~~Designation:D6352–03~~ Designation: D 6352 – 04 (Reapproved 2009)

An American National Standard

Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 700°C by Gas Chromatography[1]

This standard is issued under the fixed designation D 6352; 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 the boiling range distribution of petroleum distillate fractions. The test method is applicable to petroleum distillate fractions having an initial boiling point greater than 174°C (345°F) and a final boiling point of less than 700°C (1292°F) (C10 to C90) at atmospheric pressure as measured by this test method.

1.2 The test method is not applicable for the analysis of petroleum or petroleum products 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 D 3710, D 2887, or D 5307 for possible applicability to analysis of these types of materials.

1.3 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only and may be included as parenthetical values.

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:*[2]

D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure
D 1160 Test Method for Distillation of Petroleum Products at Reduced Pressure
D 2887 Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography
D 2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)
D 3710 Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography
D 4626 Practice for Calculation of Gas Chromatographic Response Factors
D 5307 Test Method for Determination of Boiling Range Distributions of Crude Petroleum by Gas Chromatography
E 355 Practice for Gas Chromatography Terms and Relationships
E 594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography
E 1510 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. For definitions of these terms used in this test method, refer to Practices E 355, E 594, and E 1510.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *area slice*—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.

3.2.2 *corrected area slice*—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*—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).

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[1] This test method is under the jurisdiction of ASTM Committee D02 ~~on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.~~

~~Current edition approved Nov. 1, 2003. Published November 2003. Originally approved in 1998. Last previous edition approved in 2002 as D6352–02.~~on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0H on Chromatographic Distribution Methods.

Current edition approved April 15, 2009. Published July 2009. Originally approved in 1998. Last previous edition approved in 2004 as D 6352 – 04$^{\varepsilon 1}$.

[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.

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

3.2.4 *final boiling point (FBP)*—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)*—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*—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*—the 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*—the cumulative corrected area, from the initial area point to the final area point, where the chromatographic signal has returned to baseline after complete sample elution.

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 n-C_{10} for normal-decane, i-C_{14} for iso-tetradecane).

4. Summary of Test Method

4.1 The boiling range distribution determination by distillation is simulated by the use of gas chromatography. 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 specified linear rate to ~~effect~~affect 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 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 the test method, 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 medium and heavy petroleum distillate fractions provides an insight into the composition of feed stocks and products related to petroleum refining processes (for example, hydrocracking, hydrotreating, visbreaking, or deasphalting). The gas chromatographic simulation of this determination 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 medium and heavy petroleum distillate fractions beyond the scope of Test Method D 2887 (538°C).

5.3 Boiling range distributions obtained by this test method have not been analyzed for correlation to those obtained by low efficiency distillation, such as with Test Method D 86 or D 1160.

6. Apparatus

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

6.1.1 *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.

6.1.2 *Column Oven*— Capable of sustained and linear programmed temperature operation from near ambient (for example, 30 to 35°C) up to 450°C.

6.1.3 *Column Temperature Programmer* —The chromatograph shall be capable of linear programmed temperature operation up to 450°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.

6.1.4 *Detector*—This test method requires the use of a flame ionization detector (FID). The detector shall meet or exceed the following specifications ~~as detailed in~~in accordance with Practice E 594. The flame jet should have an orifice of approximately 0.05 to 0.070 mm (0.020 to 0.030 in.).

6.1.4.1 *Operating Temperature*—100 to 450°C.

6.1.4.2 *Sensitivity*— >0.005 C/g carbon.

6.1.4.3 *Minimum Detectability*—1 × 10-11 g carbon/s.

6.1.4.4 *Linear Range*— $>10^6$

6.1.4.5 Connection of the column to the detector shall be such that no temperature below the column temperature exists between the column and the detector. Refer to Practice E 1510 for proper installation and conditioning of the capillary column.

6.1.5 *Sample Inlet System*—Any sample inlet system capable of meeting the performance specification in 7.6 and 8.2.2 may be used. Programmable temperature vaporization (PTV) and cool on-column injection systems have been used successfully.

6.2 *Microsyringe*— A microsyringe with a 23-gage 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 (see Note 1). Glass, fused silica, and stainless steel columns with 0.53 to 0.75-mm internal diameter have been successfully used. Cross-linked or bonded 100 % dimethyl-polysiloxane stationary phases with film thickness of 0.10 to 0.20 µm have been used. The column length and liquid phase film thickness shall allow the elution of at least C90 n-paraffin (BP = 700°C). The column and conditions shall provide separation of typical petroleum hydrocarbons in order of increasing boiling point and meet the column performance requirements of 8.2.1. The column shall provide a resolution between three (3) and ten (10) using the test method operating conditions.

NOTE 1—Based on recent information that suggests that true boiling points (atmospheric equivalent temperatures) versus retention times for all components do not fall on the same line, other column systems that can meet this criteria will be considered. These criteria will be specified after a round robin evaluation of the test method is completed.

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. It is, however, not a necessity if an integrator/computer data system is used.

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. 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 2—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

7.1 *Carrier Gas*— Helium, hydrogen, or nitrogen of high purity (**Warning**—Helium and nitrogen are compressed gases under high pressure). 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 FID. Hydrogen can also be ~~sued~~used as the carrier gas. (**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 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.[3] 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) is 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**—CS_2 is extremely flammable and toxic.)

7.4.2 *Cyclohexane (C_6H_{12})*—(99+ % pure) may be used in place of CS_2 for the preparation of the calibration mixture.

7.5 *Calibration Mixture*—A qualitative mixture of n-paraffins (nominally C10 to C100) dissolved in a suitable solvent. The final concentration should be approximately one part of n-paraffin mixture to 200 parts of solvent. At least one compound in the mixture shall have a boiling point lower than the initial boiling point and one shall have a boiling point higher than the final boiling point of the sample being analyzed, as defined in 1.1. The calibration mixture shall contain at least eleven known n-paraffins (for example C10, C12, C16, C20, C30, C40, C50, C60, C70, C80, and C90). Atmospheric equivalent boiling points of n-paraffins are listed in Table 1.

NOTE 3—A suitable calibration mixture can be obtained by dissolving a hydrogenated polyethylene wax (for example, Polywax 655 or Polywax 1000) in a volatile solvent (for example, CS_2 or C_6H_{12}). Solutions of 1 part Polywax to 200 parts solvent can be prepared. Lower boiling point paraffins will have to be added to ensure conformance with 7.5. Fig. 1 illustrates a typical calibration mixture chromatogram, and Fig. 2 illustrates an expanded scale of carbon numbers above 75.

7.6 *Response Linearity Mixture* —Prepare a quantitatively weighed mixture of at least ten individual paraffins (>99 % purity),

[3] *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.

TABLE 1 Boiling Points of n-Paraffins[A,B]

Carbon No.	Boiling Point, °C	Boiling Point, °F
1	–162	–259
2	–89	–127
3	–42	–44
4	0	31
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	625
20	344	651
21	356	675
22	369	696
23	380	716
24	391	736
25	402	755
26	412	774
27	422	791
28	431	808
29	440	824
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
61	619	1146
62	622	1152
63	625	1157
64	629	1164
65	632	1170
66	635	1175
67	638	1180
68	641	1186
69	644	1191
70	647	1197
71	650	1202
72	653	1207
73	655	1211

TABLE 1 *Continued*

Carbon No.	Boiling Point, °C	Boiling Point, °F
74	658	1216
75	661	1222
76	664	1227
77	667	1233
78	670	1238
79	673	1243
80	675	1247
81	678	1252
82	681	1258
83	683	1261
84	686	1267
85	688	1270
86	691	1276
87	693	1279
88	695	1283
89	697	1287
90	700	1292
91	702	1296
92	704	1299
93	706	1303
94	708	1306
95	710	1310
96	712	1314
97	714	1317
98	716	1321
99	718	1324
100	720	1328

[A] API Project 44, October 31, 1972 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 D 6352 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 D02.04.0H.

[B] Test Method D 6352 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 209°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.

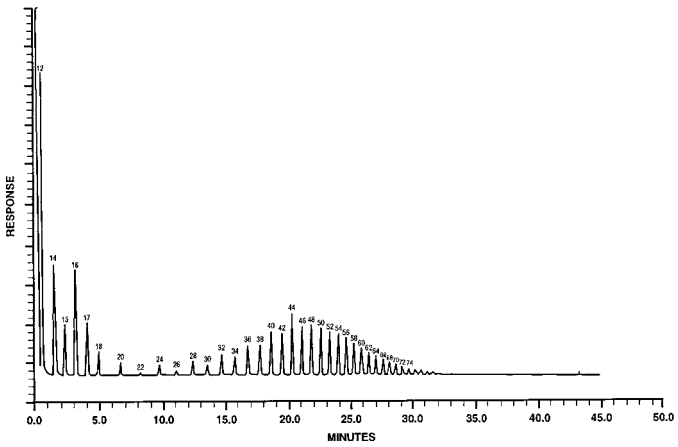

FIG. 1 Chromatogram of C_5 to C_{44} Plus Polywax 655 Used to Obtain Retention Time/Boiling Point Curve Using a 100 % Dimethylpolysiloxane Stationary Phase

covering the boiling range of the test method. The highest boiling point component should be at least n-C60. The mixture shall contain n-C40. Use a suitable solvent to provide a solution of each component at approximately 0.5 to 2.0 % by mass.

7.7 *Reference Material 5010*—A reference sample that has been analyzed by laboratories participating in the test method cooperative study. Consensus values for the boiling range distribution of this sample are given in Table 2.

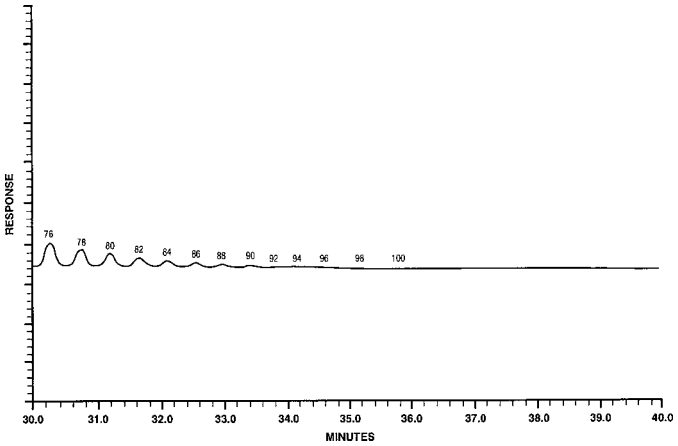

FIG. 2 Scale-Expanded Chromatogram of Latest Eluting Peaks Showing C_{76} to C_{98} Normal Paraffins on a 100 % Dimethylpolysiloxane Stationary Phase

TABLE 2 Test Method D 6352 Reference Material 5010[A]

% OFF	Average, °F	95.5% CI, °F Allowable Difference	Average, °C	95.5% CI, °C Allowable Difference
IBP	801	16	428	9
5	891	5	477	3
10	918	5	493	3
15	936	5	502	3
20	950	6	510	3
25	963	6	518	4
30	975	7	524	4
35	987	7	531	4
40	998	8	537	4
45	1008	8	543	4
50	1019	8	548	5
55	1030	8	554	4
60	1040	8	560	4
65	1051	8	566	4
70	1062	8	572	4
75	1073	9	578	5
80	1086	8	585	4
85	1099	7	593	4
90	1116	8	602	4
95	1140	7	616	4
FBP	1213	32	655	18

[A] Consensus results obtained from 14 laboratories in 2000.

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 manufacturer's instructions. Typical operating conditions are shown in Table 3.

8.1.2 Attach one of the column specified in Table 4 to the detector inlet by ensuring that the end of the column terminates as close as possible to the FID jet tip. Follow the instructions in Practice E 1510.

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.

8.1.4 If the sample inlet system is heated, a blank analysis shall be made after a new septum is installed to ensure that no extraneous peaks are produced by septum bleed. At the sensitivity levels commonly employed in this test method, conditioning of the septum at the upper operating temperature of the sample inlet system for several hours will minimize this problem. 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 to produce or generate a stable and repeatable chromatographic baseline. Follow the guidelines outlined in Practice E 1510.

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

TABLE 3 Typical Gas Chromatographic Conditions for the Simulated Distillation of Petroleum Fractions in the Boiling Range from 174 to 700°C

Instrument	a gas chromatography equipped with an on-column or temperature programmable vaporizing injector (PTV)
Column	capillary, aluminum clad fused silica 5 m × 0.53 mm id film thickness 0.1 microns of a 100 % dimethylpolysiloxane stationary phase
Flow conditions	UHP helium at 18 ml/min (constant flow)
Injection temperature	oven-track mode
Detector	flame ionization; air 400 ml/min, hydrogen 32 ml/min make-up gas, helium at 24 ml/min temperature: 450°C range: 2E5
Oven program	initial oven temperature 50°C, initial hold 0 min, program rate 10°C/min, final oven temperature 400°C, final hold 6 min, equilibration time 5 min.
Sample size	0.5 µL
Sample dilution	1 weight % in carbon disulfide
Calibration dilution	0.5 weight % in carbon disulfide

TABLE 4 Column Selection for Performing Boiling Range Distribution of Petroleum Distillates in the Range from 174 to 700°C by Gas Chromatography

Capillary Column
5 m × 0.53 mm I.D., Polymide or aluminum clad fused silica capillary column with a bonded phase of 100 % dimethylpolysiloxane of 0.1 micron film thickness.
5 m × 0.53 m I.D., stainless steel columns with a bonded phase of 100 % dimethylpolysiloxane of 0.1 micron film thickness

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). Resolution (R) should be at least two (2) and not more than four (4), using the identical conditions employed for sample analyses.

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

where:
t_1 = time (s) for the n-C_{50} peak max,
t_2 = time (s) for the n-C_{52} peak max,
w_1 = peak width (s), at half height, of the n-C_{50} peak, and
w_2 = peak width (s), 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 7.6) 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~~in accordance with Practice D 4626 and Eq 2:

$$Fn = (Cn/An)/(Cn - \mathrm{C40}/An - \mathrm{C40}) \quad (2)$$

where:
Cn = concentration of the n-paraffin in the mixture,
An = peak area of the n-paraffin in the mixture,

Cn- C40 = concentration of the n-tetracontane in the mixture, and
An-C40 = peak area of the n-tetracontane in the mixture.

The relative response factor (*Fn*) of each n-paraffin shall not deviate from unity by more than ±5 %. Results of response factor determinations by one lab are presented in Table 5.

8.2.3 *Column Temperature*—The column temperature program profile is selected such that there is baseline separation between the solvent and the first n-paraffin peak (C10) in the calibration mixture and the maximum boiling point (700°C). n-pParaffin (C90) is eluted from the column before reaching the end of the temperature program. The actual program rate used will be influenced by other operating conditions, such as column dimensions, carrier gas and flow rate, and sample size. Thin liquid phase film thickness and narrower bore columns may require lower carrier gas flow rates and faster column temperature program rates to compensate for sample component overloading (see 9.3.1).

8.2.4 *Column Elution Characteristics* —The column phase is non-polar and having McReynolds numbers of x = 15–17, y = 53–57, z = 43–46, u = 65–67, and s = 42–45.

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 shall include cooling the column oven and injector to the initial starting temperature, equilibration time, sample injection and system start, analysis, and final high 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 is being performed, use the peak detection mode. For samples and baseline compensation (with or without solvent injection), use the area slice mode operation. The recommended slice rate for this test method is 1.0 Hz (1 s). Other slice rates may be used if within the limits from 0.02 to 0.2 % of the retention time of the final calibration component (C90). Larger slice rates may be used, as may be required for other reasons, if provision is made to accumulate (bunch) the slice data to within these limits prior to determination of the boiling range distribution.

9.1.3 At the exact time set by the schedule, inject either the calibration mixture, solvent, or sample into the chromatograph; or make no injection (perform a baseline blank). At the time of injection, start the chromatograph time cycle and the integrator/computer data acquisition. Follow the analysis protocol for all subsequent repetitive analyses or calibrations. Since complete resolution of sample peaks is not expected, do not change the sensitivity setting during the analysis.

9.2 *Baseline Blank*— A blank analysis (baseline blank) shall be performed at least once per day. The blank analysis may be without injection or by injection of an equivalent solvent volume as used with sample injections, depending upon the subsequent data handling capabilities for baseline/solvent compensation. The blank analysis is typically performed prior to sample analyses, but may be useful if determined between samples or at the end of a sample sequence to provide additional data regarding instrument operation or residual sample carry over from previous sample analyses.

NOTE 4—If automatic baseline correction (see Note 2) is provided by the gas chromatograph, further correction of area slices may not be required. However, if an electronic offset is added to the signal after baseline compensation, additional area slice correction may be required in the form of offset subtraction. Consult the specific instrumentation instructions to determine if an offset is applied to the signal. If the algorithm used is unclear, the slice area data can be examined to determine if further correction is necessary. Determine if any offset has been added to the compensated signal by examining the corrected area slices of those time slices that precede the elution of any chromatographic unretained substance. If these corrected area slices (representing the true baseline) deviate from zero, subtract the average of these corrected area slices from each corrected area slice in the analysis.

9.3 *Retention Time versus Boiling Point Calibration*—A retention time versus boiling point calibration shall be performed on the same day that analyses are performed. Inject an appropriate aliquot (0.2 to 2.0 µL) of the calibration mixture (see 7.5) into the

TABLE 5 Measured Response of the Flame Ionization Detector as a Function of Carbon Number for One Laboratory Using a Fused Silica Column with 100 % Dimethylpolysiloxane Stationary Phase

Carbon No.	Measured Response Factor (nC_{40}= 1.00)
12	0.98
14	0.96
17	0.95
20	0.97
28	0.96
32	0.98
36	0.96
40	1.00
44	0.98
60	0.97

chromatograph, using the analysis schedule protocol. Obtain a normal (peak detection) data record to determine the peak retention times and the peak areas for each component. Collect a time slice area record if a boiling range distribution report is desired.

9.3.1 Inspect the chromatogram of the calibration mixture for evidence of skewed (non-Gaussian shaped) peaks. Skewness is often an indication of overloading the sample capacity of the column, which will result in displacement of the peak apex relative to non-overloaded peaks. Skewness results obtained by one laboratory are presented in Table 6. Distortion in retention time measurement and, hence, errors in boiling point temperature determination will be likely if column overloading occurs. The column liquid phase loading has a direct bearing on acceptable sample size. Reanalyze the calibration mixture using a smaller sample size or a more dilute solution if peak distortion or skewness is evident.

9.3.1.1 *Skewness Calculation*—Calculate the ratio *A/B* on specified peaks in the calibration mixture as indicated by the designations in Fig. 3. *A* is the width in seconds of the portion of the peak eluting prior to the time of the apex peak and measured at 10 % of peak height (0.10-*H*), and *B* is the width in seconds of the portion of the peak eluting after the time of the peak apex at 10 % of peak height (0.10-*H*). This ratio for the n-pentacontane (normal C_{50}) peak in the calibration mixture shall not be less than 0.5 or more than 2.0. Results of analysis in one laboratory are presented in Table 6.

9.3.2 Prepare a calibration table based upon the results of the analysis of the calibration mixture by recording the time of each peak maximum and the boiling point temperature in °C (or °F) for each component in the mixture. A typical calibration table is presented in Table 7. n-Paraffin boiling point (atmospheric equivalent temperatures) are listed in Table 1. Fig. 1 illustrates a graphic plot of typical calibration data.

9.4 *Sample Preparation*—Sample aliquots are introduced into the gas chromatograph as solutions in a suitable solvent (for example, CS_2).

9.4.1 Place approximately 0.1 to 1 g of the sample aliquot into a screw-capped or crimp-cap vial.

9.4.2 Dilute the sample aliquot to approximately 1 weight % with the solvent.

9.4.3 Seal (cap) the vial, and mix the contents thoroughly to provide a homogeneous mixture. It may be necessary to warm the mixture initially to ~~effect~~affect complete solution of the sample. However, the sample shall be in stable solution at room temperature prior to injection. If necessary, prepare a more dilute solution.

9.5 *Sample Analysis*— Using the analysis sequence protocol, inject a diluted sample aliquot into the gas chromatograph. Collect a contiguous time slice record of the entire analysis.

9.5.1 Be careful that the injection size chosen does not exceed the linear range of the detector. The typical sample size ranges from 0.2 to 2.0 µL of the diluted sample. The maximum sample signal amplitude should not exceed the maximum calibration signal amplitude found in 9.3.1. A chromatogram for round robin sample 95-3 is presented in Fig. 4.

9.5.2 Ensure that the system's return to baseline is achieved near the end of the run. If the sample chromatogram does not return to baseline by the end of the temperature program, the sample apparently has not completely eluted from the columns, and the sample is considered outside the scope of the test method.

10. Calculation

10.1 Load into a table the sample chromatogram slices.

10.2 Perform a slice offset.

10.2.1 Calculate the average slice offset at start of chromatogram as follows: Calculate the average and standard deviation of the first five area slices of the chromatogram. Throw out any of the first five slices that are not within one standard deviation of the average and recompute the average. This eliminates any area that is due to possible baseline upset from injection.

10.2.2 Subtract the average area slice from all the slices of the sample chromatogram. This will zero the chromatogram.

10.3 Load into a table the blank run chromatogram slices.

NOTE 5—For instruments that compensate the baseline directly at the detector producing an electronically corrected baseline, either process the sample chromatogram directly or do a baseline subtraction. If the compensation is made by the instrument, ~~10.4, 10.5, 10.6, and 10.7~~ 10.4-10.7 may be eliminated and proceed to 10.8.

10.4 Repeat 10.2, using the blank run table.

~~10.5Verify~~10.5 Verify that the slice width used to acquire the sample chromatogram is the same used to acquire the blank run chromatogram.

TABLE 6 Measured Resolution and Skewness for One Laboratory Using a Fused Silica Column Coated with a 100 % Dimethylpolysiloxane Stationary Phase

Resolution between: nC_{50} and nC_{52}	3.3
~~Skewness For nC_{50}~~	
Skewness for nC_{50}	
~~at 10 % of Peak height:~~	~~1.17~~
at 10 % of peak height:	1.17
~~at 50 % of Peak height:~~	~~1.00~~
at 50 % of peak height:	1.00

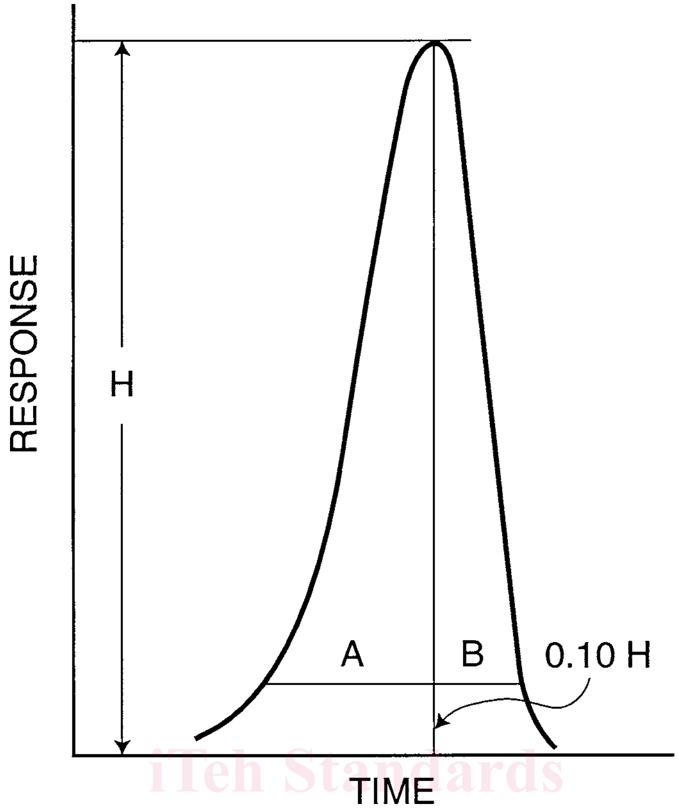

FIG. 3 Designation of Parameters for Calculation of Peak Skewness

~~10.6Subtract~~10.6 Subtract from each slice in the sample chromatogram table with its correspondent slice in the blank run chromatogram table.

~~10.7Offset~~10.7 Offset the corrected slices of the sample chromatogram by taking the smallest slice and subtracting it from all the slices. This will zero the chromatogram.

10.8 Verify the extent of baseline drift.

10.8.1 Calculate the average and standard deviation of the first five area slices of the chromatogram.

10.8.2 Eliminate any of the first five slices that are not within one standard deviation of the average and recompute the average. This eliminates any area that is due to possible baseline upset from injection.

10.8.3 Record the average area slice as *Initial Baseline Signal*.

10.8.4 Repeat 10.8.1 and 10.8.2 using the last five area slices of the chromatogram.

10.8.5 Record the average area slice as *Final Baseline Signal*.

10.8.6 Compare and report the *Initial* and *Final Baseline Signals*. These numbers should be similar.

10.9 Determine the start of sample elution time.

10.9.1 Calculate the total area. Add all the corrected slices in the table. If the sample to be analyzed has a solvent peak, start counting area from the point at which the solvent peak has eluted completely. Otherwise, start at the first corrected slice.

10.9.2 Calculate the rate of change between each two consecutive area slices, beginning at the slice set in 10.9.1 and working forward. The rate of change is obtained by subtracting the area of a slice from the area of the immediately preceding slice and dividing by the slice width. The time where the rate of change first exceeds 0.0001 % per second of the total area (see 10.9.1) is defined as the start of sample elution time.

10.9.3 To reduce the possibility of noise or an electronic spike falsely indicating the start of sample elution time, a 3-s slice average can be used instead of a single slice. For noisier baselines, a slice average larger than 3 s may be required.

10.10 Determine the end of sample elution time by using the following algorithm:

10.10.1 Calculate the sample total area. Add all the corrected slices in the table starting from the slice corresponding to the start of sample elution time.

10.10.2 Calculate the rate of change between each two consecutive area slices, beginning at the end of run and working backwards. The rate of change is obtained by subtracting the area of a slice from the area of the immediately preceding slice and dividing by the slice width. The time where the rate of change first exceeds 0.00001 % per second of the total area (see 10.10.1) is defined as the end of sample elution time.

10.10.3 To reduce the possibility of noise or an electronic spike falsely indicating the end of sample elution time, a 3-s slice average can be used instead of a single slice. For noisier baselines, a slice average larger than 3 s may be required.