Designation: D6352 – 04 (Reapproved 2009)

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 D6352; 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 D3710, D2887, or D5307 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]

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

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. For definitions of these terms used in this test method, refer to Practices E355, E594, and E1510.

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).

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.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0H on Chromatographic Distribution Methods.

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[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.

3.2.5 *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 isotetradecane).

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 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 D2887 (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 D86 or D1160.

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 in accordance with Practice E594. 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 E1510 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 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), 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.

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 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.

[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
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 D6352 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 D6352 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.

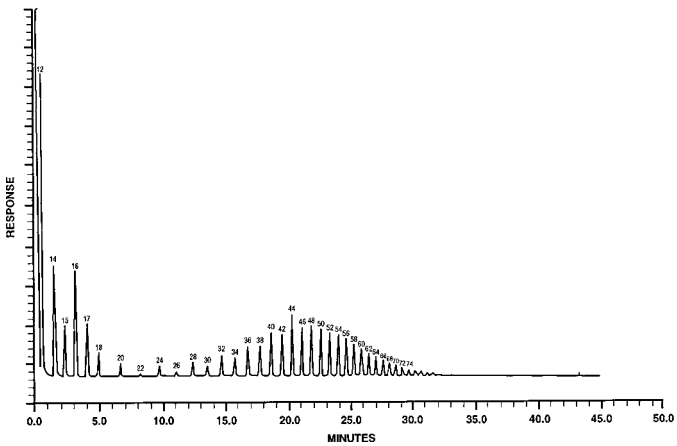

FIG. 1 Chromatogram of C_5 to C_{44} Plus Polywax 655 Used to Obtain Retention Time/Boiling Point Curve Using a 100 % Dimethylpolysiloxane Stationary Phase

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,

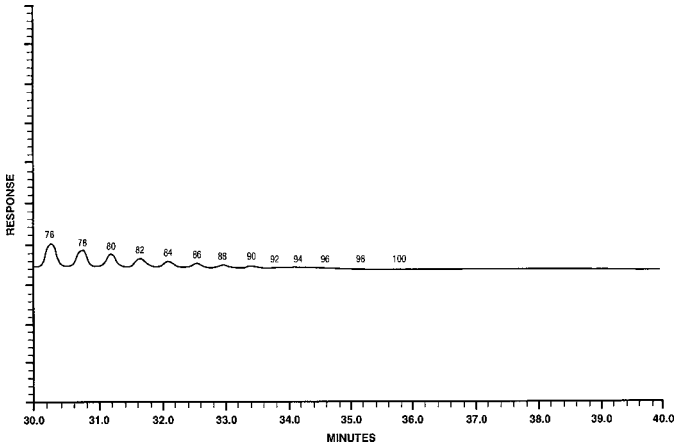

FIG. 2 Scale-Expanded Chromatogram of Latest Eluting Peaks Showing C_{76} to C_{98} Normal Paraffins on a 100 % Dimethylpolysiloxane Stationary Phase

TABLE 2 Test Method D6352 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.

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

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 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). 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) in accordance with Practice D4626 and Eq 2:

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

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-Paraffin (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.

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

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 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

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}	
at 10 % of peak height:	1.17
at 50 % of peak height:	1.00

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.

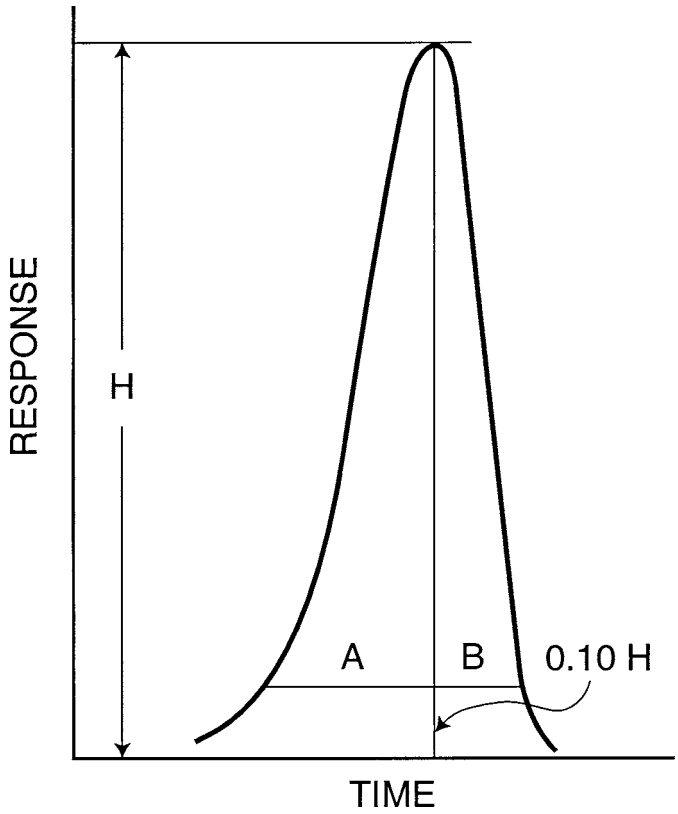

FIG. 3 Designation of Parameters for Calculation of Peak Skewness

TABLE 7 Typical Calibration Report of Retention Time and Boiling Points, °C, for Normal Paraffins on 100 % Dimethylpolysiloxane Stationary Phase

Carbon No.	Boiling Point, °C	Retention Time, min
nC10	174	0.25
nC12	216	0.58
nC14	254	1.61
nC15	271	2.40
nC16	287	3.27
nC17	302	4.18
nC18	316	5.07
nC20	344	6.78
nC22	369	8.38
nC24	391	9.84
nC26	412	11.21
nC28	431	12.48
nC30	449	13.67
nC32	466	14.79
nC34	481	15.86
nC36	496	16.88
nC38	509	17.83
nC40	522	18.74
nC42	534	19.62
nC44	545	20.46
nC46	556	21.26
nC48	566	22.02
nC50	575	22.77
nC52	584	23.47
nC54	592	24.15
nC56	600	24.82
nC58	608	25.46
nC60	615	26.08
nC62	622	26.68
nC64	629	27.25
nC66	635	27.81
nC68	641	28.35
nC70	647	28.88
nC72	653	29.39
nC74	658	29.90
nC76	664	30.39
nC78	670	30.86
nC80	675	31.31
nC82	681	31.77
nC84	686	32.22
nC86	691	32.64
nC88	695	33.05
nC90	700	34.25
nC92	704	34.32

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 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, 10.4-10.7 may be eliminated and proceed to 10.8.

10.4 Repeat 10.2, using the blank run table.

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

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

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.

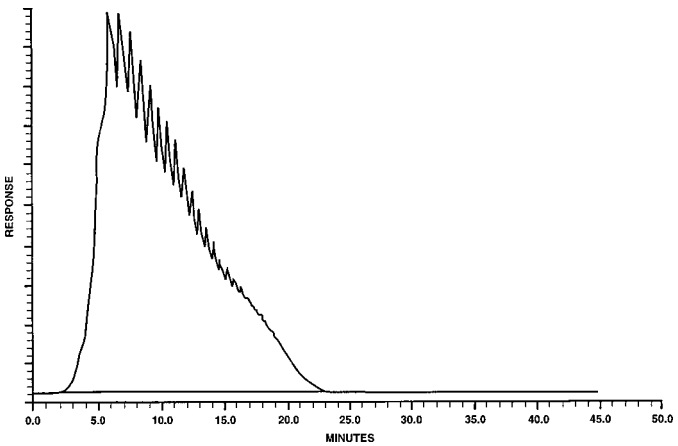

FIG. 4 Chromatogram of Round Robin Sample 95-3 Obtained Using a Fused Silica Capillary Column with 100 % Dimethylpolysiloxane Stationary Phase

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.

10.11 Calculate the sample total area. Add all the slices from the slice corresponding to the start of sample elution time to the slice corresponding to the end of run.

10.12 Normalize to area percent. Divide each slice in the sample chromatogram table by the total area (see 10.11) and multiply it by 100.

10.13 *Calculate the Boiling Point Distribution Table*:

10.13.1 *Initial Boiling Point*—Add slices in the sample chromatogram until the sum is equal to or greater than 0.5 %. If the sum is greater than 0.5 %, interpolate (refer to the algorithm in 10.15.1) to determine the time that will generate

the exact 0.5 % of the area. Calculate the boiling point temperature corresponding to this slice time using the calibration table. Use interpolation when required (refer to the algorithm in 10.15.2).

10.13.2 *Final Boiling Point*—Add slices in the sample chromatogram until the sum is equal to or greater than 99.5 %. If the sum is greater than 99.5 %, interpolate (refer to the algorithm in 10.15.1) to determine the time that will generate the exact 99.5 % of the area. Calculate the boiling point temperature corresponding to this slice time using the calibration table. Use interpolation when required (refer to the algorithm in 10.15.2).

10.13.3 *Intermediate Boiling Point*—For each point between 1 % and 99 %, find the time where the cumulative sum is equal to or greater than the area percent being analyzed. As in 10.13.1 and 10.13.2, use interpolation when the accumulated sum exceeds the area percent to be estimated (refer to the algorithm in 10.15.1). Use the calibration table to assign the boiling point.

10.14 *Report Results*:

10.14.1 Print the boiling point distribution table.

10.14.2 Print the running conditions, slice width, and start and end of analysis time.

10.15 *Calculation Algorithms*:

10.15.1 Calculations to determine the exact point in time that will generate the X percent of total area, where X = 0.5, 1, 2, ..., 99.5 %.

10.15.1.1 Record the time of the slice just prior to the slice that will generate a cumulative slice area larger than the X percent of the total area. Let us call this time, T_s, and the cumulative area at this point, A_c.

10.15.1.2 Calculate the fraction of the slice required to produce the exact X percent of the total area:

$$A_x = \frac{X - A_c}{A_{c+1} - A_c} \tag{3}$$

where:

A_x = fraction of the slice that will yield the exact percent,
A_c = cumulative percent up to the slice prior to X,
A_{c+1} = cumulative percent up to the slice right after X, and
X = desired cumulative percent.

10.15.1.3 Calculate the time required to generate the fraction of area A_x:

$$T_f = A_x \cdot W \tag{4}$$

where:

W = slice width,
A_x = fraction of the slice that will yield the exact percent, and
T_f = fraction of time that will yield A_x.

10.15.1.4 Record the exact time where the cumulative area is equal to the X percent of the total area:

$$T_t = T_s + T_f \tag{5}$$

where:

T_s = fraction of the slice that yields the cumulative percent up to the slice prior to X,
T_f = fraction of time that will yield A_x, and
T_t = time where the cumulative area is equal to X percent of the total area.

10.15.2 Interpolate to determine the exact boiling point given the retention time corresponding to a cumulative slice area.

10.15.2.1 Compare the given time against each retention time in the calibration table. Select the nearest standard having a retention time equal to or larger than the interpolation time. (**Warning—**The retention time table shall be sorted in ascending order.)

10.15.2.2 If the interpolation time is equal to the retention time of the standard, record the corresponding boiling point.

10.15.2.3 If the retention time is not equal to a retention time of the standard (see 9.3), interpolate the boiling point temperature as follows:

10.15.2.4 If the interpolation time is less than the first retention time in the calibration table, then extrapolate using the first two components in the table:

$$BP_x = m_1 \cdot (RT_x - RT_1) + BP_1 \tag{6}$$

where:

m_1 = $(BP_2 - BP_1) / (RT_2 - RT_1)$,
BP_x = boiling point extrapolated,
RT_x = retention time to be extrapolated,
RT_1 = retention time of the first component in the table,
BP_1 = boiling point of the first component in the table,
RT_2 = retention time of the second component in the table, and
BP_2 = boiling point of the second component in the table.

10.15.2.5 If the interpolation time is between two retention times in the calibration table, then interpolate using the upper and lower standard components:

$$BP_x = m_u \cdot (RT_x - RT_1) + BP_1 \tag{7}$$

where:

m_u = $(BP_u - BP_1) / (RT_u - RT_1)$,
BP_x = boiling point interpolated,
RT_x = retention time to be interpolated,
RT_1 = retention time of the lower bound component in the table,
BP_1 = boiling point of the lower bound component in the table,
RT_u = retention time of the upper bound component in the table, and
BP_u = boiling point of the upper bound component in the table.

10.15.2.6 If the interpolation time is larger than the last retention time in the calibration table, then extrapolate using the last two standard components in the table:

$$BP_x = m_n \cdot (RT_x - RT_{n-1}) + BP_{n-1} \tag{8}$$

where:

m_n = $(BP_n - BP_{n-1}) / (RT_n - RT_{n-1})$,
BP_x = boiling point extrapolated,
RT_x = retention time to be extrapolated,
RT_{n-1} = retention time of the standard component eluting prior to the last component in the calibration table,

BP_{n-1} = boiling point of the standard component eluting prior to the last component in the calibration table,
RT_n = retention time of the last standard component in the calibration table, and
BP_n = boiling point of the last standard component in the calibration table.

11. Report

11.1 Report the temperature to the nearest 0.5°C (1°F) at 1 % intervals between 1 and 99 % and at the IBP (0.5 %) and the FBP (99.5 %). Other report formats based upon users' needs may be employed.

NOTE 6—If a plot of the boiling point distribution curve is desired, use graph paper with uniform subdivisions and use either retention time or temperature as the horizontal axis. The vertical axis will represent the sample boiling range distribution from 0 to 100 %. Plot each boiling point temperature against its corresponding accumulated percent slice area. Draw a smooth curve connecting the points.

12. Precision and Bias [4]

12.1 *Precision*—The precision of this test method as determined by the statistical examination of the interlaboratory test results is as follows:

12.1.1 *Repeatability*—The differences between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values presented in Table 8 in only one case in twenty.

12.1.2 *Reproducibility*—The differences between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values presented in Table 8 in only one case in twenty.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1445.

TABLE 8 Repeatability and Reproducibility of Temperatures As a Function of Percent Recovered Using a 100 % Dimethylpolysiloxane Stationary Phase Column

Mass % Recovered	Repeatability, °C	(°F)	Reproducibility, °C	(°F)
0.5 (IBP)	8.1	(14.6)	49.1	(88.4)
2	3.7	(6.7)	15.4	(27.7)
5	2.3	(4.1)	9.0	(16.2)
10	2.8	(5.0)	7.1	(12.8)
20	2.7	(4.9)	6.2	(11.2)
30	2.4	(4.3)	5.9	(10.6)
40	2.6	(4.7)	6.0	(10.8)
50	2.7	(4.9)	6.4	(11.5)
60	2.4	(4.3)	6.4	(11.5)
70	3.0	(5.4)	7.2	(13.0)
80	3.0	(5.4)	7.8	(14.0)
90	3.4	(6.1)	10.5	(18.9)
95	4.7	(8.5)	14.3	(25.7)
98	6.3	(11.3)	21.8	(39.2)
99.5 (FBP)	13.9	(25.0)	38.1	(68.6)

12.2 *Bias*—Because the boiling point distribution can be defined only in terms of a test method, no bias for these procedures in Test Method D6352 for determining the boiling range distribution of heavy petroleum fractions by gas chromatography have been determined.

12.2.1 A rigorous, theoretical definition of the boiling range distribution of petroleum fractions is not possible due to the complexity of the mixture as well as the unquantifiable interactions among the components (for example, azeotropic behavior). Any other means used to define the distribution would require the use of a physical process, such as a conventional distillation or gas chromatographic characterization. This would therefore result in a method-dependent definition and would not constitute a true value from which bias can be calculated.

13. Keywords

13.1 boiling range distribution; distillation; gas chromatography; petroleum; petroleum distillate fractions; simulated distillation

APPENDIXES

(Nonmandatory Information)

X1. BOILING POINT BIASES OF NON-PARAFFINIC HYDROCARBONS

X1.1 By definition and convention, the basis for retention time versus boiling point for calibration of correlation in ASTM simulated distillation procedures are atmospheric equivalent boiling points of normal paraffin. In this high temperature simulated distillation procedure, the bases of these boiling points are the extrapolated data from API project 44 tables (see Table 1). The normal paraffins calibration blends consist of mixtures of normal paraffins plus an admixture of Polywax 655, which has been obtained from the Petrolyte Corporation. There are apparent discrepancies in the measured versus known boiling points of the non-normal model compounds when compared with the normal paraffin hydrocarbon curve plotted on the same basis. For a 100 % dimethylpolysiloxane stationary phase, data for several non-normal paraffin hydrocarbon model compounds whose boiling points are known are presented in Table X1.1. The measured boiling points were obtained by using a normal paraffin versus retention time calibration curve to convert the retention times of the model compounds to a corresponding temperature. These data demonstrate significant differences between known and measured boiling points, especially for the multi-ring aromatics and heteroaromatic compounds. The known or true boiling

TABLE X1.1 Comparison of Known and Measured Boiling Points of "Non-Normal Paraffinic" Hydrocarbons Based on Normal Paraffin Calibration Curve Using a 100 % Dimethylpolysiloxane

	Boiling Points, °C (°F)		
Non-Normal Paraffinics	Known	Measured	Difference
Toluene	128 (231)	127 (229)	–1 (1-2)
Pyridine	132 (240)	121 (218)	–12 (–22)
p-Xylene	157 (282)	155 (279)	–2 (–3)
Cumene	170 (306)	167 (302)	–3 (–5)
1-Decene	188 (339)	189 (341)	–1 (–2)
sec-Butylbenzene	191 (344)	186 (334)	–6 (–10)
n-Butylbenzene	201 (361)	197 (354)	–4 (–7)
trans-Decalin	203 (366)	193 (347)	–11 (–19)
cis-Decalin	212 (382)	203 (365)	–9 (–17)
1-Dodecene	231 (416)	231 (416)	0 (0)
Naphthalene	236 (424)	217 (390)	–19 (–34)
2-Methylnaphthalene	259 (466)	238 (429)	–21 (–38)
1-Methylnaphthalene	263 (473)	240 (432)	–23 (–41)
Indole	272 (489)	241 (434)	–31 (–55)
Acenaththene	297 (534)	268 (483)	–28 (–51)
1-Octadecene	332 (598)	333 (599)	+1 (+1)
Dibenzothiophene	350 (630)	307 (553)	–43 (–77)
Phenanthrene	357 (642)	311 (560)	–46 (–82)
Anthracene	359 (647)	312 (561)	–48 (–86)
Acridine	364 (655)	313 (563)	–51 (–92)
Pyrene	413 (743)	351 (631)	–62 (–112)
Triphenylene	442 (796)	391 (703)	–52 (–93)
Chrysene	465 (837)	391 (703)	–74 (–134)
Coronene	543 (977)	484 (871)	–59 (–106)

point versus retention times of the normal paraffins and the non-normal paraffin hydrocarbons are presented in Fig. X1.1. A significant divergence of these curves is evident.

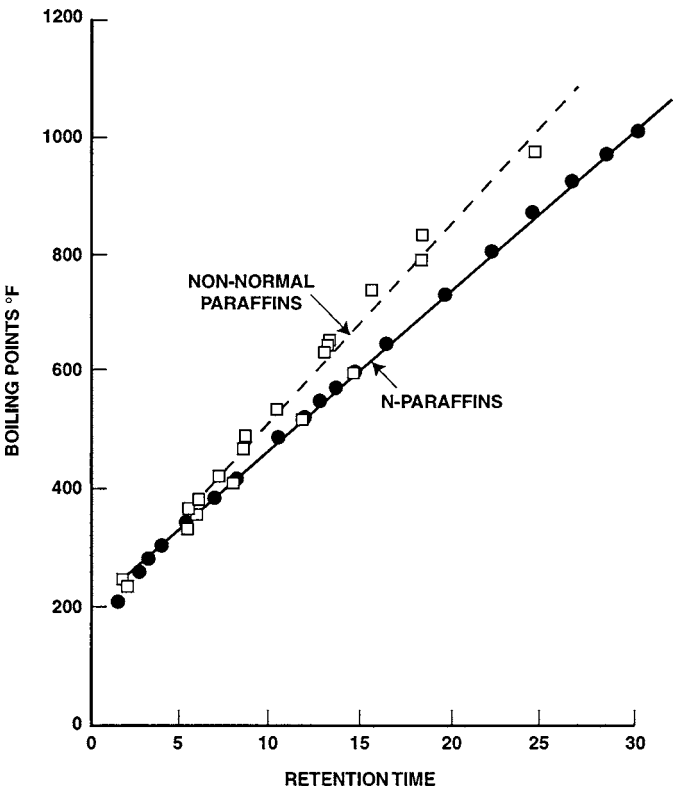

FIG. X1.1 Aromatics and Other Non-Normal Paraffins Deviate Significantly from Normal-Paraffins on 100 % Dimethylpolysiloxane Stationary Phase

X1.2 In the round robin study carried out recently in support of this procedure, three columns containing the following liquid phases were evaluated: (1) 100 % dimethylpolysiloxane, (2) polycarbonate-siloxane, (3) (50 % Phenyl) methylpolysiloxane.

X1.2.1 The same model compounds were evaluated in terms of the differences between the known (true) boiling points and the measured boiling points using the specified column liquid phases were determined. These results are summarized in Table X1.2. The data indicate that the difference between known and measured boiling points decrease in the order of 100 % dimethylpolysiloxane < polycarbonate-siloxane < (50 % Phenyl) methylpolysiloxane. The comparisons of the boiling point/retention times of the model compounds and the normal paraffins are presented in Figs. X1.2-X1.4. These data illustrate the differences between model compounds and normal paraffin curves as a function of column liquid phase. As illustrated in Fig. X1.4, the differences between the normal paraffins (•) and the model compound (□) curves are essentially indistinguishable for the (50 % Phenyl) methylpolysiloxane phase column. These results suggest that for highly aromatic systems a significant difference between simulated distillation and physical distillation would be expected from a 100 % dimethylpolysiloxane column (Fig. X1.2). On average, these differences among liquid phases are presented in Table X1.3. These differences decrease in the order of 36°C < 17°C < +8°C for 100 % dimethylpolysiloxane, polycarbonate-siloxane, and (50 % Phenyl) methylpolysiloxane, respectively.

X1.3 The differences were obtained from data on unsubstituted aromatics. Aromatic compounds typically found in petroleum have multiple alkyl substituents. Such aromatics are

TABLE X1.2 Differences in Temperatures Relative to Published Boiling Points on Non-Normal Paraffin Hydrocarbons Using Normal Paraffins As Calibrants for Several Column Stationary Phases

		Temperature Differences on the Following Stationary Phases, °C (°F)		
Compound	Boiling Point	100 % Dimethyl-Polysiloxane	Poly-Carborane-Siloxane	(50 % Phenyl) Methyl Polysiloxane
Toluene	128 (231)	–1 (–2)	8 (14)	...
Pyridine	132 (240)	–12 (–22)	9 (16)	...
p-Xylene	157 (282)	–2 (–3)	4 (8)	...
Cumene	170 (306)	–3 (–5)	3 (6)	22 (39)
1-Decene	188 (339)	1 (2)	2 (3)	5 (9)
Sec-Butyl Benzene	191 (344)	–6 (–10)	2 (3)	12 (21)
n-butyl Benzene	201 (361)	–4 (–7)	3 (6)	11 (20)
Trans Decalin	203 (366)	–11 (–19)	–2(–4)	...
1-Dodecene	231 (416)	0 (0)	1 (2)	–9 (–16)
Naphthalene	236 (424)	–19 (–34)	–4 (–8)	17 (31)
2-Methylnaphthalene	259 (466)	–21 (–37)	–5 (–9)	17 (30)
1-Methylnaphthalene	263 (473)	–23 (–41)	–6 (–11)	18 (32)
Indole	272 (489)	–31 (–55)	–21 (–37)	18 (32)
Acenaphthene	297 (534)	–28 (–51)	–11 (–19)	20 (36)
1-Octadecene	332 (598)	1 (1)	1 (2)	7 (13)
Dibenzothiaphene	350 (630)	–43 (–77)	–21 (–38)	20 (36)
Phenathrene	357 (642)	–46 (–82)	–23 (–42)	12 (21)
Anthracene	359 (647)	–48 (–86)	–26 (–46)	10 (18)
Acridine	413 (743)	–62 (–112)	–36 (–65)	7 (12)
Pyrene	413 (743)	–62 (–112)	–36 (–65)	–1 (–2)
Tryphenylene	442 (796)	–52 (–93)	–25 (–45)	7 (13)
Chrysene	465 (837)	–74 (–134)	–48 (–87)	–14 (–25)
Coronene	543 (977)	–59 (–106)	–23 (–42)	6 (10)

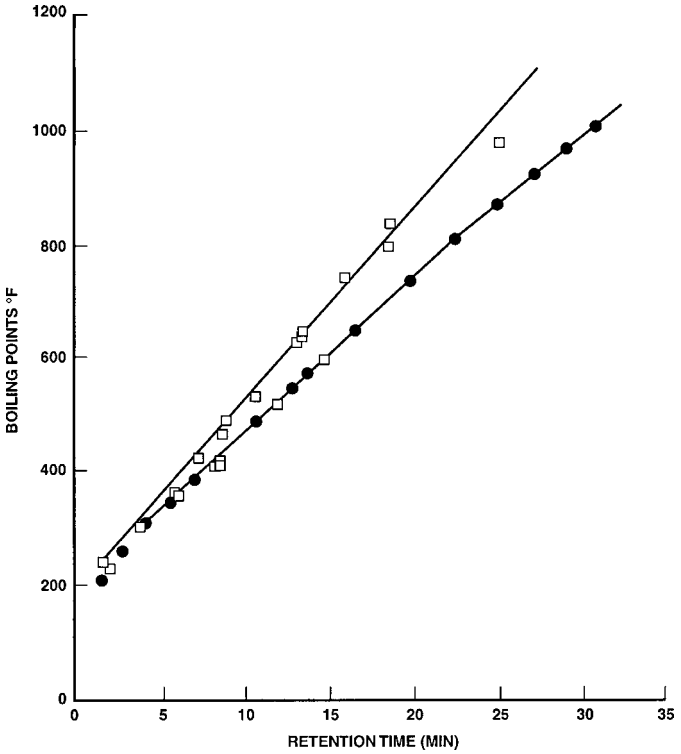

FIG. X1.2 Comparison of Measured Boiling Points of Normal Paraffins (•) and Non-Normal Paraffinic Hydrocarbons (□) Obtained on a Methylsilicone Column

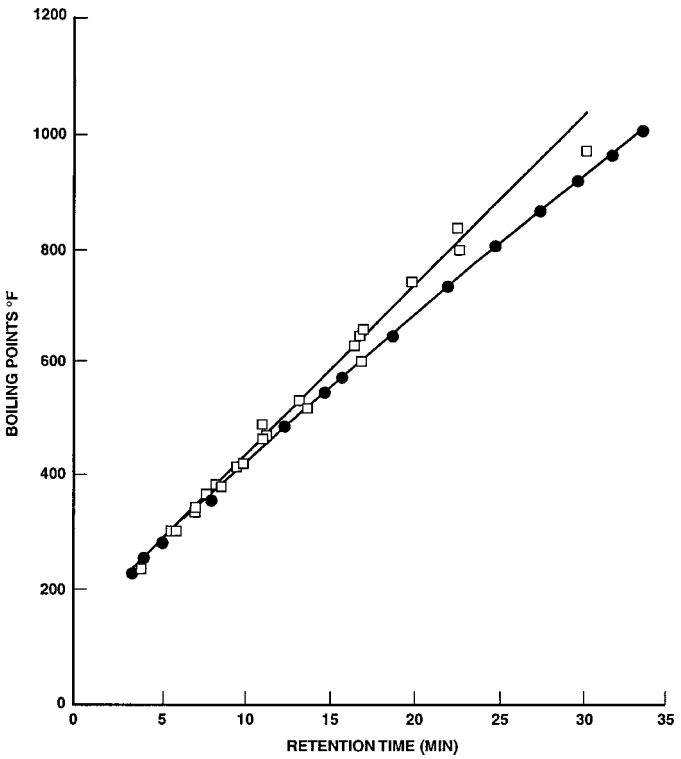

FIG. X1.3 Comparison of Measured Boiling Points of Normal Paraffins (•) and Non Paraffinic Hydrocarbons (□) Obtained on Polycarboranesiloxane Column

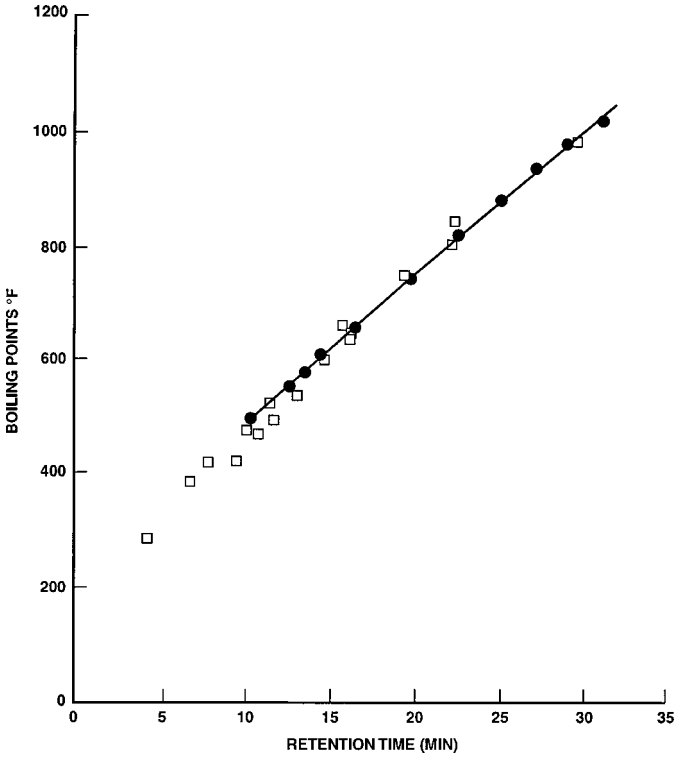

FIG. X1.4 Comparison of Measured Boiling Points of Normal Paraffins (•) and Non-Normal Paraffinic Hydrocarbons (□) Obtained on a (50 % Phenyl) Methylpolysiloxane Column

TABLE X1.3 Average Biases Between Known Boiling Points of Non-Normal Paraffinic Hydrocarbons and Those Measured on Different Column Stationary Phases in the 200°C Plus Range Using HTSD Methodology

Column Stationary Phase	Average Biases	
	°C	°F
100 % Dimethylpolysiloxane	–36	–65
Polycarborane Siloxane	–17	–31
(50 % Phenyl) Methylpolysiloxane	+8	+15

expected to have smaller differences than unsubstituted aromatics. These data also suggest that a boiling point versus retention time relationship for calibration may best be served by an aromatics or substituted aromatics basis, or both, rather than a normal paraffin hydrocarbon basis (as indicated in X1.1). However, there are insufficient alkyl by substituted aromatics available in pure form with established boiling points to test this hypothesis.

X1.4 In the recent round robin, two samples, in particular, illustrate potential differences among columns. Round robin samples HTSD-95-1 represents a refined base oil in which the major amounts of aromatic components were removed. HTSD-95-6 represents a heavy distillate fraction from the same crude source prior to aromatic component removal. The simulated distillation chromatograms on the HT-95-1 sample (basestock) using both a 100 % dimethylpolysiloxane and (50 % Phenyl) methylpolysiloxane stationary phases are presented in Fig. X1.5. These curves do not illustrate a significant difference between the two columns. The grand average simulated distillation data for this sample are presented in Table X1.4. These

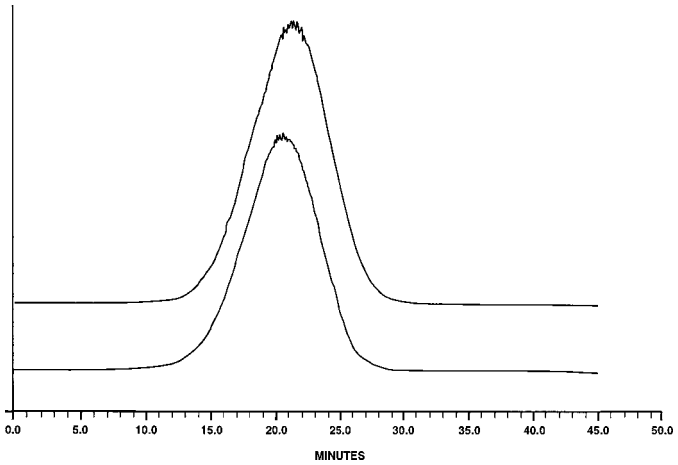

FIG. X1.5 High Temperature Simulated Distillation Chromatograms of a Refined Base Oil (HTSD-95-1) Obtained on a (50 % Phenyl) Methylpolysiloxane (Upper) and 100 % Dimethylpolysiloxane (Lower) Phases

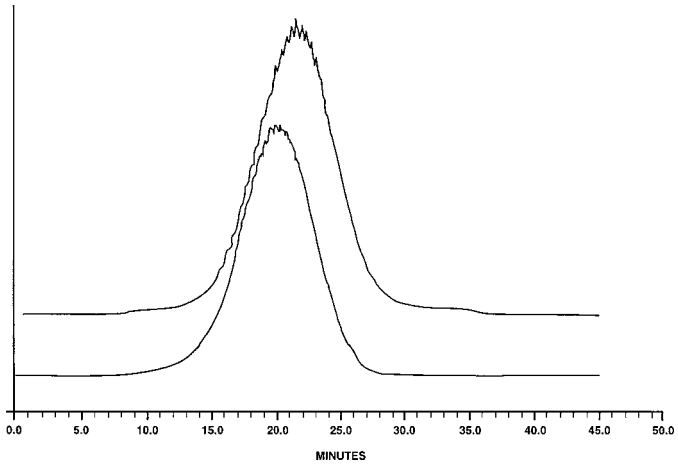

FIG. X1.6 High Temperature Simulate Distillation Chromatogram of a Heavy Distillate Fraction (HTSD-95-6) Obtained on a (50 % Phenyl) Methylpolysiloxane and 100 % Dimethylpolysiloxane

TABLE X1.4 Comparison of High Temperature Simulated Distillation Results (Grand Average) Obtained for the Refined Base Oil (HTSD-95–1) on Three Column Liquid Phases

	Temperatures, °C, on		
Mass % Recovered	100 % Dimethylpolysiloxane	Polycarboranesiloxane	(50 % Phenyl)-Methylpolysiloxane
0.5	420.5	421.5	424.5
2	451.5	453.0	457.0
5	473.0	473.5	477.5
10	491.0	491.5	495.5
20	510.5	511.0	514.5
30	526.0	525.5	529.0
40	538.0	536.5	540.0
50	545.5	546.5	550.5
60	555.0	556.5	560.0
70	565.0	566.5	570.0
80	575.0	577.0	580.5
90	588.5	591.0	594.5
95	599.5	602.5	606.5
98	611.5	615.5	619.5
99.5	626.5	632.5	636.5

TABLE X1.5 Comparison of High Temperature Simulated Distillation Results (Grand Average) Obtained for the Heavy Distillate Fraction (HTSD-95–6) on Three Column Stationary Phases

	Temperatures, °C, on		
Mass % Recovered	100 % Dimethylpolysiloxane	Polycarboranesiloxane	(50 % Phenyl)-Methylpolysiloxane
0.5	394.0	402.0	399.0
2.	435.0	445.0	448.5
5.	462.5	471.5	477.5
10	482.5	491.0	498.0
20	504.0	511.5	519.0
30	518.0	526.0	533.5
40	529.5	537.0	544.5
50	539.5	547.0	555.0
60	549.0	557.0	565.0
70	559.0	566.5	574.5
80	570.0	577.5	585.5
90	584.5	592.5	601.5
95	595.5	605.5	615.0
98	608.5	620.5	631.5
99.5	625.5	642.5	652.0

results suggest that for low aromatic streams, no significant difference in results would be expected when using any of these columns' liquid phases.

X1.5 In contrast, the simulated distillation chromatograms of the more aromatic distillate (HTSD-95-6) from the same crude sources are presented for the same two columns in Fig. X1.6 and for the three column phases employed in the round robin, the grand average simulated distillation data for HTSD-95-6 are presented in Table X1.5. These data indicate a greater difference in reported temperatures versus yield with the (50 % Phenyl) methylpolysiloxane stationary phase providing the higher boiling points. These results are consistent with differences in column liquid phases presented in X1.1 and suggest that more aromatic or heteroaromatic distillates would be expected to produce significantly different boiling point-yield data when using different column liquid phases.

X1.6 The study group has been trying to obtain samples for which good true boiling point data as generated from Test Method D2892 are available to help decide which stationary phase gives the best agreement with physical distillation. The study group also felt that consistency of this test method with Test Method D2887, which uses dimethylpolysiloxane stationary phase, was also an issue. In the absence of good physical distillation data and simulated distillation data for the same samples obtained by this test method, the test method employing dimethylpolysiloxane stationary phase was selected for use in this test method. This test method, therefore, does not claim agreement between physical distillation and simulated distillation. Efforts to resolve this question will continue. When successful resolutions of the questions are determined, this test method will be revised accordingly.

X2. CALCULATION ALGORITHM

INTRODUCTION

Test Method D6352 contains instructions on performing the calculations. This appendix is provided in order to give detailed programming information as well as to unify the algorithms used here and in Test Method D2887.

X2.1 Required Starting Elements

X2.1.1 *Sample Data Array, N Area Slices*—The data must be collected at a minimum sampling frequency of 5 to 10 Hz (that is, slice width is 0.2 to 0.1 s). In addition, the slice width must be such that no sample or solvent elutes in the first 10 to 20 slices, respectively.

X2.1.2 *Blank Data Array, N Area Slices*—The slice width for the blank and sample runs must be identical. (A blank data array may not be necessary if electronic baseline compensation is used. See X2.2.1.)

X2.1.2.1 The analysis conditions for blank and sample must be identical through the point where sample analysis is terminated.

X2.1.2.2 The number of slices in the blank array must be equal to or greater than the number of slices in the sample chromatogram. If the number of slices in the blank array is greater than the number of slices in the sample array, then drop the extra slices in the blank array. This situation could occur if a blank run extended beyond the point where the sample analysis was terminated.

X2.1.3 *Retention Times, n-Paraffins*—The retention time of each n-paraffin in the calibration mixture must be obtained from a processed (peak) data file from the analysis of the calibration mixture, run under identical conditions as the samples and blank.

X2.1.4 *Boiling Points of n-Paraffins*—The boiling point of each n-paraffin in the calibration mixture (to the nearest whole degree Celsius or Fahrenheit) can be obtained from Table 1 of this test method.

X2.1.5 *Solvent Exclusion Time*—The solvent exclusion time is that time when the signal has returned to baseline after elution of the solvent. This parameter is used to exclude area due to the solvent used, if any. If a solvent is used, the detector signal must return to baseline before any sample components start to elute.

X2.2 Subtract Blank from Sample (see Note X2.1)

X2.2.1 Subtract each blank area slice from the exactly corresponding sample area slice. This corrects the sample area slice from the blank. (**Warning—**Automatic baseline compensation is available on many instruments and is allowed by this test method. However, automatic baseline compensation may not give the same results as slice-by-slice blank subtraction. On some instruments using automatic baseline compensation, the compensated baseline has been observed to exhibit an anomalous feature at or near the point in the chromatogram where the programmed oven temperature reaches maximum and is held for some period of time. The anomalous feature appears as a slow rise in baseline, followed by a relatively sharp decrease, followed by a level baseline. While the magnitudes of the anomalies observed have been very small (only a few picoamps), the slope of the sharp decrease may be sufficient to meet the criterion for determining the end of sample elution. In such an event, this false triggering of the end of sample criterion will result in erroneously high values for the FBP. If false triggering occurs and cannot be eliminated, the user should disable automatic baseline compensation and perform blank subtractions as described in this appendix.)

NOTE X2.1—If the data was acquired on an instrument using automatic baseline compensation, skip X2.2. In this case, the zeroed sample data array contains the corrected area slices to be used in subsequent calculations.

X2.3 Zero the Data Slices

X2.3.1 Calculate the average of the first 10 to 20 (5 to 10 Hz) area slices of the blank-subtracted data array.

X2.3.2 Subtract the average slice area (X2.3.1) from each area slice in the blank-subtracted data array. Set negative numbers to zero.

X2.4 Calculate Total Chromatogram Area

X2.4.1 Starting at the first slice (or the solvent exclusion time if a solvent is used), sum all of the area slices through the last slice.

X2.4.2 Designate this sum as the total chromatogram area.

X2.5 Determine Start of Sample Elution Time

X2.5.1 Starting at the slice corresponding to the solvent exclusion time (or the first slice if no solvent was used) and working towards the end of the data array, determine where the rate of change per second between two consecutive slices first exceeds 0.00001 % of the total chromatogram area (see X2.4.2).

X2.5.1.1 For determining the start of sample elution, the rate of change is calculated by subtracting the area of a slice from the area of the immediately following slice and dividing by the slice width in seconds.

X2.5.1.2 If $(\langle slice \rangle_{N+1} - \langle slice \rangle_N)/(\text{slice width}) > 1E\text{-}7 \times$ total chromatogram area, then take slice N + 1 as the start of sample slice (see X2.2).

X2.5.2 Print the retention time corresponding to the start of sample elution.

X2.6 Determine the End of Sample Elution Time

X2.6.1 Starting at the last slice in the data array and working toward the start of sample, determine where the rate of change per second between two consecutive slices first exceeds 0.00001 % of the total chromatogram area (see X2.4.2).

X2.6.1.1 For determining the end of sample elution, the rate of change is calculated by subtracting the area of a slice from the area of the immediately preceding slice and dividing by the slice width in seconds.

X2.6.1.2 If (<slice>$_{N-1}$ – <slice>$_N$)/(slice width) > 1E-7 × total chromatogram area, then take slice N – 1 as the end of sample slice (see X2.2).

X2.6.2 Print the retention time corresponding to the end of sample elution.

NOTE X2.2—The determination of the start and end of sample elution as determined by the slope of the consecutive slices may differ according to sample properties. Thus, the sensitivity level may require adjustment.

X2.7 Calculate Total Corrected Sample Area

X2.7.1 Sum the corrected area slices from the start of sample slice (see X2.5.1.2) to the end of sample slice (see X2.6.1.2).

X2.7.2 Designate this sum as the total corrected sample area, and save it for subsequent calculations.

X2.8 Normalize to Area Percent

X2.8.1 Beginning at the start of sample slice (see X2.5.1.2) and continuing to the end of sample slice (see X2.6.1.2), divide each corrected area slice by the total corrected sample area (see X2.7.2) and multiply by 100.

X2.8.2 Save these normalized area percents in an array for subsequent calculations.

X2.9 Find Retention Time Corresponding to Percent Off

X2.9.1 For each X (where $X = 0.5, 1, 2, ..., 98, 99.5$), find the retention time corresponding to X percent off.

X2.9.1.1 Beginning with the start of sample slice and working toward the end of sample slice, determine the slice (designated $N + 1$ in the equations) at which the cumulative area percent first equals or exceeds X.

NOTE X2.3—The cumulative area percent of a given slice is the sum of the normalized area percents from the start of sample slice through the given slice.

X2.9.1.2 For the slice ($N + 1$) determined above, the following inequality should hold;

$$CA_N \leq X \leq CA_{N+1} \quad \text{(X2.1)}$$

CA_N = the cumulative area percent from start of sample slice through slice N, and
CA_{N+1} = the cumulative area percent through slice $N + 1$.

X2.9.1.3 Calculate the fraction (f) of normalized area percent in slice ($N + 1$) needed to give exactly X percent off as follows:

$$f = (X - CA_N)/A_{N+1} \quad \text{(X2.2)}$$

A_{N+1} = the normalized area percent (not cumulative) of slice $N + 1$.

X2.9.1.4 The retention time corresponding to X percent off (RT_X) is the retention time of the fractional slice ($N + f$) and is calculated as follows:

$$RT_X = (N + f) \times \text{slice width} \quad \text{(X2.3)}$$

X2.10 Convert Retention Times to Boiling Points

X2.10.1 For each retention time found in X2.9.1, calculate the boiling point equivalent to that retention time.

X2.10.1.1 Find the pair of calibration compound retention times that are closest to and bracket the percent off retention time of interest.

X2.10.1.2 Calculate the boiling point corresponding to the percent off retention time as follows:

$$BP_i = (((BP_2 - BP_1)/(RT_2 - RT_1)) \times (RT_i - RT_1)) + BP_1 \quad \text{(X2.4)}$$

BP_i = boiling point for i percent off,
RT_i = retention time for i percent off,
RT_1 = retention time of calibration compound immediately preceding RT_i,
RT_2 = retention time of calibration compound immediately following RT_i,
BP_1 = boiling point of compound at RT_1, and
BP_2 = boiling point of compound at RT_2.

NOTE X2.4—A report giving percent off at selected boiling point intervals can be calculated in an analogous manner.

X2.11 Reporting Results

X2.11.1 Report the IBP, the temperatures corresponding to 1 to 99 % off, and the FBP to the nearest whole degree Fahrenheit or nearest half a degree Celsius.