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Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography[1,2]

This standard is issued under the fixed designation D2887; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This test method covers the determination of the boiling range distribution of petroleum products. The test method is applicable to petroleum products and fractions having a final boiling point of 538 °C (1000 °F) or lower at atmospheric pressure as measured by this test method. This test method is limited to samples having a *boiling range* greater than 55.5 °C (100 °F), and having a vapor pressure sufficiently low to permit sampling at ambient temperature.

NOTE 1—Since a *boiling range* is the difference between two temperatures, only the constant of 1.8 °F/°C is used in the conversion of the temperature range from one system of units to another.

1.1.1 *Procedure A (Sections 6 – 14)*—Allows a larger selection of columns and analysis conditions such as packed and capillary columns as well as a Thermal Conductivity Detector in addition to the Flame Ionization Detector. Analysis times range from 14 min to 60 min.

1.1.2 *Procedure B (Sections 15 – 23)*—Is restricted to only 3 capillary columns and requires no sample dilution. In addition, Procedure B is used not only for the sample types described in Procedure A but also for the analysis of samples containing biodiesel mixtures B5, B10, and B20. The analysis time, when using Procedure B (Accelerated D2887), is reduced to about 8 min.

1.2 This test method is not to be used for the analysis of gasoline samples or gasoline components. These types of samples must be analyzed by Test Method D3710.

1.3 The values stated in SI units are to be regarded as standard. The inch-pound units given in parentheses are for information only.

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:*[3]

D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

D1160 Test Method for Distillation of Petroleum Products at Reduced Pressure

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 (Withdrawn 2014)[4]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

E516 Practice for Testing Thermal Conductivity Detectors Used in Gas Chromatography

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

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[2] This standard has been developed through the cooperative effort between ASTM International and the Energy Institute, London. The EI and ASTM International logos imply that the ASTM International and EI standards are technically equivalent, but does not imply that both standards are editorially identical.

[3] 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.

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

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

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

3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E260, E355, and E594.

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

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

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

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

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

3.2.7 *slice time, n*—the time associated with the end of each contiguous area slice. The slice time is equal to the slice number divided by the slice rate.

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 is considered to have returned to baseline after complete sample elution.

3.3 *Abbreviations:*

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

4. Summary of Test Method

4.1 The boiling range distribution determination by distillation is simulated by the use of gas chromatography. A nonpolar packed or open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. The column temperature is raised at a reproducible linear rate and the area under the chromatogram is recorded throughout the analysis. Boiling points are assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analyzing a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution can be obtained.

4.2 Procedure A and Procedure B yield essentially the same results. See Sections 14 and 23, and the accompanying research reports.

5. Significance and Use

5.1 The boiling range distribution of petroleum fractions provides an insight into the composition of feedstocks and products related to petroleum refining processes. 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 Boiling range distributions obtained by this test method are essentially equivalent to those obtained by true boiling point (TBP) distillation (see Test Method D2892). They are not equivalent to results from low efficiency distillations such as those obtained with Test Method D86 or D1160.

5.3 Procedure B was tested with biodiesel mixtures and reports the Boiling Point Distribution of FAME esters of vegetable and animal origin mixed with ultra low sulfur diesel.

Procedure A

6. Apparatus

6.1 *Chromatograph*—The gas chromatograph used must have the following performance characteristics:

6.1.1 *Detector*—Either a flame ionization or a thermal conductivity detector may be used. The detector must have sufficient sensitivity to detect 1.0 % dodecane with a peak height of at least 10 % of full scale on the recorder under conditions prescribed in this test method and without loss of resolution as defined in 9.3.1. When operating at this sensitivity level, detector stability must be such that a baseline drift of not more than 1 % of full scale per hour is obtained. The detector must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed. Connection of the column to the detector must be such that no temperature below the column temperature exists.

NOTE 2—It is not desirable to operate a thermal conductivity detector at a temperature higher than the maximum column temperature employed. Operation at higher temperature generally contributes to higher noise levels and greater drift and can shorten the useful life of the detector.

6.1.2 *Column Temperature Programmer*—The chromatograph must be capable of linear programmed temperature operation over a range sufficient to establish a retention time of at least 1 min for the IBP and to elute compounds up to a boiling temperature of 538 °C (1000 °F) before reaching the upper end of the temperature program. The programming rate must be sufficiently reproducible to obtain retention time repeatability of 0.1 min (6 s) for each component in the calibration mixture described in 7.8.

TABLE 1 Typical Operating Conditions

Packed Columns	1	2	3	4	Open Tubular Columns	5	6	7
Column length, m (ft)	1.2 (4)	1.5 (5)	0.5 (1.5)	0.6 (2)	Column length (m)	7.5	5	10
Column outside diameter, mm (in.)	6.4 (1/4)	3.2 (1/8)	3.2 (1/8)	6.4 (1/8)	Column inner diameter (mm)	0.53	0.53	0.53
Liquid phase	OV-1	SE-30	UC-W98	SE-30	Stationary phase	DB-1	HP-1	HP-1
Percent liquid phase	3	5	10	10	Stationary phase thickness (m)	1.5	0.88	2.65
Support material	S[A]	G[B]	P[C]	P[C]	Carrier gas	nitrogen	helium	helium
Support mesh size	60/80	60/80	80/100	60/80	Carrier gas flow rate, mL/min	30	12	12
Initial column temperature, °C	–20	–40	–30	–50	Initial column temperature, °C	40	35	35
Final column temperature, °C	360	350	360	390	Final column temperature, °C	340	350	350
Programming rate,°C/min	10	6.5	10	7.5	Programming rate, °C/min	10	10	20
Carrier gas	helium	helium	N_2	helium	Detector	FID	FID	FID
Carrier gas flow, mL/min	40	30	25	60	Detector temperature, °C	350	380	370
Detector	TC	FID	FID	TC	Injector temperature, °C	340	cool on-column	cool on-column
Detector temperature, °C	360	370	360	390	Sample size, µL	0.5	1	0.1–0.2
Injection port temperature, °C	360	370	350	390	Sample concentration mass %	25	2	neat
Sample size, µ	4	0.3	1	5				

[A] Diatoport S; silane treated.
[B] Chromosorb G (AW-DMS).
[C] Chromosorb P, acid washed.

6.1.3 *Cryogenic Column Cooling*—Column starting temperatures below ambient will be required if samples with IBPs of less than 93 °C (200 °F) are to be analyzed. This is typically provided by adding a source of either liquid carbon dioxide or liquid nitrogen, controlled through the oven temperature circuitry. Excessively low initial column temperature must be avoided to ensure that the stationary phase remains liquid. The initial temperature of the column should be only low enough to obtain a calibration curve meeting the specifications of the method.

6.1.4 *Sample Inlet System*—The sample inlet system must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed, or provide for on-column injection with some means of programming the entire column, including the point of sample introduction, up to the maximum temperature required. Connection of the column to the sample inlet system must be such that no temperature below the column temperature exists.

6.1.5 *Flow Controllers*—The gas chromatograph must be equipped with mass flow controllers capable of maintaining carrier gas flow constant to ±1 % over the full operating temperature range of the column. The inlet pressure of the carrier gas supplied to the gas chromatograph must be sufficiently high to compensate for the increase in column backpressure as the column temperature is raised. An inlet pressure of 550 kPa (80 psig) has been found satisfactory with the packed columns described in Table 1. For open tubular columns, inlet pressures from 10 kPa to 70 kPa (1.5 psig to 10 psig) have been found to be suitable.

6.1.6 *Microsyringe*—A microsyringe is needed for sample introduction.

NOTE 3—Automatic sampling devices or other sampling means, such as indium encapsulation, can be used provided: the system can be operated at a temperature sufficiently high to completely vaporize hydrocarbons with atmospheric boiling points of 538 °C (1000 °F), and the sampling system is connected to the chromatographic column avoiding any cold temperature zones.

6.2 *Column*—Any column and conditions may be used that provide separation of typical petroleum hydrocarbons in order of increasing boiling point and meet the column performance requirements of 9.3.1 and 9.3.3. Successfully used columns and conditions are given in Table 1.

6.3 *Data Acquisition System:*

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

6.3.2 *Integrator*—Means must 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 must have normal chromatographic software for measuring the retention time and areas of eluting peaks (peak detection mode). In addition, the system must 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) must be within the linear range of the detector/electrometer system used. The system must be capable of subtracting the area slice of a blank run from the corresponding area slice of a sample run.

NOTE 4—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 analyses to compensate for any baseline offset. Some integration systems also store and automatically subtract a blank analysis from subsequent analytical determinations.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where

such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Liquid Phase for Columns*—Methyl silicone gums and liquids provide the proper chromatographic hydrocarbon elution characteristics for this test method.

7.3 *Solid Support for Packed Columns*—Chromatographic grade diatomaceous earth solid support material within a particle size range from 60 to 100 sieve mesh size is recommended.

7.4 *Carrier Gas*—Helium 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 must be sufficient to ensure a constant carrier gas flow rate (see 6.1.5).

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

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

7.7 *Column Resolution Test Mixture*—For packed columns, a nominal mixture of 1 mass % each of *n*-C_{16} and *n*-C_{18} paraffin in a suitable solvent, such as *n*-octane, for use in testing the column resolution. (**Warning**—*n*-octane is flammable and harmful if inhaled.) The calibration mixture specified in 7.8.2 may be used as a suitable alternative, provided the concentrations of the *n*-C_{16} and *n*-C_{18} components are nominally 1.0 mass % each. For open tubular columns, use the mixture specified in 7.8.3.

7.8 *Calibration Mixture*—An accurately weighed mixture of approximately equal mass quantities of *n*-hydrocarbons dissolved in carbon disulfide (CS_2). (**Warning**—Carbon disulfide is extremely volatile, flammable, and toxic.) The mixture shall cover the boiling range from *n*-C_5 to *n*-C_{44}, but does not need to include every carbon number (see Note 5).

7.8.1 At least one compound in the mixture must have a boiling point lower than the IBP of the sample and at least one compound in the mixture must have a boiling point higher than the FBP of the sample. Boiling points of *n*-paraffins are listed in Table 2.

7.8.1.1 If necessary, for the calibration mixture to have a compound with a boiling point below the IBP of the sample, propane or butane can be added to the calibration mixture, non-quantitatively, by bubbling the gaseous compound into the calibration mixture in a septum sealed vial using a gas syringe.

[5] *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 2 Boiling Points of Normal Paraffins[A,B]

Carbon Number	Boiling Point, °C	Boiling Point, °F	Carbon Number	Boiling Point, °C	Boiling Point, °F
1	−162	−259	23	380	716
2	−89	−127	24	391	736
3	−42	−44	25	402	755
4	0	31	26	412	774
5	36	97	27	422	791
6	69	156	28	431	808
7	98	209	29	440	825
8	126	258	30	449	840
9	151	303	31	458	856
10	174	345	32	466	870
11	196	385	33	474	885
12	216	421	34	481	898
13	235	456	35	489	912
14	254	488	36	496	925
15	271	519	37	503	937
16	287	548	38	509	948
17	302	576	39	516	961
18	316	601	40	522	972
19	330	626	41	528	982
20	344	651	42	534	993
21	356	674	43	540	1004
22	369	695	44	545	1013

[A] API Project 44, October 31, 1972 is believed to have provided the original normal paraffin boiling point data that are listed in Table 2. However, over the years some of the data contained in both API Project 44 (Thermodynamics Research Center Hydrocarbon Project) and Test Method D2887 have changed, and they are no longer equivalent. Table 2 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 D2887 has traditionally used *n*-paraffin boiling points rounded to the nearest whole degree for calibration. The boiling points listed in Table 2 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 result will not agree with the table value 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.

NOTE 5—Calibration mixtures containing normal paraffins with the carbon numbers 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 20, 24, 28, 32, 36, 40, and 44 have been found to provide a sufficient number of points to generate a reliable calibration curve.

7.8.2 *Packed Columns*—The final concentration should be approximately ten parts of the *n*-paraffin mixture to one hundred parts of CS_2.

7.8.3 *Open Tubular Columns*—The final concentration should be approximately one part of the *n*-paraffin mixture to one hundred parts of CS_2.

7.9 *Reference Gas Oil No. 1 or No. 2*—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 Tables 3 and 4.

8. Sampling

8.1 Samples to be analyzed by this test method must be obtained using the procedures outlined in Practice D4057.

8.2 The test specimen to be analyzed must be homogeneous and free of dust or undissolved material.

9. Preparation of Apparatus

9.1 *Chromatograph*—Place in service in accordance with the manufacturer's instructions. Typical operating conditions are shown in Table 1.

TABLE 3 Test Method D2887 Reference Gas Oil No. 1[A]

% Off	Batch 1		Allowable Difference		Batch 2		Allowable Difference	
	°C	°F	°C	°F	°C	°F	°C	°F
IBP	114	238	7.5	13.6	115	240	7.6	13.7
5	143	289	3.6	6.6	151	304	3.8	6.8
10	169	336	4.0	7.3	176	348	4.1	7.4
15	196	384	4.4	8.0	201	393	4.5	8.1
20	221	429	4.8	8.7	224	435	4.9	8.7
25					243	470		
30	258	496	4.7	8.4	259	499	4.7	8.4
35					275	527		
40	287	548	4.3	7.7	289	552	4.3	7.7
45					302	576		
50	312	594	4.3	7.7	312	594	4.3	7.7
55					321	611	4.3	7.7
60	332	629	4.3	7.7	332	629	4.3	7.7
65	343	649	4.3	7.7	343	649	4.3	7.7
70	354	669	4.3	7.7	354	668	4.3	7.7
75	364	688	4.3	7.7	365	690	4.3	7.7
80	376	709	4.3	7.7	378	712	4.3	7.7
85	389	732	4.3	7.7	391	736	4.3	7.7
90	404	759	4.3	7.7	407	764	4.3	7.7
95	425	797	5.0	9.0	428	803	5.0	9.0
FBP	475	887	11.8	21.2	475	888	11.8	21.2

[A] Consensus results for Batch 2 obtained from 30 laboratories in 1995 (supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1407).

TABLE 4 Test Method D2887 Reference Gas Oil No. 2[A]

	Allowable Difference		Allowable Difference	
% Off	°C	°F	°C	°F
IBP	106	223	7.0	12.6
5	173	343	4.1	7.4
10	196	384	4.4	8.0
15	216	420	4.7	8.5
20	233	452	5.0	9.0
25	251	483	...	...
30	267	512	4.8	8.6
35	283	541	...	...
40	298	568	4.3	7.7
45	310	590	...	...
50	321	610	4.3	7.7
55	331	629	4.3	7.7
60	342	647	4.3	7.7
65	350	662	4.3	7.7
70	358	677	4.3	7.7
75	368	694	4.3	7.7
80	378	712	4.3	7.7
85	390	734	4.3	7.7
90	406	763	4.3	7.7
95	431	808	5.0	9.0
FBP	496	925	11.8	21.2

[A] Consensus results for Reference Gas Oil No. 2 obtained from 32 laboratories in 2009.

9.1.1 When a FID is used, regularly remove the deposits formed in the detector from combustion of the silicone liquid phase decomposition products. These deposits will change the response characteristics of the detector.

9.1.2 If the sample inlet system is heated above 300 °C (572 °F), a blank analysis must be made after a new septum is installed to ensure that no extraneous detector response is produced by septum bleed. At the sensitivity levels commonly employed in this test method, conditioning of the septum at the operating temperature of the sample inlet system for several hours will minimize this problem. A recommended practice is to change the septum at the end of a series of analyses rather than at the beginning of the series.

9.2 *Column Preparation:*

9.2.1 *Packed Columns*—Any satisfactory method that will produce a column meeting the requirements of 9.3.1 and 9.3.3 can be used. In general, use liquid phase loadings of 3 % to 10 %. Condition the column at the maximum operating temperature to reduce baseline shifts due to bleeding of the column substrate. The column can be conditioned very rapidly and effectively using the following procedure:

9.2.1.1 Connect the column to the inlet but leave the detector end free.

9.2.1.2 Purge the column thoroughly at ambient temperature with carrier gas.

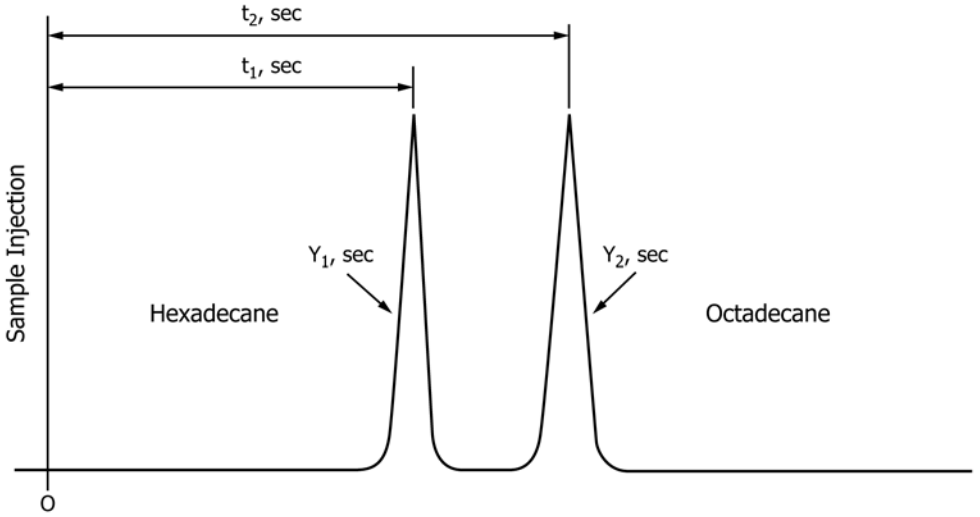

FIG. 1 Column Resolution Parameters

9.2.1.3 Turn off the carrier gas and allow the column to depressurize completely.

9.2.1.4 Seal off the open end (detector) of the column with an appropriate fitting.

9.2.1.5 Raise the column temperature to the maximum operating temperature.

9.2.1.6 Hold the column at this temperature for at least 1 h with no flow through the column.

9.2.1.7 Cool the column to ambient temperature.

9.2.1.8 Remove the cap from the detector end of the column and turn the carrier gas back on.

9.2.1.9 Program the column temperature up to the maximum several times with normal carrier gas flow. Connect the free end of the column to the detector.

9.2.1.10 An alternative method of column conditioning that has been found effective for columns with an initial loading of 10 % liquid phase consists of purging the column with carrier gas at the normal flow rate while holding the column at the maximum operating temperature for 12 h to 16 h, while detached from the detector.

9.2.2 *Open Tubular Columns*—Open tubular columns with cross-linked and bonded stationary phases are available from many manufacturers and are usually pre-conditioned. These columns have much lower column bleed than packed columns. Column conditioning is less critical with these columns but some conditioning may be necessary. The column can be conditioned very rapidly and effectively using the following procedure.

9.2.2.1 Once the open tubular column has been properly installed into the gas chromatograph and tested to be leak free, set the column and detector gas flows. Before heating the column, allow the system to purge with carrier gas at ambient temperature for at least 30 min.

9.2.2.2 Increase the oven temperature about 5 °C to 10 °C per minute to the final operating temperature and hold for about 30 min.

9.2.2.3 Cycle the gas chromatograph several times through its temperature program until a stable baseline is obtained.

9.3 *System Performance Specification:*

9.3.1 *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_{16} and C_{18} paraffins from a column resolution test mixture analysis (see 7.7 and Section 10), and is illustrated in Fig. 1. Resolution (R) should be at least three, using the identical conditions employed for sample analyses:

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

where:

R = resolution,
t_1 = time(s) for the n-C_{16} peak maximum,
t_2 = time(s) for the n-C_{18} peak maximum,
w_1 = peak width(s), at half height, of the n-C_{16} peak, and
w_2 = peak width(s), at half height, of the n-C_{18} peak.

9.3.2 *Detector Response Calibration*—This test method assumes that the detector response to petroleum hydrocarbons is proportional to the mass of individual components. This must be verified when the system is put in service, and whenever any changes are made to the system or operational parameters. Analyze the calibration mixture using the identical procedure to be used for the analysis of samples (see Section 10). Calculate the relative response factor for each n-paraffin (relative to n-decane) in accordance with Practice D4626 and Eq 2:

$$F_n = (M_n/A_n)/(M_{10}/A_{10}) \quad (2)$$

where:

F_n = relative response factor,
M_n = mass of the n-paraffin in the mixture,
A_n = peak area of the n-paraffin in the mixture,
M_{10} = mass of the n-decane in the mixture, and
A_{10} = peak area of the n-decane in the mixture.

The relative response factor (F_n) of each n-paraffin must not deviate from unity (1) by more than ±10 %.

9.3.3 *Column Elution Characteristics*—The column material, stationary phase, or other parameters can affect the elution order of non-paraffinic sample components, resulting in deviations from a TBP versus retention time relationship. If stationary phases other than those referenced in 7.3 are used, the retention times of a few alkylbenzenes (for example, *o*-xylene, *n*-butyl-benzene, 1,3,5-triisopropylbenzene, *n*-decyl-benzene, and tetradecylbenzene) across the boiling range should be analyzed to make certain that the column is separating in accordance with the boiling point order (see Appendix X1).

10. Calibration and Standardization

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

10.1.1 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.

10.1.2 During the cool down and equilibration time, ready the integrator/computer system. If a retention time or detector response calibration is being performed, use the peak detection mode. For samples and baseline compensation determinations, use the area slice mode of integration. The recommended slice rate for this test method is given in 12.1.2. Other slice rates may be used if within the limits of 0.02 % and 0.2 % of the retention time of the final calibration component (C_{44}). 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.

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

10.2 *Baseline Compensation Analysis*—A baseline compensation analysis, or baseline blank, is performed exactly like an analysis except no injection is made. A blank analysis must be performed at least once per day. The blank analysis is necessary due to the usual occurrence of chromatographic baseline instability and is subtracted from sample analyses to remove any nonsample slice area from the chromatographic data. 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 carryover from previous sample analyses. Attention must be given to all factors that influence baseline stability, such as column bleed, septum bleed, detector temperature control, constancy of carrier gas flow, leaks, instrument drift, and so forth. Periodic baseline blank analyses should be made, following the analysis sequence protocol, to give an indication of baseline stability.

NOTE 6—If automatic baseline correction (see Note 4) 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.

10.3 *Retention Time Versus Boiling Point Calibration* —In order to analyze samples, a retention time versus boiling point calibration must be performed. Inject an appropriate aliquot (0.2 µL to 2.0 µL) of the calibration mixture (see 7.8) into the chromatograph, using the analysis sequence protocol. Obtain a normal (peak detection) data record in order 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.

10.3.1 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 that will result in displacement of the peak apex relative to nonoverloaded peaks. Distortion in retention time measurement and hence errors in boiling point temperature determination will be likely if column overloading occurs. The column liquid phase loading has a direct bearing on acceptable sample size. Reanalyze the calibration mixture using a smaller sample size or a more dilute solution to avoid peak distortion.

10.3.2 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 degrees Celsius (or Fahrenheit) for every component in the mixture. *n*-Paraffin boiling point temperatures are listed in Table 2.

10.3.3 Plot the retention time of each peak versus the corresponding normal boiling point temperature of that component in degrees Celsius (or Fahrenheit) as shown in Fig. 2.

10.3.4 Ideally, the retention time versus boiling point temperature calibration plot would be linear, but it is impractical to operate the chromatograph such that curvature is eliminated completely. The greatest potential for deviation from linearity will be associated with the lower boiling point paraffins. They will elute from the column relatively fast and have the largest difference in boiling point temperature. In general, the lower the sample IBP, the lower will be the starting temperature of the analysis. Although extrapolation of the curve at the upper end is more accurate, calibration points must bracket the boiling range of the sample at both the low and high ends.

10.4 *Reference Gas Oil Analysis*—The Reference Gas Oil sample is used to verify both the chromatographic and calculation processes involved in this test method. Perform an

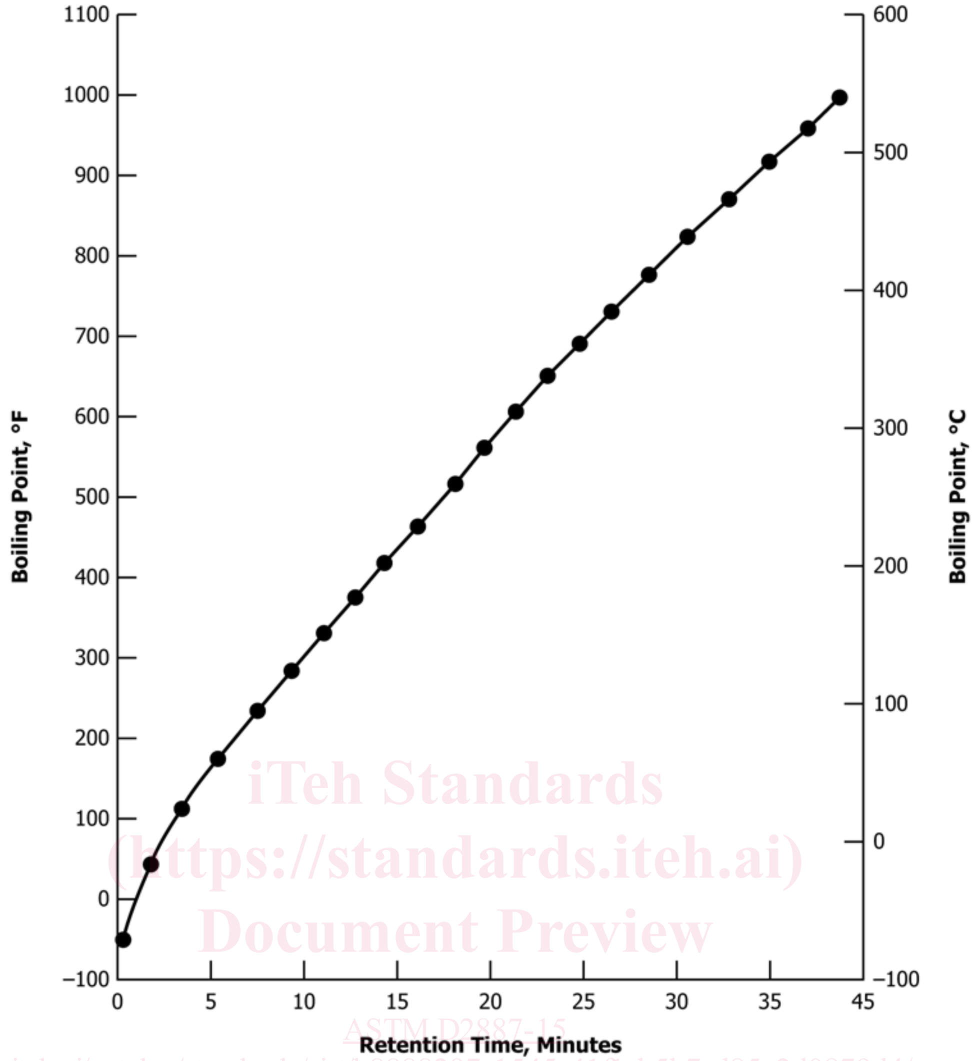

FIG. 2 Typical Calibration Curve

analysis of the gas oil following the analysis sequence protocol. Collect the area slice data and provide a boiling point distribution report as in Sections 12 and 13.

10.4.1 The results of this reference analysis must agree with the values given in Table 3 within the range specified by the test method reproducibility (see 14.1.2). If it does not meet the criteria in Table 3, 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.

10.4.2 Perform this reference gas oil confirmation test at least once per day or as often as required to establish confidence in consistent compliance with 10.4.1.

11. Procedure

11.1 *Sample Preparation:*

11.1.1 The amount of sample injected must not overload the column stationary phase nor exceed the detector linear range. A narrow boiling range sample will require a smaller amount injected than a wider boiling range sample.

11.1.1.1 To determine the detector linear range, refer to Practice E594 for flame ionization detectors or Practice E516 for thermal conductivity detectors.

11.1.1.2 The column stationary phase capacity can be estimated from the chromatogram of the calibration mixture (see 9.3.2). Different volumes of the calibration standard can be injected to find the maximum amount of a component that the stationary phase can tolerate without overloading (see 10.3.1). Note the peak height for this amount of sample. The maximum sample signal intensity should not exceed this peak height.

11.1.2 Samples that are of low enough viscosity to be sampled with a syringe at ambient temperature may be injected

neat. This type of sample may also be diluted with CS_2 to control the amount of sample injected to comply with 11.1.1.

11.1.3 Samples that are too viscous or waxy to sample with a syringe may be diluted with CS_2.

11.1.4 Typical sample injection volumes are listed below.

Packed Columns:	
Stationary Phase Loading, %	Neat Sample Volume, µL
10	1.0
5	0.5
Open Tubular Columns:	
Film Thickness, µ	Neat Sample Volume, µL
0.8 to 1.5	0.1 to 0.2
1.8 to 3.0	0.1 to 0.5
3.0 to 5.0	0.2 to 1.0

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

12. Calculations[6]

12.1 *Acquisition Rate Requirements:*

12.1.1 The number of slices required at the beginning of data acquisition depends on chromatographic variables such as the column flow, column film thickness, and initial column temperature as well as column length. In addition the detector signal level has to be as low as possible at the initial temperature of the analysis. The detector signal level for both the sample signal and the blank at the beginning of the run has to be similar for proper zeroing of the signals.

12.1.2 The sampling frequency has to be adjusted so that at least a significant number of slices are acquired prior to the start of elution of sample or solvent. For example, if the time for start of sample elution is 0.06 min (3.6 s), a sampling rate of 5 Hz would acquire 18 slices. However a rate of 1 Hz would only acquire 3.6 slices which would not be sufficient for zeroing the signals. Rather than specifying number of slices, it is important to select an initial time segment that is, one or two seconds. Ensure that the smallest number of slices is 5 or greater.

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

12.2 *Chromatograms Offset for Sample and Blank*—Perform a slice offset for the sample chromatogram and blank chromatogram. This operation is necessary so that the signal is corrected from its displacement from the origin. This is achieved by determining an average slice offset from the slices accumulated in the first segment (that is, first s) and performing a standard deviation calculation for the first N slices accumulated. It is carried out for both sample signal and baseline signal.

12.2.1 *Sample Offset:*

12.2.1.1 Calculate the average slice offset of sample chromatogram using the first second of acquired slices. Insure that no sample has eluted during this time and that the number of slices acquired is at least 5. Throw out any of the first N slices selected 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.

12.2.1.2 Subtract the average slice offset from all the slices of the sample chromatogram. Set negative slices to zero. This will zero the chromatogram.

12.2.2 *Blank Offset:*

NOTE 7—If you are using electronic baseline compensation proceed to 12.4. It is strongly recommended that the offset method use the slices acquired by running a blank with or without solvent according on how the sample was prepared. Use these acquired blank slices for the offset or zero calculations.

12.2.2.1 Repeat 12.2.1 using the blank run table.

12.3 *Offset the Sample Chromatogram with Blank Chromatogram*—Subtract from each slice in the sample chromatogram table with its correspondent slice in the blank run chromatogram table. Set negative slices to zero.

12.4 *Determine the Start of Sample Elution Time:*

12.4.1 *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.

12.4.2 *Calculate the Rate of Change between each Two Consecutive Area Slices*—Begin at the slice set in 12.4.1 and work 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 12.4.1) is defined as the start of the sample elution time. To reduce the possibility of noise or an electronic spike falsely indicating the start of sample elution time, a 1 s slice average can be used instead of a single slice. For noisier baselines, a slice average larger than 1 s may be required.

12.5 *Determine the End of Sample Elution Time:*

12.5.1 *Calculate the Rate of Change between each Two Consecutive Area Slices*—Begin at the end of run and work backward. 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 12.4.1) is defined as the end of sample elution time. To reduce the possibility of noise or an electronic spike falsely indicating the end of sample elution a 1 s slice average can be used instead of a single slice. For noisier baselines a slice average larger than 1 s may be required.

12.6 *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 sample elution time.

12.7 *Normalize to Area Percent*—Divide each slice in the sample chromatogram table by the total area (see 12.6) and multiply it by 100.

12.8 *Calculate the Boiling Point Distribution Table:*

12.8.1 *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

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1477.

12.9.1) 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 12.9.2).

12.8.2 *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 12.9.1) 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 12.9.2).

12.8.3 *Intermediate Boiling Point*—For each point between 1 % and 99 %, find the time where the accumulative sum is equal to or greater than the area percent being analyzed. As in 12.8.1 and 12.8.2, use interpolation when the accumulated sum exceeds the area percent to be estimated (refer to the algorithm in 12.9.1). Use the calibration table to assign the boiling point.

12.9 *Calculations Algorithms:*

12.9.1 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 %.

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

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

$$A_x = \frac{X - A_c}{A_{c+1} - A_c} \quad (3)$$

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.

12.9.1.3 Calculate the time required to generate the fraction of area Ax:

$$T_f = A_x \cdot W \quad (4)$$

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.

12.9.1.4 Record the exact time where the accumulative area is equal to the X percent of the total area:

$$T_t = T_s + T_f \quad (5)$$

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.

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

12.9.2.1 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.)

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

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

12.9.2.4 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:

$$BP_x = m_1 \cdot (RT_x - RT_1) + BP_1 \quad (6)$$

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 calibration table,
BP_1 = boiling point of the first component in the calibration table,
RT_2 = retention time of the second component in the calibration table, and
BP_2 = boiling point of the second component in the calibration table.

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

$$BP_x = m_u \cdot (RT_x - RT_1) + BP_1 \quad (7)$$

where:

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

12.9.2.6 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:

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

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 component in the calibration table, and

TABLE 5 Repeatability

NOTE 1—x = the average of the two results in °C and y = the average of the two results in °F.

% Off	Repeatability	
	°C	°F
IBP	0.011 x	0.011 (y – 32)
5 %	0.0032 (x + 100)	0.0032 (y + 148)
10 %–20 %	0.8	1.4
30 %	0.8	1.4
40 %	0.8	1.4
50 %–90 %	1.0	1.8
95 %	1.2	2.2
FBP	3.2	5.8

TABLE 6 Reproducibility

NOTE 1—x = the average of the two results in °C and y = the average of the two results in °F.

% Off	Reproducibility	
	°C	°F
IBP	0.066 x	0.066 (y – 32)
5 %	0.015 (x + 100)	0.015 (y + 148)
10 %–20 %	0.015 (x + 100)	0.015 (y + 148)
30 %	0.013 (x + 100)	0.013 (y + 148)
40 %	4.3	7.7
50 %–90 %	4.3	7.7
95 %	5.0	9.0
FBP	11.8	21.2

BP_n = boiling point of the standard component in the calibration table.

13. Report

13.1 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 8—If a plot of the boiling point distribution curve is desired, use a spreadsheet with uniform subdivisions and use either retention time or temperature as the horizontal axis. The vertical axis will represent the boiling range distribution (0 % to 100 %). Plot each boiling temperature against its corresponding normalized percent. Draw a smooth curve connecting the points.

14. Precision and Bias[7]

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

14.1.1 *Repeatability*—The difference 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 following values by only one case in twenty (see Table 5).

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only one case in twenty (see Table 6).

NOTE 9—This precision estimate is based on the analysis of nine samples by 19 laboratories using both packed and open tubular columns. The range of results found in the round robin are listed in Table 7.

14.2 *Bias*—The procedure in Test Method D2887 for determining the boiling range distribution of petroleum fractions by gas chromatography has no bias because the boiling range distribution can only be defined in terms of a test method.

14.2.1 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.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1406.

TABLE 7 Round Robin Range of Results

% Off	Range of Results, °C	Range of Results, °F
IBP	112–213	234–415
5 %	133–286	271–547
10 %	139–312	282–594
20 %	151–341	304–646
30 %	161–358	322–676
40 %	171–370	340–698
50 %	182–381	360–718
60 %	196–390	385–734
70 %	206–401	403–754
80 %	219–412	426–774
90 %	233–426	451–799
95 %	241–437	466–819
FBP	274–475	525–887

Procedure B, Accelerated Method

15. Introduction

15.1 Procedure B was developed for carrying out Test Method D2887 in an accelerated mode. By changing variables such as carrier flow, oven heating and type of column, it is possible to significantly reduce the analysis time. The term accelerated is used here to distinguish this technique from ultrafast chromatography, which requires direct heating of the column only. In addition, the precision study involved mixtures of ultra low sulfur diesel and B100. The need to use solvent for sample dilution is not required.

15.2 Procedure B requires the use of a Flame Ionization detector only. Sections common to both procedures are referenced in Procedure B.

16. Apparatus

16.1 *Chromatograph*—The gas chromatograph used shall have the following performance characteristics:

16.1.1 *Detector*—A flame ionization detector (FID) must be used. The detector must have a Minimum Detectable Quantity of 2.0 pg carbon/s for n-C13 or better. The detector requires a sensitivity of 0.005C/g-0.010C/g of Carbon. Operating at this sensitivity level, detector stability must be such that a baseline drift of not more than 10^{-12} to 10^{-13} A/h(Pico Amps/Hour).