration dilution	1 wt % in carbon disulfide

^{A} Hydrogen was used in the precision study. Results were found to be "statistically equivalent." See Research Report RR:D02-1725.

8.1.4 The inlet liner and initial portion of the column shall be periodically inspected and replaced if necessary to remove extraneous deposits or sample residue.

8.1.5 *Column Conditioning*—A new column will require conditioning at the upper test method operating temperature to reduce or eliminate significant liquid phase bleed, resulting in a stable chromatographic baseline. Follow the guidelines outlined in Practice E1510.

8.2 *System Performance Specification:*

8.2.1 *Column Resolution*—The column resolution, influenced by both the column physical parameters and operating conditions, affects the overall determination of boiling range distribution. Resolution is therefore specified to maintain equivalence between different systems (laboratories) employing this test method. Resolution is determined using Eq 1 and the C_{50} and C_{52} paraffins from a calibration mixture analysis (or a polywax retention time boiling point mixture) (see 7.6). Resolution (*R*) should be at least one and not more than ten, using the identical conditions employed for sample analyses.

$$R = 2\,(t_2 - t_1)/(1.699\,(w_2 + w_1)) \qquad (1)$$

where:

R = resolution,
t_1 = time for the n-C_{50} peak maximum,
t_2 = time for the n-C_{52} peak maximum,
w_1 = peak width, at half height, of the n-C_{50} peak and,
w_2 = peak width, at half height, of the n-C_{52} peak.

8.2.2 *Detector Response Calibration*—This test method assumes that the FID response to petroleum hydrocarbons is proportional to the mass of individual components. This shall be verified when the system is put in service, and whenever any changes are made to the system or operational parameters. Analyze the response linearity mixture (see 7.7) using the identical procedure to be used for the analysis of samples (see Section 9). Calculate the relative response factor for each *n*-paraffin (relative to *n*-tetracontane) as per Practice D4626 and Eq 2:

$$F_n = (M_n/A_n)/(M_{40}/A_{40}) \qquad (2)$$

where:

F_n = relative response factor,
M_n = mass of the *n*-paraffin in the mixture,
A_n = peak area of the *n*-paraffin in the mixture,
M_{40} = mass of the *n*-tetracontane in the mixture, and
A_{40} = peak area of the *n*-tetracontane in the mixture.

8.2.2.1 The relative response factor (F_n) of each *n*-paraffin shall not deviate from unity by more than ±5 %.

8.2.3 *Column Temperature*—The column temperature program profile is selected such that the C_5 peak can be differentiated from the solvent and that the maximum boiling point (615°C) *n*-paraffin (C_{60}) is eluted from the column before reaching the end of the temperature program. The actual program rate used will be influenced by other operating variables such as column dimensions, liquid phase film thickness, carrier gas and flow rate, and sample size.

8.2.4 *Column Elution Characteristics*—The recommended column liquid phase is a non-polar phase such as 100 % dimethyl-polysiloxane.

9. Procedure

9.1 *Analysis Sequence Protocol*—Define and use a predetermined schedule of analysis events designed to achieve maximum reproducibility for these determinations. The schedule will include cooling the column oven and injector to the initial starting temperature, equilibration time, sample injection and system start, analysis, and final temperature hold time.

9.1.1 After chromatographic conditions have been set to meet performance requirements, program the column temperature upward to the maximum temperature to be used and hold that temperature for the selected time. Following the analysis sequence protocol, cool the column to the initial starting temperature.

9.1.2 During the cool down and equilibration time, ready the integrator/computer system. If a retention time calibration