



Designation: D2887 – 08



Designation: 406

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 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.

1.2 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

[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

[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*:

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.

Current edition approved Dec. 1, 2008. Published January 2009. Originally approved in 1973. Last previous edition approved in 2006 as D2887–06a. DOI: 10.1520/D2887-08.

² This standard has been developed through the cooperative effort between ASTM and the Institute of Petroleum, London. The IP and ASTM logos imply that the ASTM and IP standards are technically equivalent, but their use 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.

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

3.2.1 *area slice*—the area, resulting from the integration of the chromatographic detector signal, within a specified retention time interval. In area slice mode (see 6.3.2), 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*—an area slice corrected for baseline offset, by subtraction of the exactly corresponding area slice in a previously recorded blank (non-sample) analysis.

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

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

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

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

3.2.7 *slice time*—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*—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 = $n\text{-C}_{10}$; isotetradecane = $i\text{-C}_{14}$).

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.

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.

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.

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 $\pm 1\%$ over the full operating

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.

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 back-pressure 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 to 70 kPa (1.5 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 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.⁴ 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

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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.

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*-C₁₆ and *n*-C₁₈ 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*-C₁₆ and *n*-C₁₈ 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 (CS₂). (**Warning**—Carbon disulfide is extremely volatile, flammable, and toxic.) The mixture shall cover the boiling range from *n*-C₅ to *n*-C₄₄, 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.

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 CS₂.

7.8.3 Open Tubular Columns—The final concentration should be approximately one part of the *n*-paraffin mixture to one hundred parts of CS₂.

7.9 Reference Gas Oil No. 1—A reference sample that has been analyzed by laboratories participating in the test method cooperative study. Consensus values for the boiling range distribution of this sample are given in [Table 3](#).

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](#).

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.

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.

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

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

^A Consensus results for Batch 2 obtained from 30 laboratories in 1995.⁹

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 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 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 C₁₆ and C₁₈ 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*-C₁₆ peak maximum,

*t*₂ = time(s) for the *n*-C₁₈ peak maximum,

*w*₁ = peak width(s), at half height, of the *n*-C₁₆ peak, and

*w*₂ = peak width(s), at half height, of the *n*-C₁₈ 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.

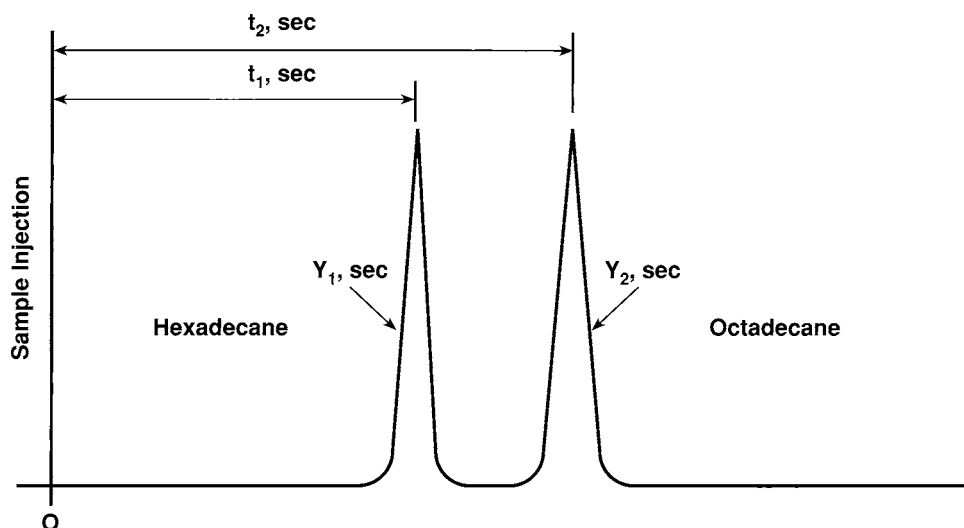


FIG. 1 Column Resolution Parameters

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

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 1.0 Hz (one slice per second). 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 to 2.0 μL) of the calibration mixture (see [7.8](#)) into the

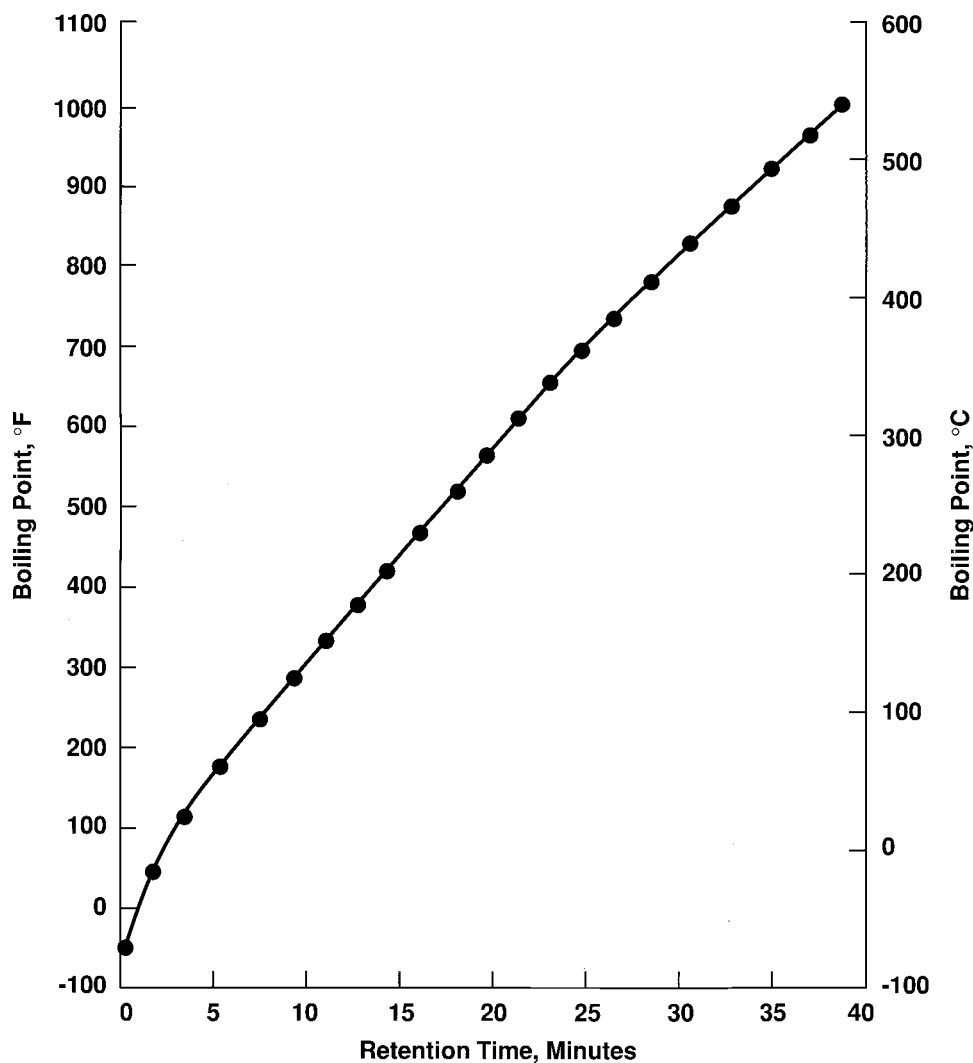


FIG. 2 Typical Calibration Curve

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 No. 1 sample is used to verify both the chromatographic and calculation processes involved in this test method. Perform an 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. Calculation

NOTE 7—See **Appendix X3** for the recommended calculation algorithm.⁵

12.1 Correct the sample area slices for nonsample detector response by subtracting each blank analysis area slice (as determined in **10.2**) from each sample area slice at the equivalent slice time. Also see **Note 6** regarding automatic baseline correction. Sum the corrected area slices to obtain the cumulative corrected areas for each time interval during the run.

12.2 At the point on the chromatogram where the baseline at the end of the run first becomes steady as the total area point, record the total cumulative corrected area counts. Move back along the chromatogram until a cumulative area equals 99.5 % of the total area. Mark this point as the FBP.

NOTE 8—Location of the FBP may be the most difficult step in this test method. Some samples have extremely long tailing end portions due to gradually decreasing quantities of heavy materials. This fact, coupled with the natural tendency of the chromatographic baseline to rise at the end of the run due to septum or column bleed or elution of traces of heavy compounds from previous samples, can preclude the possibility of the chromatogram returning precisely to the original baseline established prior to the IBP of the sample. Thus, the most satisfactory procedure is to inspect the chromatogram and the area counts at each interval near the end of the run to determine the point at which the rate of change per second of the chromatographic signal has reached a constant low value of no greater than 0.00001 % of the total area counts. In some rather unusual cases, a sample may have individual peaks, separated at the end of the run, which return to baseline between the peaks. In such cases, the total area point of the sample obviously is somewhere beyond the last detectable peak.

12.3 Observe the area counts at the start of the run, until the point is reached where the cumulative area count is equal to 0.5 % of the total area (see **12.2**). Mark this point as the IBP of the sample.

12.4 Divide the cumulative area at each interval between the initial and FBPs by the total area (see **12.2**) and multiply by 100. This will give the cumulative percent of the sample recovered at each time interval.

12.5 Tabulate the cumulative percent recovered at each interval and the retention time at the end of the interval. Using linear interpolation where necessary, determine the retention time associated with each percent between 1 and 99.

12.6 For each percent and its associated retention time, determine the corresponding boiling temperature from the calibration table (see **10.3.2**).

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 %).

NOTE 9—If a plot of the boiling point distribution curve is desired, use graph paper with uniform subdivisions and use either retention time or temperature as the horizontal axis. The vertical axis will represent the 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 ⁶

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

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report D02-1477.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report D02-1406.

TABLE 4 Repeatability

NOTE— 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

operation of the test method, exceed the following values by only one case in twenty (see [Table 4](#)).

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 5](#)).

NOTE 10—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 6](#).

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

TABLE 5 Reproducibility

NOTE— 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	0.06 ($y - 32$)
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

TABLE 6 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

definition and would not constitute a true value from which bias can be calculated.

15. Keywords

15.1 boiling range distribution; correlation; distillation; gas chromatography; petroleum; petroleum fractions; petroleum products; simulated distillation

APPENDIXES

(Nonmandatory Information)

X1. BOILING POINTS OF NONPARAFFINIC HYDROCARBONS

X1.1 There is an apparent discrepancy in the boiling point of multiple ring-type compounds. When the retention times of these compounds are compared with n -paraffins of equivalent atmospheric boiling point, these ring compounds appear to be eluted early from methyl silicone rubber columns. A plot showing 36 compounds other than n -paraffins plotted along the calibration curve for n -paraffins alone is shown in [Fig. X1.1](#). The numbered dots are identified in [Table X1.1](#). In this figure, the atmospheric boiling points are plotted against the observed retention times. If columns containing different percentages of stationary phase or different temperature programming rates were used, the slope and curvature of the n -paraffin curve (solid line) would change, but the relative relationships would remain

essentially the same. Deviations of simulated distillation boiling points, as estimated from the curve, from actual boiling points for a few compounds are shown in [Table X1.2](#). The deviations obtained by plotting boiling points at 10 mm rather than 760 mm are tabulated also. It is apparent that the deviation is much less at 10 mm pressure. This indicates that the distillation data produced by gas chromatography closely approximates those obtained in reduced pressure distillation. Since the vapor-pressure-temperature curves for multiple-ring type compounds do not have the same slope or curvature as those of n -paraffins, an apparent discrepancy would exist when n -paraffin boiling points at atmospheric pressure are used.

X1.2 However, this discrepancy does not introduce any significant error when comparing with laboratory distillation because the pressure must be reduced in such procedures when overhead temperatures reach approximately 260°C (500°F) to prevent cracking of the sample. Thus, distillation data are subject to the same deviations experienced in simulated distillation by gas chromatography. A comparison of data obtained from TBP distillation with those obtained from simulated

distillation of three high boiling petroleum fractions is shown in Table X1.3. The TBP distillations were made on 100 theoretical plate spinning band columns at 1 mm Hg pressure.

X1.3 The decanted oil is of particular interest because it contains a high presence of polycyclic aromatic compounds and the high sulfur coker gas oil should contain ring-type sulfur compounds and complex olefinic types.

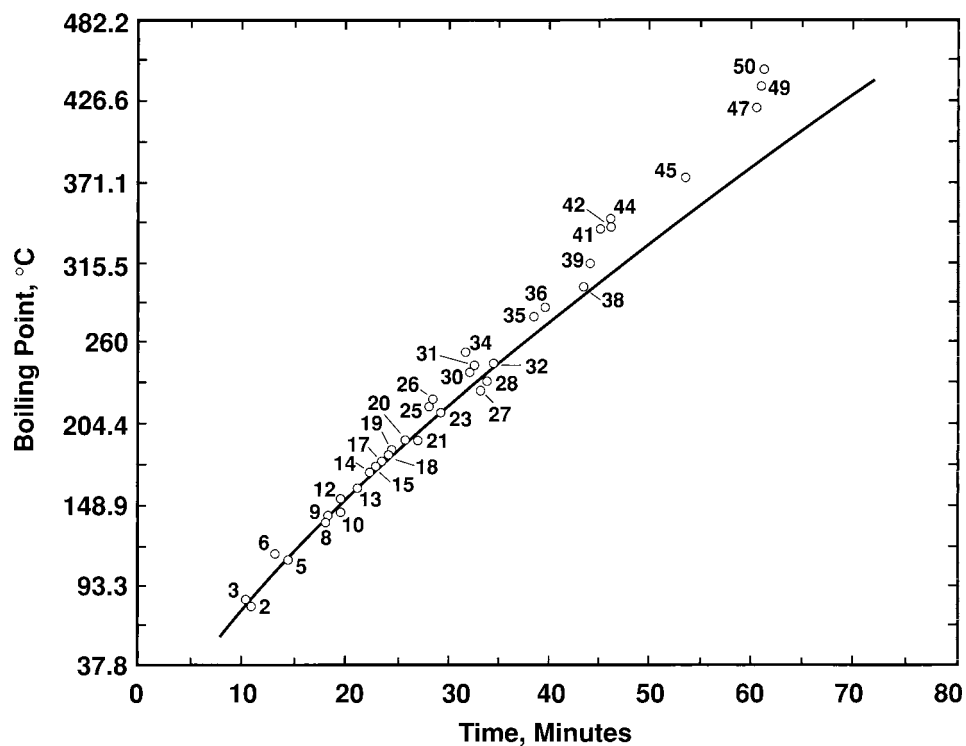


FIG. X1.1 Boiling Point—Retention Time Relationships for Several High-Boiling Multiple-Ring Type Compounds (see Table X1.1)

TABLE X1.1 Compound Identification—Numbered Dots (see Fig. X1.1)

No.	Boiling Point, °C (°F)	Compound	Number	Boiling Point, °C (°F)	Compound
2	80 (176)	benzene	27	227 (441)	di- <i>n</i> -amylsulfide
3	84 (183)	thiophene	28	234 (453)	tri-isopropylbenzene
5	111 (231)	toluene	30	241 (466)	2-methylnaphthalene
6	116 (240)	pyridine	31	295 (473)	1-methylnaphthalene
8	136 (277)	2,5-dimethylthiophene			
9	139 (282)	<i>p</i> -xylene	34	254 (489)	indole
10	143 (289)	di- <i>n</i> -propylsulfide	35	279 (534)	acenaphthene
12	152 (306)	cumene			
13	159 (319)	1-hexahydroindan	38	298 (568)	<i>n</i> -decylbenzene
14	171 (339)	1-decene	39	314 (598)	1-octadecene
15	173 (344)	<i>sec</i> -butylbenzene			
17	178 (352)	2,3-dihydroindene	41	339 (642)	phenanthrene
18	183 (361)	<i>n</i> -butylbenzene	42	342 (647)	anthracene
19	186 (366)	<i>trans</i> -decalin			
20	194 (382)	<i>cis</i> -decalin	44	346 (655)	acridine
21	195 (383)	di- <i>n</i> -propyldisulfide	45	395 (743)	pyrene
23	213 (416)	1-dodecene	47	404 (796)	triphenylene
25	218 (424)	naphthalene	49	438 (820)	naphthacene
26	221 (430)	2,3-benzothiophene	50	447 (837)	chrysene

TABLE X1.2 Deviations of Simulated Distillation Boiling Points From Actual Boiling Points

Compound	Boiling Point, °C (°F) (760 mm)	Deviations from Actual Boiling Point, °C (°F)	
		(760 mm)	(10 mm)
Benzene	80 (176)	+ 3 (+ 6)	- 2 (-4)
Thiophene	84 (183)	+ 4 (+ 7)	+ 1 (+ 2)
Toluene	111 (231)	+ 2 (+ 3)	- 1 (-2)
<i>p</i> -Xylene	139 (282)	0 (0)	+ 2 (+ 4)
1-Dodecene	213 (416)	0 (0)	0 (0)
Naphthalene	218 (424)	- 11 (-20)	- 4 (-8)
2,3-Benzothiophene	221 (430)	- 13 (-23)	0 (0)
2-Methylnaphthalene	241 (466)	- 12 (-21)	- 2 (-3)
1-Methylnaphthalene	245 (473)	- 12 (-21)	- 1 (-1)
Dibenzothiophene	332 (630)	- 32 (-58)	- 6 (-10)
Phenanthrene	339 (642)	- 35 (-63)	- 9 (-16)
Anthracene	342 (647)	- 36 (-64)	- 8 (-15)
Pyrene	395 (743)	- 48 (-87)	- 16 (-29)
Chrysene	447 (837)	- 60 (-108)	^A

^A No data at 10 mm for chrysene.

TABLE X1.3 Distillation of Heavy Gas Oils

Weight Percent Off ^A	Virgin Gas Oil		High-Sulfur Coker Gas Oil		"Decanted" Oil	
	TBP, ^A °C (°F)	SD, ^B °C (°F)	TBP, °C (°F)	SD, °C (°F)	TBP, °C (°F)	SD, °C (°F)
IBP ^C	230 (446)	215 (419)	223 (433)	209 (409)	190 (374)	176 (348)
10	269 (517)	265 (506)	274 (526)	259 (498)	318 (605)	302 (575)
20	304 (580)	294 (562)	296 (565)	284 (544)	341 (645)	338 (640)
30	328 (622)	321 (610)	316 (600)	312 (593)	357 (675)	358 (676)
40	343 (650)	348 (659)	336 (636)	344 (651)	377 (710)	375 (707)
50	367 (693)	373 (704)	356 (672)	364 (688)	390 (734)	391 (736)
60	394 (742)	409 (749)	377 (710)	386 (727)	410 (770)	409 (768)
70	417 (783)	424 (795)	399 (751)	410 (770)	425 (797)	425 (797)
80	447 (836)	451 (844)	421 (800)	434 (814)	445 (833)	443 (830)
90	...	488 (910)	462 (863)	467 (872)	...	469 (876)
95	...	511 (951)	482 (900)	494 (922)	...	492 (918)
100	...	543 (1009)	...	542 (1007)	...	542 (1007)

^A TBP = True boiling point.

^B SD = Simulated distillation boiling point.

^C IBP = Initial boiling point.

X2. AGREEMENT WITH CONVENTIONAL DISTILLATION

X2.1 Test Method **D2892** is the standard for conventional distillation of petroleum products.

X2.2 This test method has been compared with Test Method **D2892** on the same samples by a number of laboratories **(1-3)**⁷. In all cases, agreement between the two test

⁷ The boldface numbers in parentheses refer to the list of references at the end of this standard.

methods has been very good for petroleum products and fractions within the scope of this test method.

X2.3 The time required for analysis by this test method is approximately one tenth of that required for Test Method **D2892**, and Test Method **D2892** has difficulty establishing the IBP and FBP accurately.

X3. CALCULATION ALGORITHM

X3.1 Required Starting Elements

X3.1.1 *Sample Data Array, N Area Slices*—The data must be collected at a minimum sampling frequency of 1 Hz (that is, maximum slice width is 1 s). In addition, the slice width must be such that no sample or solvent elutes in the first five slices.

X3.1.2 *Blank Data Array, N Area Slices*—The slice width for the blank and sample runs must be identical. (A blank data array is not necessary if electronic baseline compensation is used.)

X3.1.2.1 The analysis conditions for blank and sample must be identical through the point where sample analysis is terminated.

X3.1.2.2 The number of slices in the blank array must be equal to or greater than the number of slices in the sample chromatogram. If the number of slices in the blank array is greater than the number of slices in the sample array, then drop the extra slices in the blank array. This situation could occur if

a blank run extended beyond the point where the sample analysis was terminated.

X3.1.3 Retention Times, *n*-Paraffins—The retention time of each *n*-paraffin in the calibration mixture must be obtained from a processed (peak) data file from the analysis of the calibration mixture, run under identical conditions as the samples and blank.

X3.1.4 Boiling Points of *n*-Paraffins—The boiling points of each *n*-paraffin in the calibration mixture (to the nearest whole degree Celsius or Fahrenheit) can be obtained from **Table 2** of this test method.

X3.1.5 Solvent Exclusion Time—The solvent exclusion time is that time when the signal has returned to baseline after elution of the solvent. This parameter is used to exclude area due to the solvent used, if any. If a solvent is used, the detector signal must return to baseline before any sample components start to elute.

X3.2 Subtract Blank from Sample (see **Note X3.1)**

X3.2.1 Subtract each blank area slice from the exactly corresponding sample area slice. This corrects the sample area slices for the blank. (**Warning**—Automatic baseline compensation is available on many instruments and is allowed by this test method. However, automatic baseline compensation may not give the same results as slice-by-slice blank subtraction. On some instruments using automatic baseline compensation, the compensated baseline has been observed to exhibit anomalous features at (or near) the point in the chromatogram where the programmed oven temperature reaches maximum and is held for some period of time. The anomalous feature appears as a slow rise in baseline, followed by a relatively sharp decrease, followed by a level baseline. While the magnitudes of the anomalies observed have been very small (only a few picoamps), the slope of the sharp decrease may be sufficient to meet the criterion for determining the end of sample elution. In such event, this false triggering of the end of sample criterion will result in erroneously high values for the FBP and other percent off values near the FBP. If false triggering occurs and can not be eliminated, the user should disable automatic baseline compensation and perform blank subtractions as described in this appendix.)

NOTE X3.1—If the data was acquired on an instrument using automatic baseline compensation, **X3.2** must be skipped. In this case, the zeroed and bunched sample data array (see **X3.3.3**) contains the corrected area slices to be used in subsequent calculations.

X3.3 Zero and Bunch Data Slices

X3.3.1 Calculate the average of the first five area slices of the blank-subtracted data array.

X3.3.2 Subtract the average slice area (see **X3.3.1**) from each area slice in the blank-subtracted data array. Set negative numbers to zero.

X3.3.3 If the data sampling frequency was 1.5 Hz or greater, bunch (add together) an integral number of area slices to obtain a bunched slice width as close to 1 s as possible. Drop any extra area slices at the end of the sample data array.

NOTE X3.2—As an example, if data was collected at 3 Hz, add the areas of slices 1, 2, and 3 and use the retention time of slice 3. Add the area of

slices 4, 5, and 6 and use the retention time of slice 6. Continue to the end of the data array.

X3.3.4 Calculate the bunched slice width by multiplying the original slice width by the number of slices added to form each bunch.

X3.4 Calculate Total Chromatogram Area

X3.4.1 Starting at the first slice (or the solvent exclusion time if a solvent is used), sum all of the area slices through the last bunched slice.

X3.4.2 Designate this sum as the total chromatogram area.

X3.5 Determine Start of Sample Elution Time

X3.5.1 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 bunched slices first exceeds 0.00001 % of the total chromatogram area (see **X3.4.2**).

X3.5.1.1 For determining 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 bunched slice width (see **X3.3.4**) in seconds.

X3.5.1.2 If $(\langle \text{slice} \rangle_{N+1} - \langle \text{slice} \rangle_N) / (\text{bunched slice width}) > 1E-7 * \text{total chromatogram area}$, then take slice *N*+1 as the start of sample slice.

X3.5.2 Print the retention time corresponding to the start of sample elution.

X3.6 Determine End of Sample Elution Time

X3.6.1 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 bunched slices first exceeds 0.00001 % of the total chromatogram area (see **X3.4.2**).

X3.6.1.1 For determining 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 bunched slice width (see **X3.3.4**) in seconds.

X3.6.1.2 If $(\langle \text{slice} \rangle_{N-1} - \langle \text{slice} \rangle_N) / (\text{bunched slice width}) > 1E-7 * \text{total chromatogram area}$, then take slice *N*-1 as the end of sample slice.

X3.6.2 Print the retention time corresponding to end of sample elution.

X3.7 Calculate Total Corrected Sample Area

X3.7.1 Sum the corrected area slices from start of sample slice (see **X3.5.1.2**) to end of sample slice (see **X3.6.1.2**).

X3.7.2 Designate this sum as the total corrected sample area, and save for subsequent calculations.

X3.8 Normalize to Area Percent

X3.8.1 Starting at the start of sample slice (see **X3.5.1.2**) and continuing to the end of sample slice (see **X3.6.1.2**), divide each corrected area slice by the total corrected sample area (see **X3.7.2**) and multiply by 100.

X3.8.2 Save these normalized area percents in an array for subsequent calculations.

X3.9 Find Retention Time Corresponding to Percent Off

X3.9.1 For each X (where $X = 0.5, 1, 2, \dots, 98, 99, 99.5$), find the retention time corresponding to X percent off.

X3.9.1.1 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 X3.3—The cumulative area percent of a given slice is the sum of the normalized area percents from the start of sample slice through the given slice.

X3.9.1.2 For the slice ($N+1$) determined above, the following inequality should hold:

$$CA_N \leq X \leq CA_{N+1} \quad (X3.1)$$

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 $N+1$.

X3.9.1.3 Calculate the fraction (f) of normalized area percent in slice ($N+1$) needed to give exactly X percent off as follows:

$$f = (X - CA_N) / A_{N+1} \quad (X3.2)$$

where:

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

X3.9.1.4 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:

$$RT_X = (N+f) \times \text{bunched slice width} \quad (X3.3)$$

X3.10 Convert Retention Times to Boiling Points

X3.10.1 For each retention time found in X3.9.1, calculate the boiling point equivalent to that retention time.

X3.10.1.1 Find the pair of calibration compound retention times that are closest to and bracket the percent off retention time of interest.

X3.10.1.2 Calculate the boiling point corresponding to the percent off retention time as follows:

$$BP_i = (((BP_2 - BP_1) / (RT_2 - RT_1)) \times (RT_i - RT_1)) + BP_1 \quad (X3.4)$$

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 X3.4—A report giving percent off at selected boiling point intervals can be calculated in an analogous manner.

X3.11 Reporting Results

X3.11.1 Report the IBP, the temperatures corresponding to 1 to 99 % off, and the FBP to the nearest whole degree Fahrenheit or nearest half degree Celsius.

X4. CALCULATION OF D86 CORRELATED DATA FROM D2887 DATA

X4.1 Correlations

X4.1.1 The resulting data obtained from carrying out an analysis by Test Method D2887 can be used to obtain Test Method D86 data via a correlation. The correlations used to convert selected Test Method D2887 distillation points (percent off) to Test Method D86 (percent off) are mathematical equations. There are two correlations presented in this appendix: the STP 577 correlation and the API correlation.

X4.2 STP 577 Correlation

X4.2.1 The correlation that has been used for a number of years is called the Atlantic Richfield correlation, which was published in an ASTM Special Technical Publication (STP 577) (4). See Table X4.1.

X4.2.2 The application of this correlation was also published by Kennard (5), which showed how the correlation can be optimized for a particular type of sample.

X4.2.3 This correlation has not been subjected to recent ASTM statistical treatment since its origin precedes the newer

TABLE X4.1 STP 577 Correlation

D86-IBP	46.566 + 0.58289 (D2887 10 %) + 0.34795 (D2887 IBP)
D86-10 %	33.308 + 0.61562 (D2887 10 %) + 0.35110 (D2887 20 %)
D86-20 %	22.411 + 0.48903 (D2887 30 %) + 0.27528 (D2887 20 %) + 0.21713 (D2887 10 %)
D86-30 %	14.431 + 0.47035 (D2887 30 %) + 0.28369 (D2887 20 %) + 0.22784 (D2887 50 %)
D86-50 %	4.876 + 0.97597 (D2887 50 %)
D86-70 %	0.911 + 0.51975 (D2887 80 %) + 0.33260 (D2887 70 %) + 0.10159 (D2887 30 %)
D86-80 %	0.279 + 0.75936 (D2887 80 %) + 0.28333 (D2887 95 %) - 0.09975 (D2887 FBP)
D86-90 %	-1.973 + 0.61459 (D2887 90 %) + 0.31909 (D2887 95 %)
D86-FBP	34.179 + 1.14826 (D2887 95 %) - 0.59208 (D2887 90 %) + 0.31542 (D2887 FBP)

statistical methodologies. However, a limited number of comparisons of the use of the correlation is presented in Reference (4).

X4.3 API Correlation

X4.3.1 A second correlation that has been used is the API Procedure 3A3.2 (see Reference (6)).

X5. CORRELATION FOR JET AND DIESEL FUEL

X5.1 The resulting data obtained from carrying out an analysis by Test Method D2887 can be used to obtain Test Method D86 data via a correlation. The correlations used to convert selected Test Method D2887 distillation points (percent off) to Test Method D86 (percent off) are mathematical equations.

X5.2 A correlation model is presented here for the calculation of Test Method D86 correlated data from boiling range distribution analysis by gas chromatography according to Test Method D2887. This correlation model is only valid for diesel and jet fuels, excluding biodiesels.

X5.3 This correlation model was validated by an analysis of variance procedure in accordance with Practice D6708.

X5.4 Significance and Use

X5.4.1 Valid data for conversion to Test Method D86 correlated data can be obtained by Test Method D2887. The model is only valid for diesel or jet fuel and samples must meet the specifications given in Test Method D2887.

X5.5 Summary of the Procedure

X5.5.1 Test Method D86 correlated data is calculated from Test Method D2887 data using Eq X5.1 and the coefficients specified in Table X5.1.

$$t_n = a_0 + a_1 \cdot T_{n-1} + a_2 \cdot T_n + a_3 \cdot T_{n+1} \quad (\text{X5.1})$$

where:

t_n = n th boiling point temperature of Test Method D86 correlated,

a_i = i th coefficient from Table X5.1, and
 T_n = n th boiling point temperature of D2887.

X5.6 Basis

X5.6.1 This correlation model is based on data for 46 jet fuel samples and 39 diesel fuel samples analyzed in accordance with both Test Method D86 and D2887. From these results, a correlation model was determined using regression, specifying coefficients per recovery. A model of the remaining bias was determined by use of Practice D6708 on a dataset from the ASTM Interlaboratory Crosscheck Program of five jet fuels and six diesels analyzed by 38 laboratories by Test Method D2887 and 201 laboratories by Test Method D86.

X5.6.2 The bias correction model was used to correct the results from the correlation model, resulting in a new correlation matrix given in Table X5.1.

X5.6.3 Based on statistical significance tests, no sample specific biases were observed in the dataset used for the bias correction.

X5.6.4 Both methods were found sufficiently precise to distinguish among the samples.

X5.6.5 *Precision and Bias*⁸—Reproducibility after conversion of Test Method D2887 data into Test Method D86 data is equivalent to the reproducibility of Test Method D2887.

X5.6.6 Cross-method reproducibility after conversion of Test Method D2887 data into Test Method D86 correlated data is given in Table X5.2.

⁸ Supporting data have been filed at ASTM International Headquarters, and may be obtained by requesting Research Reports D02-1553 and D02-1564.

TABLE X5.1 Correlation Coefficients

t_n °C	a_0	a_1	a_2	a_3	T_{n-1}	T_n °C	T_{n+1}
IBP	25.351	0.32216	0.71187	-0.04221	T_{IBP}	T_5	T_{10}
5 %	18.822	0.06602	0.15803	0.77898	T_{IBP}	T_5	T_{10}
10 %	15.173	0.20149	0.30606	0.48227	T_5	T_{10}	T_{20}
20 %	13.141	0.22677	0.29042	0.46023	T_{10}	T_{20}	T_{30}
30 %	5.7766	0.37218	0.30313	0.31118	T_{20}	T_{30}	T_{50}
50 %	6.3753	0.07763	0.68984	0.18302	T_{30}	T_{50}	T_{70}
70 %	-2.8437	0.16366	0.42102	0.38252	T_{50}	T_{70}	T_{80}
80 %	-0.21536	0.25614	0.40925	0.27995	T_{70}	T_{80}	T_{90}
90 %	0.09966	0.24335	0.32051	0.37357	T_{80}	T_{90}	T_{95}
95 %	0.89880	-0.09790	1.03816	-0.00894	T_{90}	T_{95}	T_{FBP}
FBP	19.444	-0.38161	1.08571	0.17729	T_{90}	T_{95}	T_{FBP}

TABLE X5.2 Cross-Method Reproducibility, °C

	IBP	5 %	10 %	20 %	30 %	50 %	70 %	80 %	90 %	95 %	FBP
R °C	13.71	11.80	10.73	8.83	7.39	6.96	7.03	7.62	8.85	17.32	12.94

X6. ACCELERATED TEST METHOD D2887

X6.1 This section has been added to the test method to provide guidance for carrying out Test Method D2887 in an accelerated mode. Without instrumental adaptation, it is possible to significantly reduce analysis times. The term accelerated is used here to distinguish this technique from fast chromatography, which requires direct heating of the column only.

X6.2 The development of gas chromatographic ovens, which allow reproducible heating rates from 10 to 35°C/min, allows the chromatography to be carried out in shorter periods of time, by decreasing the run time from about 20 min to 8 to 9 min. Two sets of typical operating conditions are provided in **Table X6.1**.

X6.3 **Figs. X6.1 and X6.2** show chromatograms of the retention time standard analyzed at an oven-heating rate of 35°C/min with Columns 2 and 1, respectively.

X6.4 **Figs. X6.3 and X6.4** show chromatograms of the reference gas oil eluting in about 8 min for Columns 2 and 1, respectively.

X6.5 **Table X6.2** shows the results obtained by analyzing the reference gas oil in three different instruments by injecting the reference gas oil in duplicate by three different operators utilizing Column 2. **Table X6.2** also shows the comparison of the reference gas oil values obtained under accelerated condi-

TABLE X6.1 Typical Operating Parameters for Accelerated Test Method D2887

	Column 1	Column 2
Column length (m)	10	5
Column ID (mm)	0.53	0.53
Stationary phase thickness (μm) ^A	0.88	2.65
Carrier gas	helium	helium
Carrier gas flow rate (mL/min)	26	35
Initial column temperature (°C)	40	40
Final column temperature (°C)	360	350
Oven programming rate (°C/min)	35	35
Detector	FID	FID
Detector temperature (°C)	360	360
Injector	cold on-column	cold on-column
Injector initial temperature (°C)	100	100
Injector programming rate (°C/min)	35	35
Injector final temperature (°C)	360	350
Sample size (μL)	0.1	0.1
Dilution concentration	neat	neat
Analysis time (minutes)	8	7.8

^A All columns contain a polydimethylsiloxane stationary phase.

tions with the results listed in Test Method D2887 as shown in the column labeled Delta which tabulates the difference. From the average of the duplicate runs, the repeatability standard deviation is given in **Table X6.2**. This temporary repeatability standard deviation is determined so as to comply with Section A.21.2.3 of the *Form and Style Manual for ASTM Standards*. Final repeatability and reproducibility precision will be available on or before 2010 by completing an interlaboratory study.

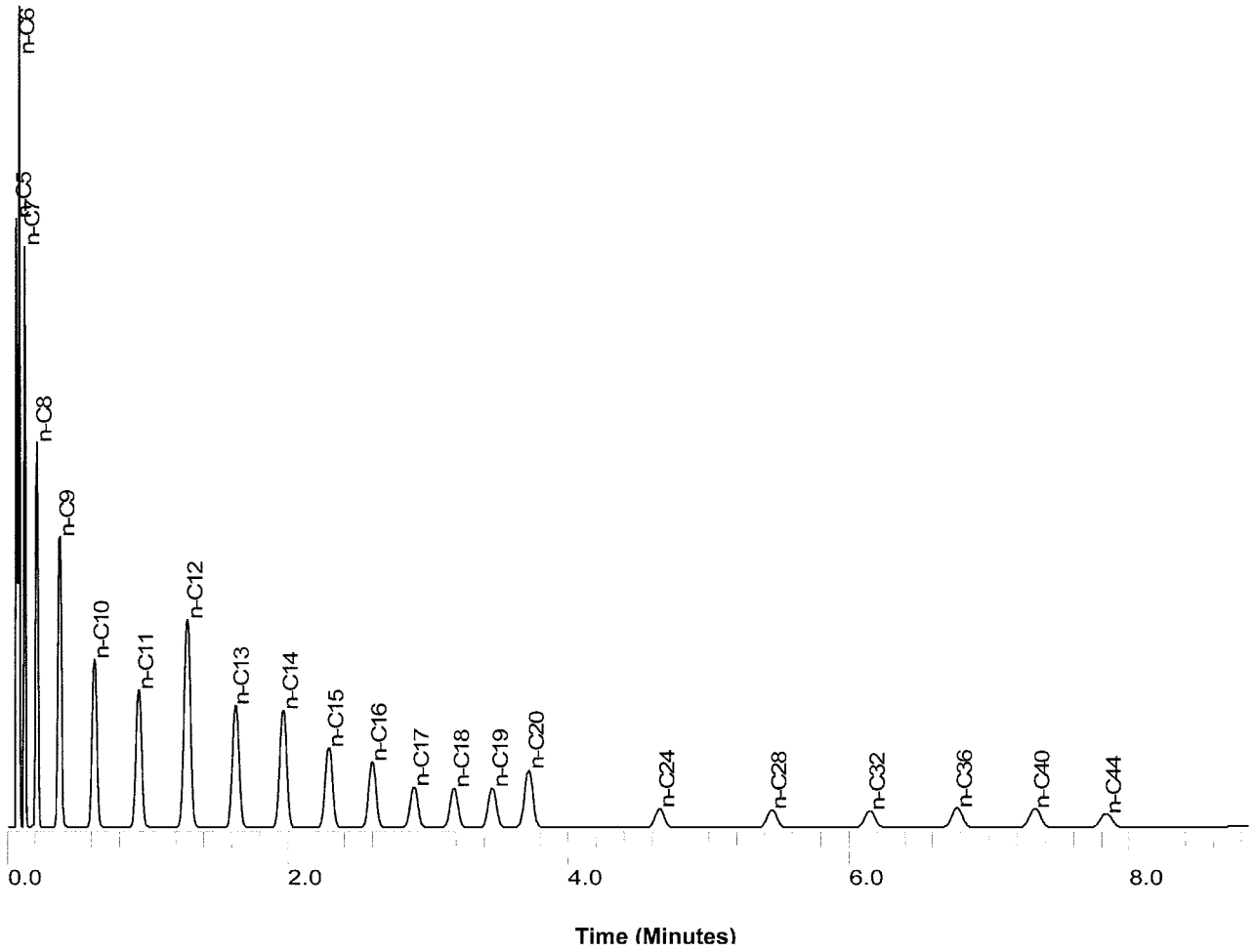


FIG. X6.1 Retention Time Standard (Column 2)

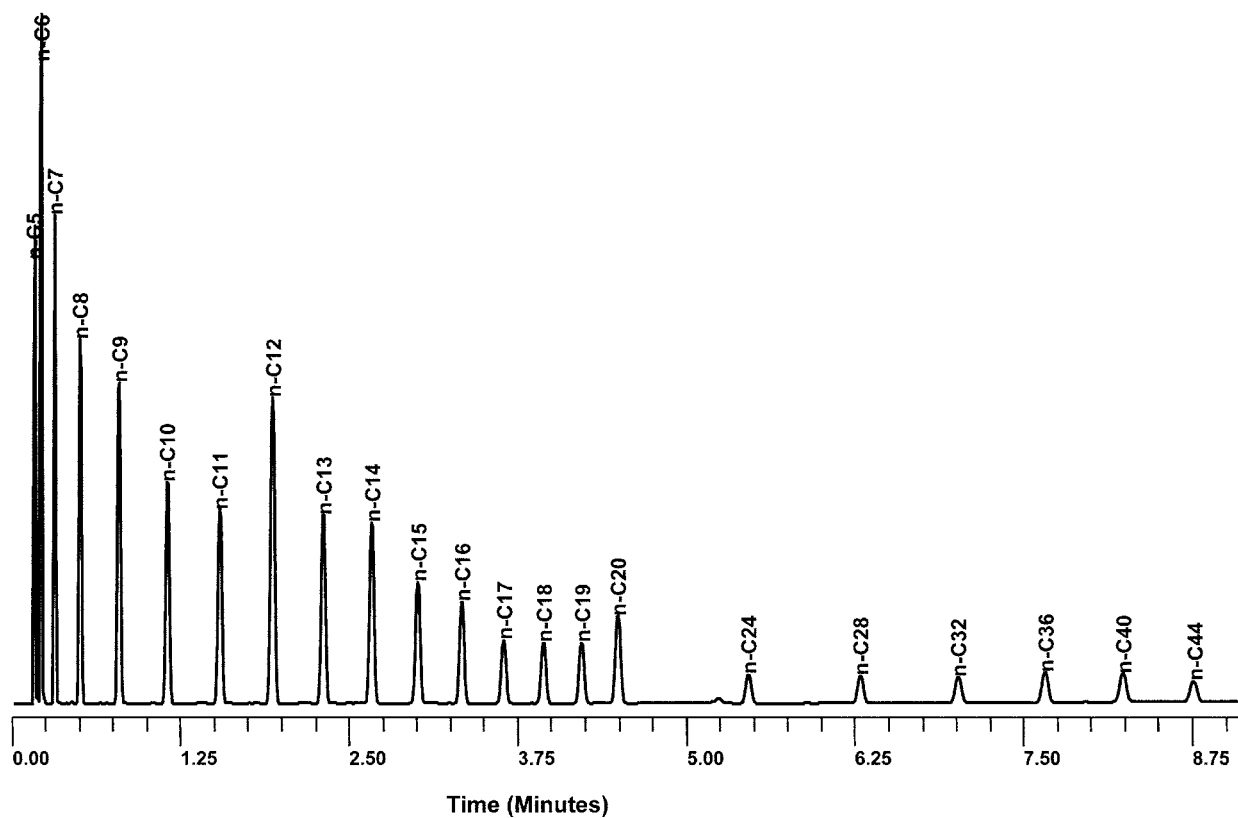


FIG. X6.2 Retention Time Standard (Column 1)

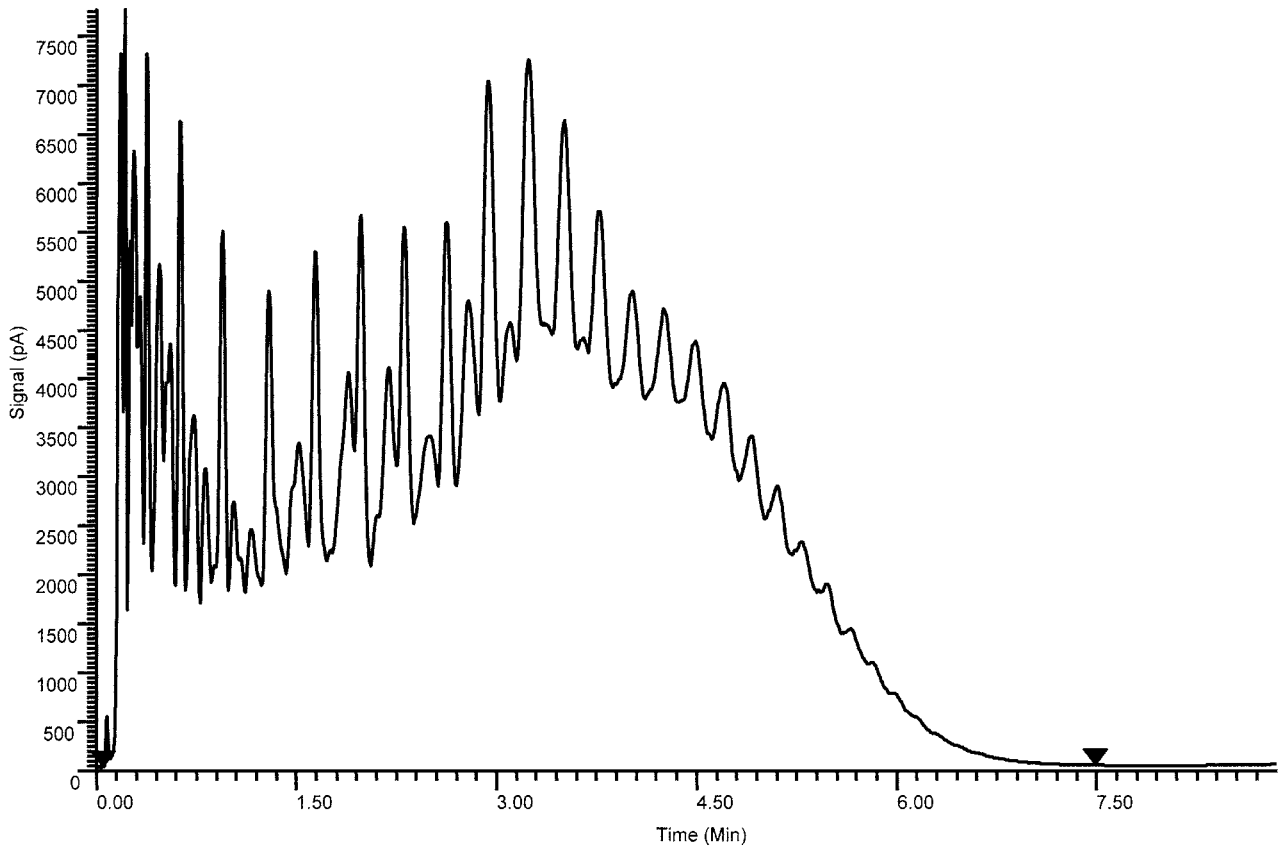


FIG. X6.3 Analysis of the Reference Gas Oil Under Accelerated Conditions (Column 2)

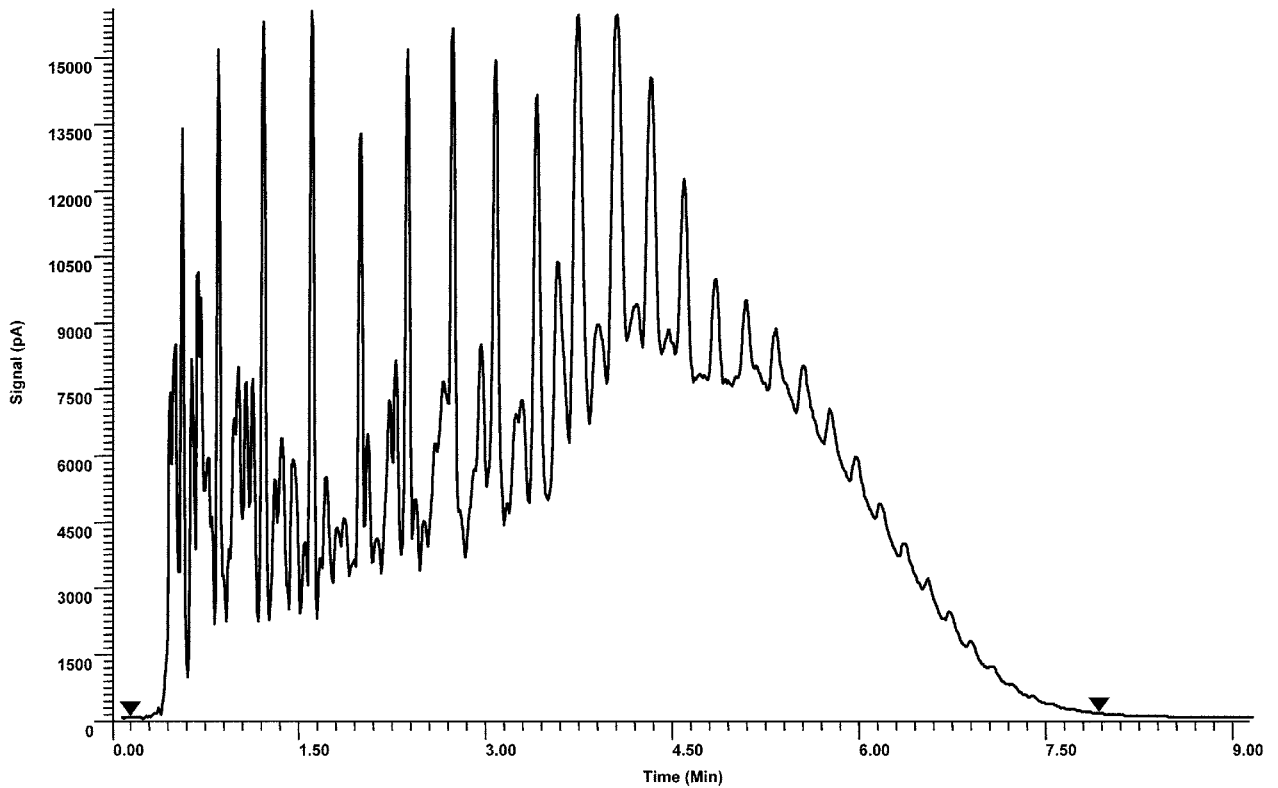


FIG. X6.4 Analysis of the Reference Gas Oil Under Accelerated Conditions (Column 1)

TABLE X6.2 Boiling Point Distribution (°F) Results Obtained for the Reference Gas Oil (Batch 2) Using an Accelerated Mode (Column 2)

% Off	BP (°F)	Repeatability Std Deviation		Accepted Reference Gas Oil Values		Delta Values
		(°F)	(°C)	(°F)	(°F)	(°F)
IBP	236.3	1.5	0.8	240		-3.7
5	304.3	1.2	0.7	304		0.3
10	348.2	1.4	0.8	348		0.2
15	393.9	1.2	0.7	393		0.9
20	436.3	2.0	1.1	435		1.3
25	470.9	2.9	1.6
30	500.3	2.3	1.3	499		1.3
35	527.7	2.3	1.3
40	554.4	1.1	0.6	552		2.4
45	577.1	2.1	1.2
50	595.3	2.0	1.1	594		1.3
55	611.4	2.8	1.6
60	630.1	1.6	0.9	629		1.1
65	649.9	1.7	1.0	649		0.9
70	669.8	1.5	0.8	668		1.8
75	691.5	1.4	0.8	690		1.5
80	713.8	1.1	0.6	712		1.8
85	737.9	0.9	0.5	736		1.9
90	765.6	1.4	0.8	764		1.6
95	804.1	1.7	1.0	803		1.1
FBP	887.6	3.7	2.0	888		-0.4

X7. PREVIOUS CHANGES

X7.1 Subcommittee D02.04 has identified the location of selected changes to this standard since the last issue (D2887-01a) that may impact the use of this standard.

X7.1.1 Changes:

(1) Corrected selected Fahrenheit boiling point values in **Table 2** and added a note explaining the derivation of the corrected values.

(2) Corrected Footnote A in **Table 2**.

(3) Removed Column Resolution requirement.

(4) Added **Appendix X3**, Calculation Algorithm.

(5) Corrected rate of change of chromatographic signal in **Note 8**.

(6) Modified paragraph **6.1.5** to address inlet pressure for open tubular columns.

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- (2) Hickerson, J. F., *ASTM STP 577M*, ASTM International, 1973, p. 71.
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- (5) Kennard, C., "Correlated ASTM Distillation Distribution Based on Simulated Distillation (ASTM D2887) Data," Hewlett Packard, Avondale, PA, Application Note AN230-5, April 1979.
- (6) API Technical Data Book for Petroleum Refining, Chapter 3, Petroleum Fraction Distillation Interconversions, 1999.

SUMMARY OF CHANGES

Subcommittee D02.04.0H has identified the location of selected changes to this standard since the last issue (D2887–06a) that may impact the use of this standard.

- (1) Added **Note 1**.
- (2) Replaced 55°C with 55.5°C in **1.1**.
- (3) Revised **10.3**.
- (4) Revised **10.4.1**.

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