Designation: D7500 – 08

Standard Test Method for Determination of Boiling Range Distribution of Distillates and Lubricating Base Oils—in Boiling Range from 100 to 735°C by Gas Chromatography[1]

This standard is issued under the fixed designation D7500; 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 products by capillary gas chromatography using flame ionization detection. This standard test method has been developed through the harmonization of two test methods, Test Method D6352 and IP 480. As both of these methods cover the same scope and include very similar operating conditions, it was agreed that a single standard method would benefit the global simulated distillation community.

1.2 This test method is not applicable for the analysis of petroleum or petroleum products containing low molecular weight components (for example naphthas, reformates, gasolines, diesel). Components containing hetero atoms (for example alcohols, ethers, acids, or esters) or residue are not to be analyzed by this test method. See Test Methods D7096, D2887, or D7213 for possible applicability to analysis of these types of materials. This method is also not suitable for samples that will not elute completely from the gas chromatographic column, leaving residues. For such samples as crude oils and residues, see Test Methods D5307 and D7169.

1.3 This test method is applicable to distillates with initial boiling points above 100ºC and final boiling points below 735ºC (carbon 110); for example, distillates (IBP > 100°C), base oils and lubricating base stocks.

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

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

D1160 Test Method for Distillation of Petroleum Products at Reduced Pressure

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

D5307 Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography

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

D7096 Test Method for Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography

D7169 Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography

D7213 Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100 to 615°C by Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

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

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

2.2 *ISO Standard:*

[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.

ISO 3170 Petroleum Liquids Manual Sampling[3]

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*, *n*—the area resulting from the integration of the chromatographic detector signal within a specified retention time interval. In area slice mode (see 6.4.1), 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*, *n*—an area slice corrected for baseline offset by subtraction of the exactly corresponding area slice in a previously recorded blank (non-sample) analysis.

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

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

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

3.2.6 *slice rate*, *n*—the frequency used in sampling (analog) the chromatographic detector signal during an analysis. The slice rate is expressed in Hz (for example integrations or slices per second).

3.2.7 *slice time*, *n*—the inverse function of the acquisition rate. It is the time duration of each sampling pulse usually expressed in seconds. The slice time is the time at the end of each contiguous area slice.

3.2.8 *total sample area*, *n*—the cumulative corrected area, from the initial 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 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 distillates (IBP > 100°C) 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. This test method does not claim agreement between these physical distillations 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.

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 to ±1 % 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 430°C.

6.1.3 *Column Temperature Programmer*—The chromatograph shall be capable of linear programmed temperature operation up to 430°C at selectable linear rates up to 10°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.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

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. Check the detector according the instrument manufacturers instructions.

6.1.4.1 *Operating Temperature*—100 to 430°C.

6.1.4.2 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 Annex A3 and execute the conditions of Table 2. Programmable temperature vaporization (PTV) and cool on-column (COC) injection systems have been used successfully.

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

6.2.1 Automatic syringe injection is recommended to achieve best precision.

6.3 *Column*—This test method is limited to the use of non-polar wall coated open tubular (WCOT) columns of high thermal stability. Fused silica (aluminum coated) 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 0.09 to 0.17 µm have been used. The column length and liquid phase film thickness shall allow the elution of C_{110} *n*-paraffin (BP = 735°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 A3.2.1. The column shall provide a resolution not less than 2 and not higher than 4 using the test method operating conditions in Table 2.

6.4 *Data Acquisition System*:

TABLE 1 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 as reported in Test Method D6352.

TABLE 2 Typical Operating Conditions for Gas Chromatograph

Column length, m	5
Column internal diameter, mm	0.53
Column material	Metal
Stationary phase type	methyl silicone
Film thickness, µm	0.09 to 0.17
Initial column temperature, °C	35
Initial hold time, min	0
Final column temperature, °C	430
Final hold time, min	10
Program rate, °C/min	10
Injector initial temperature, °C	100
Injector final temperature, °C	430
Injector program rate, °C/min	15
Detector temperature, °C	450
Make-up gas flow, He or N2, mL/min[A]	20
Hydrogen Flow, mL/min[A]	45
Air Flow, mL/min[A]	450
Carrier gas	He
Carrier gas flow rate, constant flow, mL/min	19
Sample size, µL[A,B]	1.0
Sample concentration, % (m/m)	2
Injector	PTV or COC

[A] Consult with the manufacturer's operations manual.
[B] Monitor skewness when varying the injection volume.

6.4.1 *Integrator/Computer System*—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 processing mode). In addition, the system shall be capable of converting the continuously integrated detector signal into area slices of fixed duration (slice mode). These contiguous area slices, collected for the entire analysis, are stored for later processing. A similar collection of contiguous slices is also collected for the blank run. It is necessary that the number of slices collected for sample and blank analysis are the same. The electronic range of the integrator/computer (for example 1 V, 10 V) shall be operated within the linear range of the detector/electrometer system used.

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

7. Reagents and Materials

7.1 *Liquid Stationary Phase*—A methyl silicone stationary phase for the column.

7.2 *Carrier Gases*—Helium, of at least 99.999 % (v/v) purity. Any oxygen present is removed by a chemical resin filter. (**Warning—**Follow the safety instructions from the filter supplier.) Total impurities not to exceed 10 mL/m^3. Helium or Nitrogen (99.999 %) can also be used as detector makeup gas.

7.3 *Hydrogen*—99.999 % Grade suitable for flame ionization detectors. Total impurities not to exceed 10 mL/m^3.

7.4 *Compressed Air*—Regulated for flame ionization detectors. Total impurities not to exceed 10 mL/m^3.

7.5 *Alkanes*—Normal alkanes of at least 98 % (m/m) purity from C_5 to C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{24}, C_{26}, and C_{28}, are

to be used with Polywax 655 or 1000.[4] A solution of these alkanes is prepared by adding 500 mg of each alkane into a 20 mL vial. Additionally *n*-tetracontane (C_{40}) can also be added to for ease of carbon counting. This solution is used to spike the Polywax[4] solution.

7.6 *Polywax 655 or 1000.*[4]

7.7 *Carbon Disulfide*—Purity 99.7 % (v/v) minimum. (**Warning—**Extremely flammable and toxic by inhalation.)

7.8 *Calibration Mix*—A suitable calibration mixture can be obtained by dissolving a hydrogenated polyethylene wax (for example, Polywax 655[4] or Polywax 1000[4]) in a volatile solvent (for example, CS_2 or cyclohexane). Solutions of 1 part Polywax[4] to 200 parts solvent can be prepared. Lower boiling point paraffins will have to be added to as specified in 7.5. Fig. 5 illustrates a typical calibration mixture chromatogram. The calibration mix is used to determine the column resolution, skewness of components, and retention time versus boiling point calibration curve. Add 10 µL of the mixture of alkanes prepared in 7.5.

NOTE 2—Commercially available alkane standards are suitable for column performance checks.

NOTE 3—Calibration mixtures are commercially available.

7.9 *Reference Oil 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 Table 1.

NOTE 4—The 5010 reference oil is available commercially.

7.10 *Cyclohexane (C_6H_{12})*—(99+ % pure) if necessary, use in place of CS_2 for the preparation of the calibration mixture.

7.11 A Gravimetric blend consisting of 2 distillation fractions is used for system performance check (see A3.3).

8. Sampling and Sample Preparation

8.1 Unless otherwise specified, obtain the laboratory samples by the procedures specified in ISO 3170 and place in glass or metal containers. Do not use plastic containers for sample storage to avoid contamination of the sample because of possible leaching of the plasticizer.

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

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

8.4 Dilute the sample aliquot to approximately 1–3 weight % with the solvent, depending on the boiling point distribution.

8.5 Seal (cap) the vial, and mix the contents thoroughly to provide a homogeneous mixture. Warm the vial if necessary initially to affect complete solution of the sample. Inspect the sample to ensure it is in stable solution at room temperature prior to injection. If necessary, prepare a more dilute solution.

9. Preparation of Apparatus

9.1 *Gas Chromatograph Setup*—Set up and operate the gas chromatograph in accordance with the manufacturer's instructions.

NOTE 5—Typical operating conditions are shown in Table 2.

[4] Polywax is a registered trademark of Baker Petrolite, 12645 West Airport Blvd., Sugar Land, TX 77478.

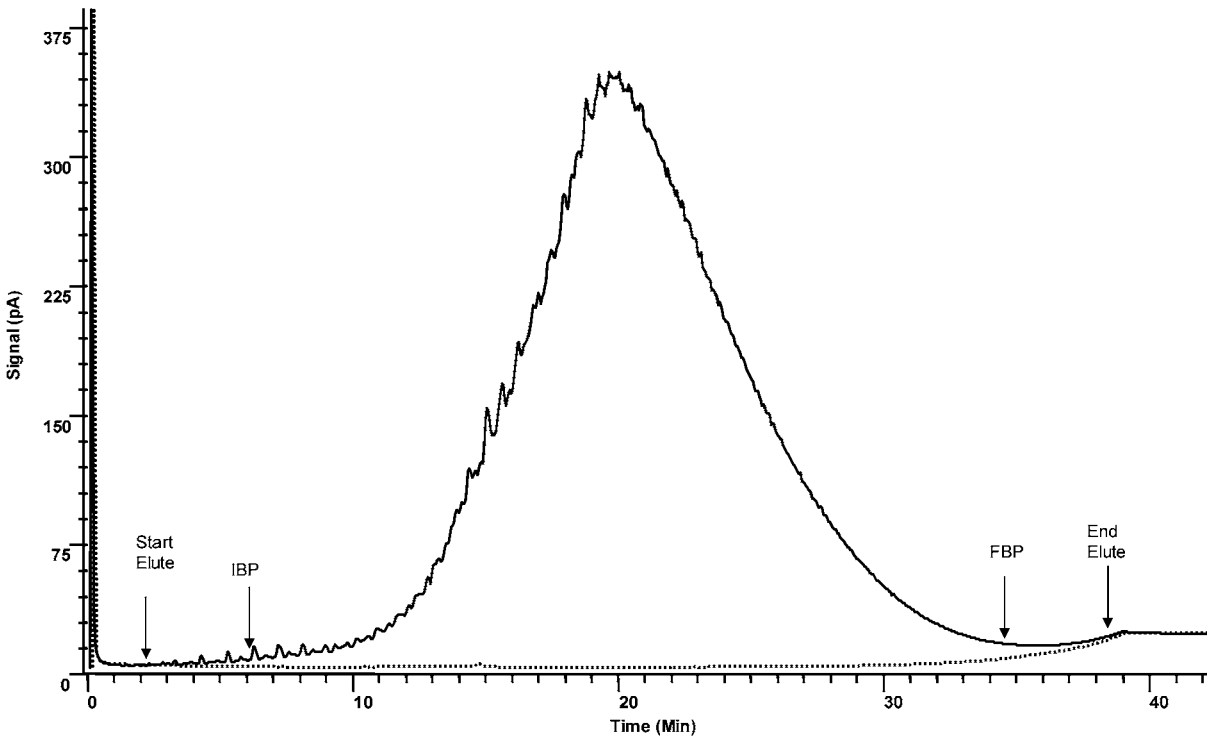


FIG. 1 Typical Sample Chromatogram which has a FBP of 700ºC

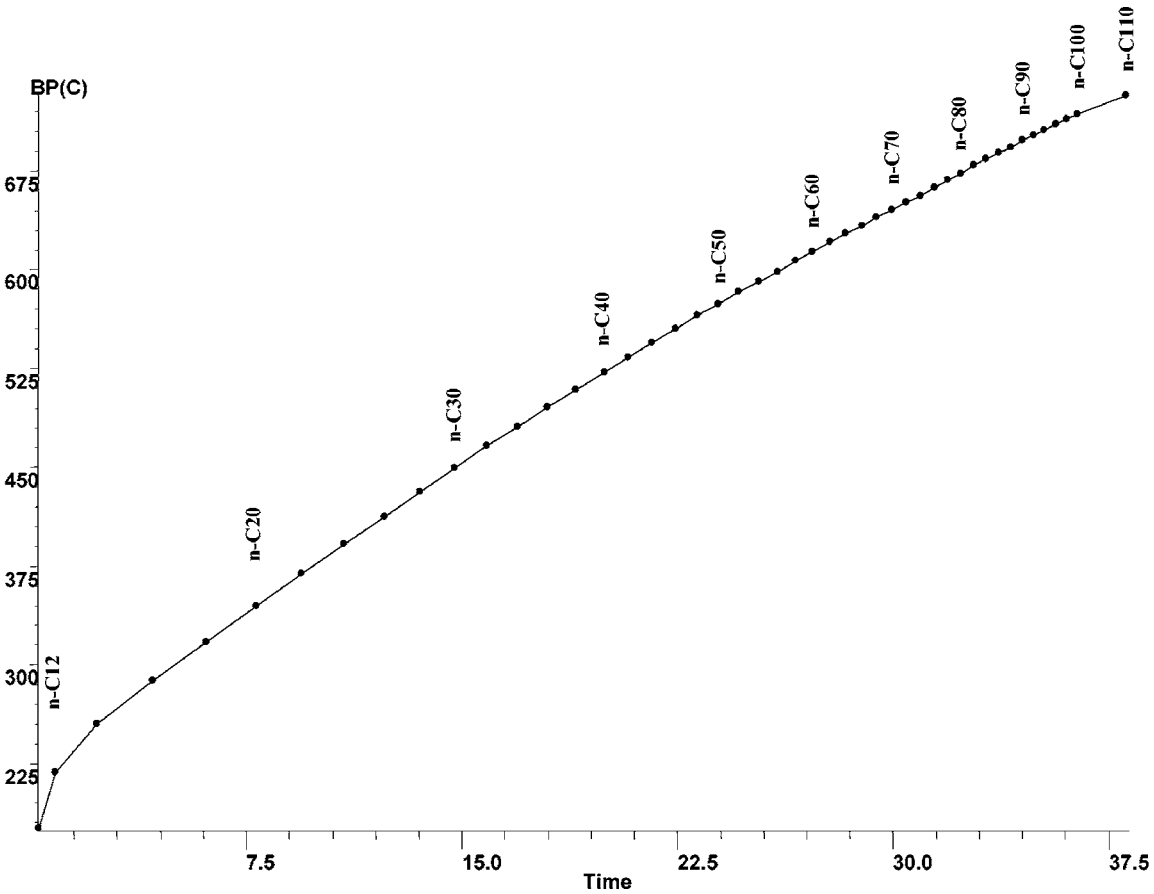


FIG. 2 Typical Calibration Curve of Retention Time versus Boiling Point

9.2 A new column will require conditioning at the upper test method operating temperature to reduce or eliminate significant liquid phase bleed so that a stable and repeatable chromatographic baseline can be generated. Disconnecting the column will require conditioning prior to calibration and analysis.

9.3 The inlet liner (PTV) and or the initial section of the column (COC and PTV) shall be periodically inspected and replaced in order to remove extraneous deposit or sample residue.

9.4 Perform a blank analysis after a new septum is installed to ensure that no extraneous peaks are produced by the septum. The blank analysis shall be carried out whenever the column is disconnected from carrier flow.

9.5 Ensure that the system's return to baseline is achieved near the end of the run and that the baseline shows no drift at the final isothermal oven temperature.

9.6 Inspect and clean the jet periodically to avoid deposits that form on the jet from combustion of decomposition products from the column liquid stationary phase. These deposits will affect the characteristics of the detector response.

NOTE 6—The following parameters are affected by deposits on the jet: increase in inlet pressure, FID difficulty in lighting, increase in the CS_2 response, and off-specification reference oil. To clean the jet, place it in an ultrasonic cleaner with a suitable solvent and use a cleaning wire if necessary to remove column deposits.

9.7 Check the system performance requirements at installation and at the intervals given and by the procedures specified in Annex A3 with regards to frequency of calibration, check column resolution, peak skewness and verify the detector response with the gravimetric blend.

10. Calibration

10.1 The first run of the day shall be a clean up run and not a usable blank because of the possible elution of extraneous components that have concentrated in the inlet while the instrument is idle. However, a retention time calibration mix (7.8) can be used as first injection.

10.2 Run the calibration mixture (7.8) and confirm the elution of C_{110} within the oven temperature program.

NOTE 7—When C_{110} does not elute within the temperature program, it is recommended to shorten the column. See manufacturer's instructions.

10.3 Ensure the injection volume (or sample concentration) chosen does not allow any peak to exceed the linear range of the detector or overload the column. The skewness of all peaks shall be maintained between 0.8–1.8. Values greater than 1.8 indicate the sample is too concentrated and a skew less than 0.8 indicate severe tailing due to an old column or dirty liner or a poorly focused sample. As a guide, 0.2 to 1.0 µL of the calibration mixture (7.8) has been found to be suitable for columns with a film thickness ranging from 0.09 to 0.17 µm or less. (See A3.4.)

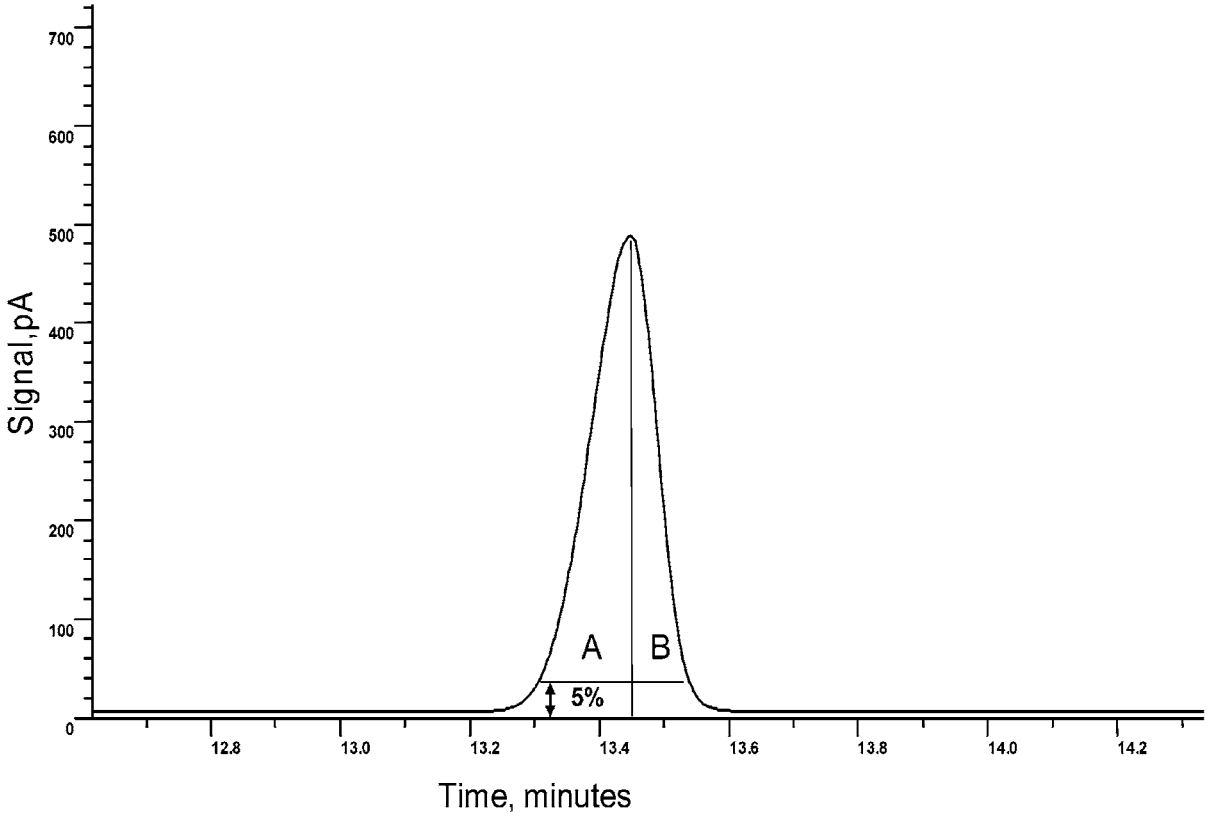


FIG. 3 Peak Skewness for Calibration Mix Peak C_{20}

10.4 Record the retention time of each component and plot the retention time versus the atmospheric boiling point for each component using the boiling points from Table 4. Typical results of the calibration are shown in Table 5 and Fig. 2.

10.5 Inject the Reference Oil 5010 (7.9) using the specified procedure (Section 11). Visually inspect the chromatogram. Using the data system, load the chromatogram (Fig. 6) of the reference oil 5010 and overlay the blank baseline. Enlarge the section of the chromatogram at the end of sample elution and compare the relative magnitudes of the sample and blank baseline with the examples shown in Fig. 7. Ensure that the end of the run merges with the sample chromatogram as shown in Fig. 7. Calculate the boiling range distribution of the reference material by the procedures specified in Annex A1 and compare this with the consensus values for the reference material used as listed in Table 1.

NOTE 8—Fig. 6 shows a typical chromatogram of the 5010 reference oil. Table 6 shows typical boiling point values obtained for the reference oil.

10.6 If the consensus values as shown in Table 1 are not met, check that all hardware is operating properly and all instrument settings are as recommended by the manufacturer. Rerun the retention boiling point calibration as described in 10.3.

11. Sample Analyses Procedure

11.1 Run a solvent (blank) baseline analysis before the first sample analysis and then after every five samples.

11.2 Inspect the baseline at the end of the run for each solvent (blank) injected to ensure that it is constant and stable and is void of extraneous peaks.

NOTE 9—The identification of a constant baseline at the end of the run is critical to the analysis. Constant attention should be given to all factors that influence baseline stability, for example, column substrate bleed, septum bleed, and detector temperature control, constancy of carrier gas flow, leaks, and instrument drift.

11.3 Prepare a Sequence analysis listing all samples and blank to be injected as described in 11.1.

NOTE 10—A sequence is a series of analysis. The length of the sequence depends on the system stability.

11.4 Cool the column and inlet to the starting temperature and inject the selected sample volume.

11.5 Immediately start programming the column temperature and the temperature of the PTV or COC inlet.

11.6 Visually inspect the chromatogram. Using the data system, load each sample chromatogram overlay the nearest blank baseline obtained after the sample as listed in the Sequence. Enlarge the section of the chromatogram at the end of sample elution and compare the relative magnitudes of the sample and blank baseline with the examples shown in Fig. 7. Insure that the end of the run merges with the sample chromatogram as shown in Fig. 7. If the sample baseline has an abrupt break and does not join the blank baseline, it is possible that the sample has not eluted completely from thee column and the sample is considered outside of the scope of this method.

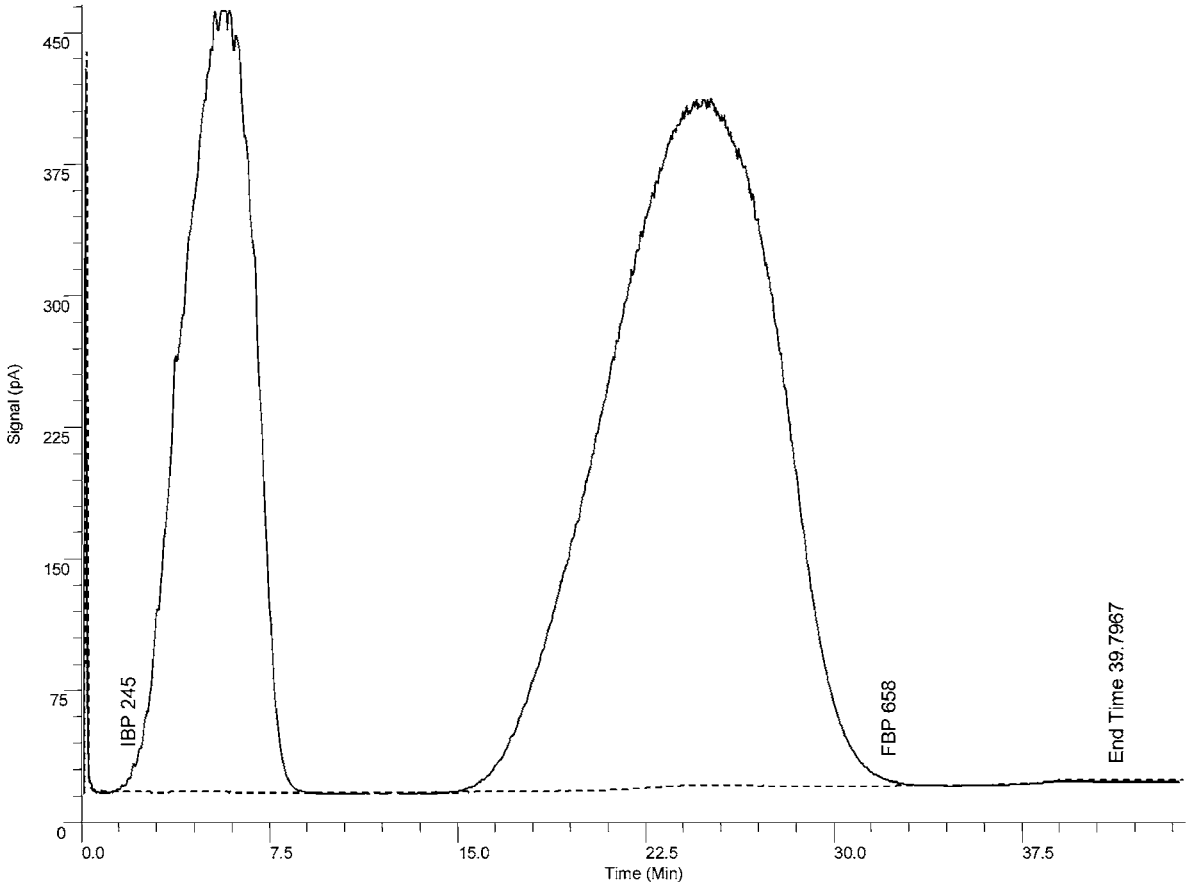


FIG. 4 Typical Chromatogram of Gravimetric Blend

11.6.1 Identify the start of the area of interest by selecting a point on the baseline where the blank and the sample baselines are merged. This is taken before the start of the sample and after the end of the solvent (Fig. 8).

11.6.2 Identify the end of the area of interest by selecting a point on the baseline where the blank and the sample baselines are merged. This is taken after the end of the sample and at or before the end of run (Fig. 8).

11.6.3 The start of the sample is determined by the software as given in A1.5.

11.6.4 The end of the sample is determined by the software as given in A1.6.

12. Calculation

12.1 The following calculations are performed in this sequence. For detailed information see Annex A1.

12.1.1 Subtract blank from sample.

12.1.2 Zero the data slices.

12.1.3 Calculate total chromatogram area.

12.1.4 Determine start of sample elution time.

12.1.5 Determine the end of sample elution time.

12.1.6 Calculated total corrected sample area.

12.1.7 Normalize to area percent.

12.1.8 Find retention time corresponding to percent off.

12.1.9 Convert retention time to boiling points.

12.1.10 Report the results.

13. Report

13.1 Report the tabulated results as follows:

13.1.1 Report all temperatures to the nearest 1ºC (1°F),

13.1.2 Report all percentages to the nearest 1 % (m/m),

13.1.3 Report the 0.5 % (m/m) point as the initial boiling point and the 99.5 % (m/m) point as the final boiling point, and

13.1.4 Report intermediate percentages as required at intervals of not less than 1 % (m/m).

13.2 The test report shall contain at least the following information:

13.2.1 A reference to this test method,

13.2.2 The type and complete identification of the material tested,

13.2.3 The result of the test (see Section 12),

13.2.4 Any deviation, by agreement or otherwise, from the standard procedures specified, and

13.2.5 The date of the test.

14. Precision and Bias

14.1 *Precision*:

14.1.1 *Repeatability*—The repeatability standard deviation was determined from 4 laboratories each analyzing the 5010 Reference oil in duplicate. The values are shown in Table 3.

14.1.2 *Reproducibility*—The reproducibility of this test method is being determined and will be available on or before September 2013.

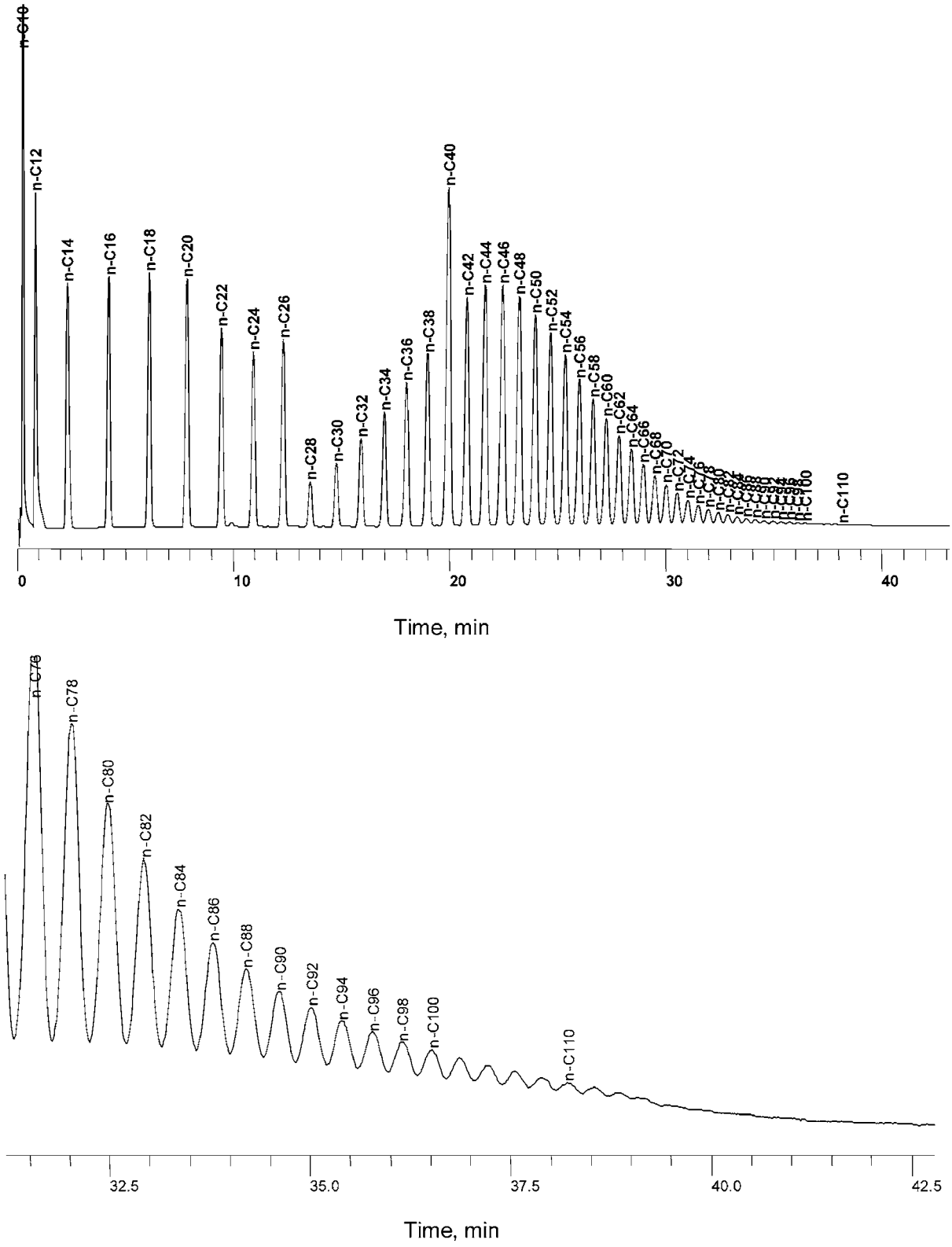


FIG. 5 Typical Chromatogram of Calibration Mix

TABLE 3 Repeatability Standard Deviation Determined for the 5010 Reference Oil[A]

m/m %	°C	Repeat Std Dev °C
IBP	426.5	1.1
5	475.8	0.2
10	491	0.3
15	500.6	0.2
20	508.2	0.2
25	515.4	0.2
30	522.2	0.2
35	528.4	0.2
40	534.5	0.2
45	540.2	0.2
50	545.9	0.2
55	551.9	0.2
60	557.9	0.2
65	563.9	0.1
70	569.8	0.2
75	575.9	0.2
80	583	0.1
85	590.8	0.1
90	600	0.2
95	614.2	0.3
FBP	654.4	2.7

[A] Repeatability standard deviation was determined from 4 laboratories each analyzing the 5010 Reference oil in duplicate.

14.2 *Bias*—Because the boiling point distribution can be defined only in terms of a test method, no bias for the procedures in this test method as determined by gas chromatography has been determined.

15. Keywords

15.1 boiling range distribution; capillary gas chromatography; distillates; flame ionization detection; lubricating base oils; petroleum products; simulated distillation

TABLE 4 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 4 *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
110[C]	735	1355

[A] API Project 44, October 31, 1972 is believed to have provided the original normal paraffin boiling point data that are listed in this table. 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. The values listed here as well as in Test Method D6352 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 this table 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.

[C] The boiling point of carbon 110 has been obtained by graphical extrapolation of the retention time versus boiling point curve shown in Fig. 3.

TABLE 5 Retention Time Data Corresponding to Fig. 5

Component	Time	BP (°C)	Skewness
n-C10	0.227	174.1	1.077
n-C12	0.811	216.3	0.703
n-C14	2.301	253.9	0.788
n-C16	4.218	287.2	1.474
n-C18	6.098	316.1	1.471
n-C20	7.842	343.9	1.473
n-C22	9.437	368.3	1.353
n-C24	10.919	391.1	1.347
n-C26	12.306	412.2	1.447
n-C28	13.553	431.1	1.116
n-C30	14.763	449.7	1.134
n-C32	15.906	466.1	1.152
n-C34	16.991	481.1	1.248
n-C36	18.019	496.1	1.322
n-C38	19.003	508.9	1.472
n-C40	19.987	522.2	1.672
n-C42	20.833	533.9	1.748
n-C44	21.675	545	1.683
n-C46	22.489	556.1	1.819
n-C48	23.257	566.1	1.71
n-C50	23.997	575	1.692
n-C52	24.706	583.9	1.623
n-C54	25.383	592.2	1.481
n-C56	26.043	600	1.506
n-C58	26.668	607.8	1.324
n-C60	27.274	615	1.235
n-C62	27.872	622.2	1.322
n-C64	28.441	628.9	1.251
n-C66	28.993	635	1.195
n-C68	29.527	641.1	1.133
n-C70	30.058	647.2	1.213
n-C72	30.558	652.8	1.107
n-C74	31.054	657.8	1.097
n-C76	31.538	663.9	1.115
n-C78	32.009	670	1.089
n-C80	32.456	675	0.942
n-C82	32.91	681.1	0.995
n-C84	33.343	686.1	0.922
n-C86	33.775	691.1	1.005
n-C88	34.188	695	0.909
n-C90	34.606	700	1.005
n-C92	35.003	703.9	1.011
n-C94	35.377	707.8	0.775
n-C96	35.767	712.2	0.945
n-C98	36.142	716.1	0.972
n-C100	36.507	720	0.983
n-C110	38.202	735	0.774

TABLE 6 Typical Values Obtained for Reference Oil 5010

% Off	BP (°C)	QC (°C)	(–) Diff	Limit
IBP	429.2	427.2	1.9	8.9
5	477.4	477.2	0.2	2.8
10	492.8	492.2	0.6	2.8
15	502.4	502.2	0.1	2.8
20	510.1	510	0.1	3.3
25	517.3	517.2	0.1	3.3
30	524.1	523.9	0.2	3.9
35	530.5	530.6	0	3.9
40	536.6	536.7	-0.1	4.4
45	542.4	542.2	0.2	4.4
50	548.2	548.3	-0.1	4.4
55	554.2	554.4	-0.2	4.4
60	560.1	560	0.1	4.4
65	566.1	566.1	0	4.4
70	571.8	572.2	-0.4	4.4
75	578	578.3	-0.3	5
80	585	585.6	-0.6	4.4
85	592.7	592.8	-0.1	3.9
90	602	602.2	-0.2	4.4
95	615.8	615.6	0.3	3.9
FBP	656.7	656.1	0.6	17.8

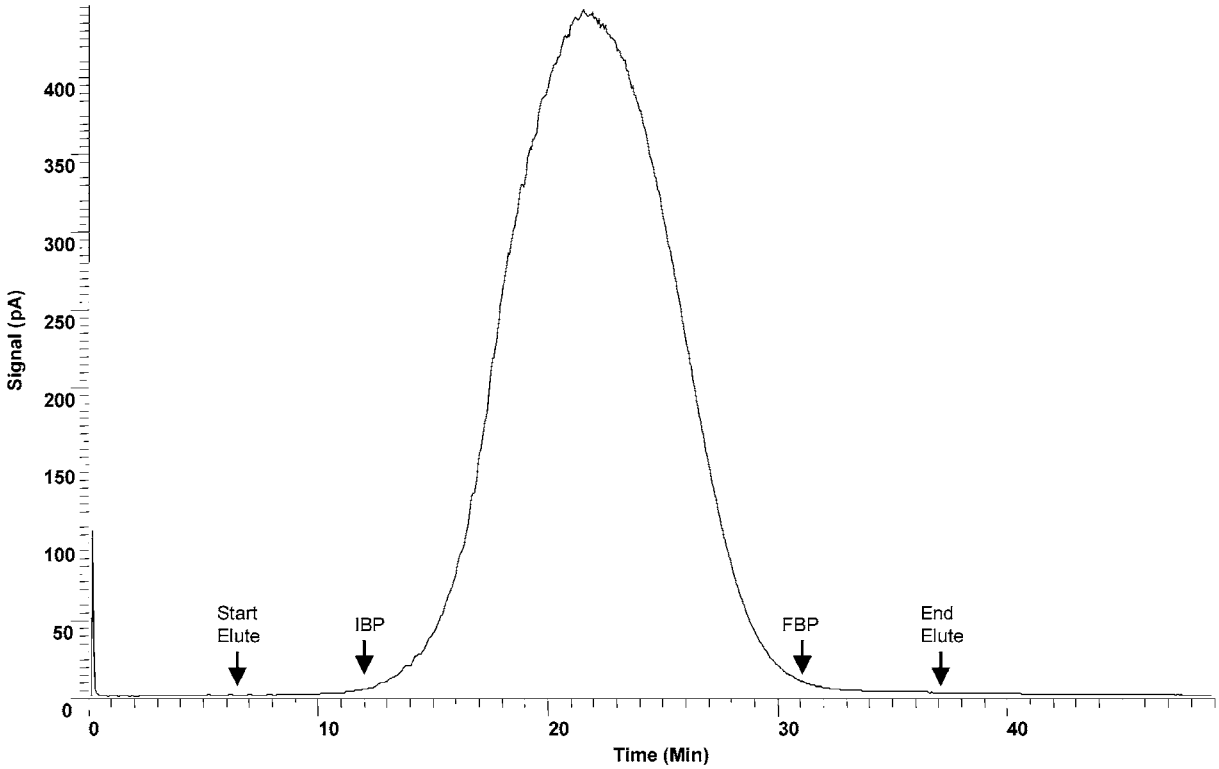
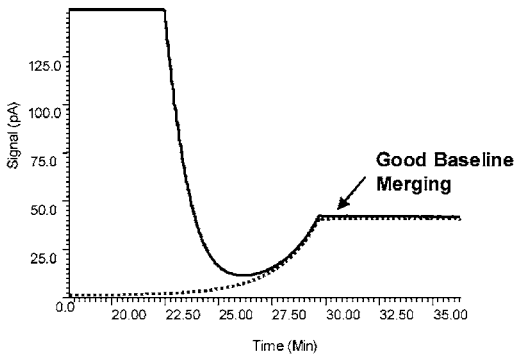
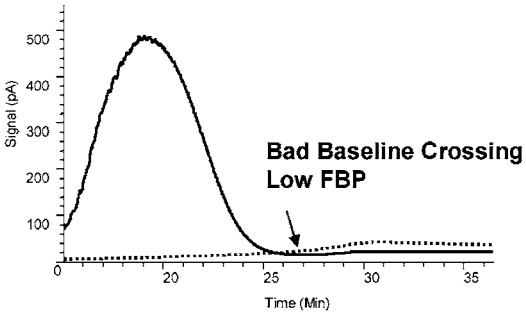


FIG. 6 Typical Chromatogram of Reference Oil 5010





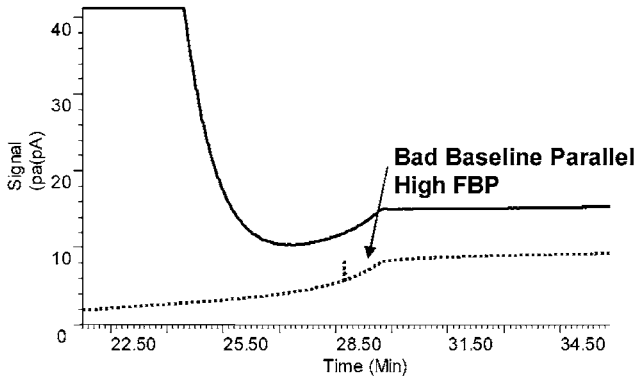


FIG. 7 Correct and Incorrect Positioning of Baseline Signal with Respect to Sample Signal

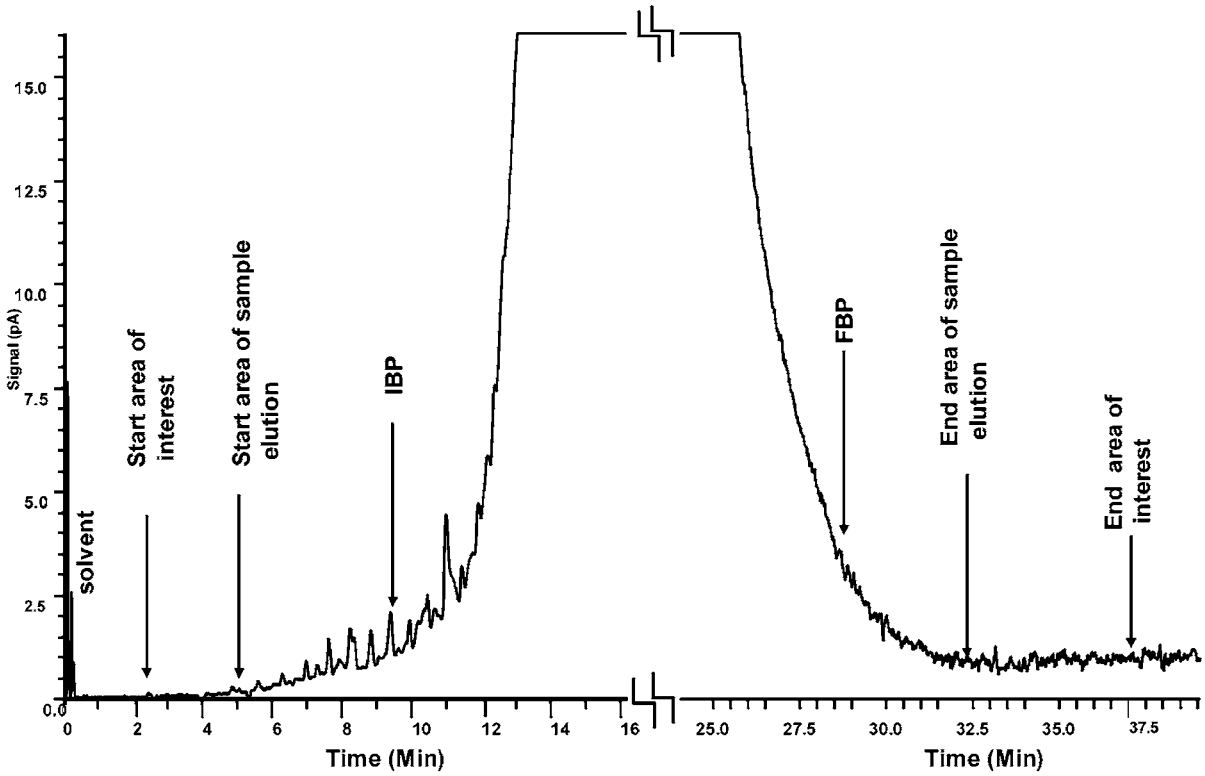


FIG. 8 Regions of the Enlarged Chromatogram to be Considered in the Developing of the Algorithm

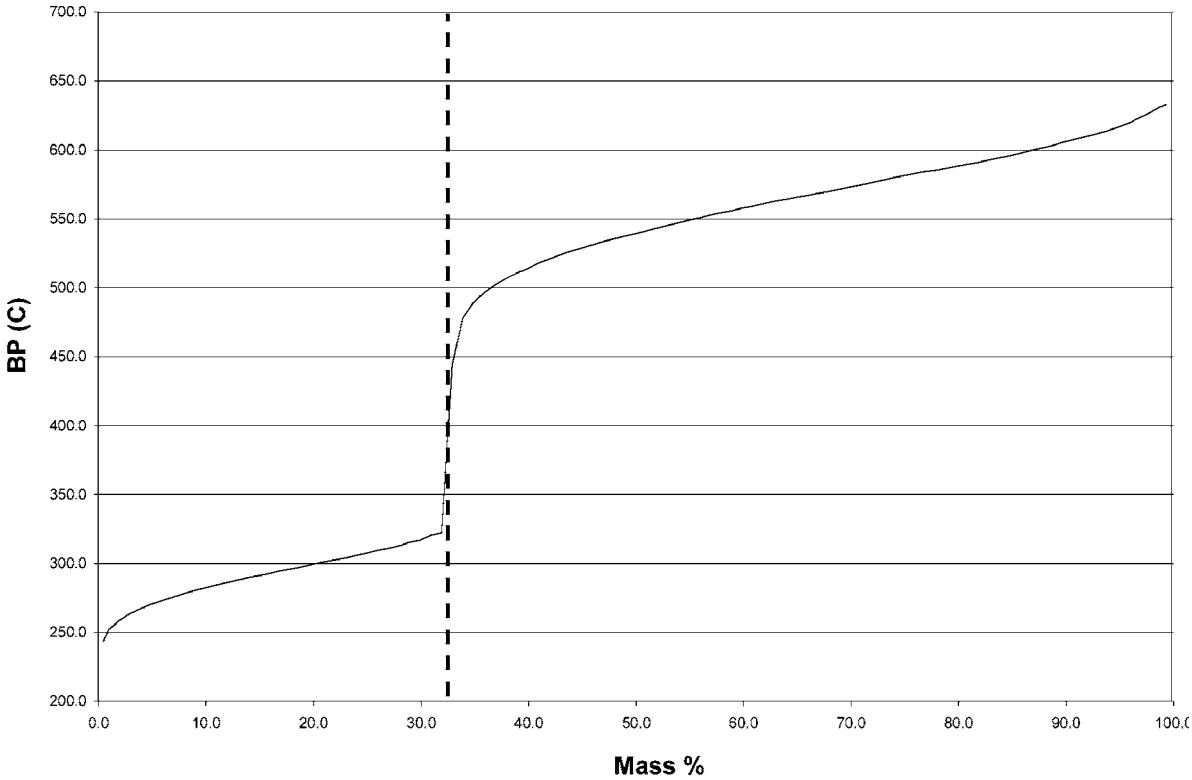


FIG. 9 Boiling Point Curve of the Gravimetric Blend

ANNEXES

(Mandatory Information)

A1. 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.

A1.1 Required Starting Elements

A1.1.1 *Sample Data Array, N Area Slices*—Collect the data at a minimum sampling frequency of 5 to 10 Hz (that is, slice width is 0.2 to 0.1 s). In addition, select a slice width that no sample or solvent elutes in the first 10 to 20 slices, respectively.

A1.1.2 *Blank Data Array, N Area Slices*—The slice width for the blank and sample runs needs to be identical.

NOTE A1.1—A blank data array may not be necessary if electronic baseline compensation is used. See A1.2.1.

A1.1.2.1 The analysis conditions for blank and sample needs to be identical through the point where sample analysis is terminated.

A1.1.2.2 The number of slices in the blank array shall 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.

A1.1.2.3 *Retention Times, n-Paraffins*—Obtain the retention time of each *n*-paraffin in the calibration mixture from a processed (peak) data file from the analysis of the calibration mixture, run under identical conditions as the samples and blank.

A1.1.2.4 *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 4 of this test method.

A1.1.2.5 *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 needs to return to baseline before any sample components start to elute.

A1.2 Subtract Blank from Sample (see Note A1.2)

A1.2.1 Subtract each blank area slice from the exactly corresponding sample area slice. This corrects the sample area slice from the blank. (**Caution:** Automatic baseline compensation is available on many instruments and is allowed by this test method. However, automatic baseline compensation does not always 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 is often 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, disable the automatic baseline compensation and perform blank subtractions as described in this appendix.)

NOTE A1.2—If the data was acquired on an instrument using automatic baseline compensation, skip A1.2. In this case, the zeroed sample data array contains the corrected area slices to be used in subsequent calculations.

A1.3 Zero the Data Slices

A1.3.1 Calculate the average of the first 10 to 20 (5 to 10 Hz) area slices of the blank-subtracted data array.

A1.3.2 Subtract the average slice area (A1.3.1) from each area slice in the blank-subtracted data array. Set negative numbers to zero.

A1.4 Calculate Total Chromatogram Area

A1.4.1 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.

A1.4.2 Designate this sum as the total chromatogram area.

A1.5 Determine Start of Sample Elution Time

A1.5.1 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 A1.4.2).

A1.5.1.1 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.

A1.5.1.2 If $(\text{<slice>}_{N+1} - \text{<slice>}_{N})/(\text{slice width}) > 1\text{E-}7 \times$ total chromatogram area, then take slice $N + 1$ as the start of sample slice (see A1.2).

A1.5.2 Print the retention time corresponding to the start of sample elution.

A1.6 Determine the End of Sample Elution Time

A1.6.1 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 A1.4.2).

A1.6.1.1 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.

A1.6.1.2 If $(<slice>_{N-1} - <slice>_N)/(\text{slice width}) > 1E\text{-}7 \times$ total chromatogram area, then take slice $N - 1$ as the end of sample slice (see A1.2).

A1.6.2 Print the retention time corresponding to the end of sample elution.

NOTE A1.3—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.

A1.7 Calculate Total Corrected Sample Area

A1.7.1 Sum the corrected area slices from the start of sample slice (see A1.5.1.2) to the end of sample slice (see A1.6.1.2).

A1.7.2 Designate this sum as the total corrected sample area, and save it for subsequent calculations.

A1.8 Normalize to Area Percent

A1.8.1 Beginning at the start of sample slice (see A1.5.1.2) and continuing to the end of sample slice (see A1.6.1.2), divide each corrected area slice by the total corrected sample area (see A1.7.2) and multiply by 100.

A1.8.2 Save these normalized area percents in an array for subsequent calculations.

A1.9 Find Retention Time Corresponding to Percent Off

A1.9.1 For each X (where $X = 0.5, 1, 2, ..., 98, 99.5$), find the retention time corresponding to X percent off.

A1.9.1.1 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 A1.4—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.

A1.9.1.2 For the slice $(N + 1)$ determined above, the following inequality shall hold:

$$CA_N \le X \le CA_{N+1} \quad \text{(A1.1)}$$

where:

CA_N = the cumulative area percent from start of sample slice through slice N, and

CA_{N+1} = the cumulative area percent through slice $N + 1$.

A1.9.1.3 Calculate the fraction (f) of normalized area percent in slice $(N + 1)$ needed to give exactly X percent off as follows:

$$f = (X - CA_N)/A_{N+1} \quad \text{(A1.2)}$$

where:

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

A1.9.1.4 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:

$$RT_X = (N + f) \times \text{slice width} \quad \text{(A1.3)}$$

A1.10 Convert Retention Times to Boiling Points

A1.10.1 For each retention time found in A1.9.1, calculate the boiling point equivalent to that retention time.

A1.10.1.1 Find the pair of calibration compound retention times that are closest to and bracket the percent off retention time of interest.

A1.10.1.2 Calculate the boiling point corresponding to the percent off retention time as follows:

$$BP_i = (((BP_2 - BP_1)/(RT_2 - RT_1)) \times (RT_i - RT_1)) + BP_1 \quad \text{(A1.4)}$$

where:

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 A1.5—A report giving percent off at selected boiling point intervals is calculated in an analogous manner.

A1.11 Reporting Results

A1.11.1 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.

A2. BOILING POINTS OF NORMAL ALKANES

A2.1 The boiling points of normal alkanes used for construction of the calibration curve are given in Table 4.

A3. SYSTEM PERFORMANCE CHECK

A3.1 Frequency

A3.1.1 Carry out a run on the calibration mix (7.8), using identical conditions, and injection volumes to those used for the sample analysis at the start of an analysis. Periodically inject this mix to verify the shift in retention time. Also this calibration mix shall be injected if the analytical system and conditions have been altered in any way since the last performance check was carried out or whenever the results obtained for the reference oil 5010 fall outside the permitted limits.

A3.1.2 A typical chromatogram of the calibration mix is shown in Fig. 5.

NOTE A3.1—This procedure may be carried out as part of the boiling range calibration (see Section 10).

A3.2 Column Resolution

A3.2.1 Determine the column resolution, R, using the C_{50} and C_{52} peaks and the following equation:

$$R = \frac{2(t_2 - t_1)}{1.699\,(W_1 + W_2)} \quad \text{(A3.1)}$$

where:

t_1 = the retention time, in seconds, for the C_{50} peak,
t_2 = the retention time, in seconds, for the C_{52} peak,
W_1 = the width, in seconds, at half-height of C_{50} peak, and
W_2 = the width, in seconds, at half-height of C_{52} peak.

A3.2.2 Resolution as determined above shall be at least 2, but no greater than 4.

A3.3 Detector Response

A3.3.1 Use a binary gravimetric blend distillate to determine the detector response as well as to determine the quality of the baseline. Since the most critical area of the chromatogram is where column bleeding occurs, the binary blend is also used as a recovery of the baseline test. The binary blend shall have the following characteristics:

A3.3.2 It shall consists of two fractions: The first fraction 1 shall have an IBP 240.5ºC and a FBP 362ºC. The second fraction 2 shall have an IBP of 459ºC and a FBP of 652ºC.

A3.3.3 Ensure that the two fractions have similar height response and follow the criteria of not exceeding linearity nor overloading the column.

A3.3.4 The ratio of the area's of the two distillates shall be constant and meet the following conditions:

A3.3.4.1 The lower boiling distillate shall not interfere with the solvent.

A3.3.4.2 There shall be a baseline between distillates.

A3.3.4.3 The higher boiling point distillate shall elute totally and as close to the end of the temperature program as possible.

A3.3.4.4 The two fractions shall preferably contain no aromatics so that the detector response is due to saturates only.

A3.3.5 A typical chromatogram of the gravimetric blend with its superimposed baseline is shown in Fig. 4.

A3.3.6 With the example given this is best achieved with a mixture of fraction 1 of 32 %. The determined mass % is obtained from the distillation curve which presents a break at 32.4 ± 0.6 % at 400ºC which corresponds to the midpoint of the distillation curve of the composite fractions as shown in Fig. 9.

A3.4 Peak Skewness

A3.4.1 Determine the skewness of the calibration mix peaks as the ratio *A/B* as shown in Fig. 3, for the C_{20} peak,

where:

A = the width of the leading part of the peak at 5 % of the peak height, and
B = the width of the following part of the peak at 5 % of the peak height.

A3.4.2 The ratio shall for all peaks be between 0.8 and 1.8.

A3.4.3 Verify that the skewness of all peaks does not exceed the limits. Typical skewness data for the calibration mix chromatogram of Fig. 5 is shown in Table 5.