Designation: D7798 – 13

StandardTest Method for
Boiling Range Distribution of Petroleum Distillates with Final Boiling Points up to 538°C by Ultra Fast Gas Chromatography (UF GC)[1]

This standard is issued under the fixed designation D7798; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the boiling range distribution of petroleum products and biodiesel formulations, B5, B10, and B20. It is applicable to petroleum distillates having a final boiling point not greater than 538°C or lower at atmospheric pressure as measured by this test method. The difference between the initial boiling point and the final boiling point shall be greater than 55°C.

1.2 The test method is not applicable for analysis of petroleum distillates containing low molecular weight components (for example naphthas, reformates, gasolines, full range crude oils). Materials containing heterogeneous mixtures (for example, alcohols, ethers, acids or esters, except biodiesels) or residue are not to be analyzed by this test method. See Test Methods D3710, D7096, D6352, or D7169.

1.3 This test method uses the principles of simulated distillation methodology. This test method uses gas chromatographic components that allow the entire analysis from sample to sample to occur in 5 min or less. In these instruments the column is heated directly at rates 10–15 times that of a conventional gas chromatograph and thus the analysis time is reduced from sample to sample.

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

1.4.1 *Exception*—Appendix X1 includes temperatures in Fahrenheit for information only.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

D1160 Test Method for Distillation of Petroleum Products at Reduced Pressure

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

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)[3]

D4626 Practice for Calculation of Gas Chromatographic Response Factors

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

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

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

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

E355 Practice for Gas Chromatography Terms and Relationships

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

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

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[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] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

3. Terminology

3.1 *Definitions:*

3.1.1 This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E355, E594, and E1510.

3.1.2 *area slice, n—in gas chromatography*, the area, resulting from the integration of the chromatographic detector signal, within a specified retention time interval.

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

3.1.4 *cumulative corrected area, n—in gas chromatography*, the accumulated sum of corrected area slices from the beginning of the analysis through to a given retention time, ignoring any non-sample areas (for example, solvent peak area).

3.1.5 *Final Boiling Point (FBP), n—in gas chromatography*, 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.

3.1.6 *Initial Boiling Point (IBP), n—in gas chromatography*, 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.

3.1.7 *slice rate, n—in gas chromatography*, the time interval used to integrate the continuous (analog) chromatographic detector response during an analysis, expressed in Hz.

3.1.7.1 *Discussion*—for example, integrations or slices per second.

3.1.8 *slice time, n—in gas chromatography*, the time duration of the slice, in seconds. The slice time is the time at the end of each contiguous area slice.

3.1.9 *total sample area, n—in gas chromatography*, the cumulative corrected area, from the initial area point to the final area point.

3.2 *Abbreviations:*

3.2.1 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, n-C_{10} normal decane; iC_{14} = iso tetradecane).

4. Summary of Test Method

4.1 The boiling range distribution of hydrocarbon fractions obtained by physical distillation is simulated by the use of gas chromatography (GC). The GC column heating is accomplished by supplying heat to the column directly instead of an oven with a consequence that the elution time is considerably shortened. Thus, cycle times of 5 min or less (heating and cooling) is achieved. A non-polar capillary gas chromatographic column is used to separate the hydrocarbon compo-

nents of the sample and cause them to elute in order of increasing boiling point.

4.2 Depending on the analyzer and column used, a sample aliquot is diluted with a viscosity reducing solvent or introduced neat into the chromatographic system. Sample vaporization is provided by separate heating of the point of injection or in conjunction with column oven heating.

4.3 The column temperature is raised at a reproducible linear rate to effect separation of the hydrocarbon components in order of increasing boiling point. The elution of sample components is quantitatively determined using a flame ionization detector. The detector signal integral is recorded as area slices for consecutive retention time intervals during the analysis.

4.4 Retention times of known normal paraffin hydrocarbons, spanning the scope of the test method (C_5–C_{44}), are determined and correlated to their boiling point temperatures. (Refer to Table 1.) The normalized cumulative corrected sample areas for each consecutive recorded time interval are used to calculate the boiling range distribution. The boiling point temperature at each reported percent off increment is calculated from the retention time calibration.

5. Significance and Use

5.1 The boiling range distribution of petroleum distillate fractions provides an insight into the composition of feed stocks and products related to petroleum refining processes. A major advantage of the fast analysis time obtained by this test method is increasing product through put and reduced lab testing time by a minimum factor of 3. This gas chromatographic determination of boiling range may be used to replace conventional distillation methods for control of refining operations and 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 chromatographic system used shall have the following performance characteristics:

6.1.1 *Column Heating Assembly*—Capable of sustaining a programmed temperature operation from 40°C up to 400°C.

6.1.2 *Column Temperature Programmer*—The column should be capable of linear programmed temperature operation up to 400°C at selectable linear rates from a minimum of 60°C/min up to 350°C/min. The programming rate shall be sufficiently reproducible to obtain the retention time repeatability for the mixture described in 7.6.

6.1.3 *Detector*—This test method requires a flame ionization detector (FID). The detector shall meet or exceed the following specifications as detailed in Practice E594. The flame jet should have an orifice of approximately 0.018 inches or 0.45 mm or as specified by the manufacturer.

6.1.3.1 Operating Temperature approximately 380–400°C.

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

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

[A] API Project 44, October 31, 1972 is believed to have provided the original normal paraffin boiling point data that are listed in Table 1. However, over the years some of the data contained in both API Project 44 (Thermodynamics Research Center Hydrocarbon Project) and Test Method D2887 have changed, and they are no longer equivalent. Table 1 represents the current normal paraffin boiling point values accepted by Subcommittee D02.04 and found in all test methods under the jurisdiction of Section D02.04.0H.

[B] Test Method D2887 has traditionally used n-paraffin boiling points rounded to the nearest whole degree for calibration. The boiling points listed in Table 1 are correct to the nearest whole number in both degrees Celsius and degrees Fahrenheit. However, if a conversion is made from one unit to the other and then rounded to a whole number, the 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.

6.1.3.2 Sensitivity >0.005 coulombs/ g carbon.

6.1.3.3 Minimum Detectability 1×10^{-12} g carbon / s for n-C_{13}.

6.1.3.4 Linear Range >10^6.

6.1.3.5 Connection of the column to the detector shall be such that no temperature below the column inlet temperature exists. Refer to E1510 for proper installation and conditioning of the capillary column.

6.1.4 *Sample Inlet System*—Any sample inlet system capable of operating continuously at a temperature equivalent to the maximum column temperature employed. Programmed temperature vaporization (PTV) and programmable cool on-column injection and split injection systems have been used successfully. Table 2 gives some examples of operating conditions of commercially available instrumentation. The inlet should be capable to continuously deliver the sample components in to the column by maintaining the temperature higher than the column temperature.

6.1.5 *Carrier Gas Flow Control*—The chromatograph shall be equipped with carrier gas pressure or flow control capable of maintaining constant carrier gas flow control through the column throughout the column temperature program cycle. The flow shall not vary by more than 1 % from the initial temperature to the end column temperature.

6.2 *Microsyringe*—Syringes of 0.1 to 5 µL capacity are suitable for this test method. Consult manufacturer for specific details on requirements for syringes compatible with autosampler and injection technique used.

6.2.1 Automatic syringe injection is required to achieve best precision.

6.3 *Column*—This test method is limited to the use of non-polar wall coated open tubular (WCOT) columns of high thermal stability. Fused silica, and stainless steel columns, with a 0.32–0.18 mm inside diameter have been successfully used. Cross-linked or bonded 100 % dimethyl-polysiloxane stationary phases with film thickness of 0.1 to 1.0 µm have been used. It is required that the choice of these two variables (column i.d. and phase thickness) allow the elution of C_5 to C_{44} during the temperature programming phase of the column. The column and conditions shall provide separation of typical petroleum hydrocarbons in order of increasing boiling point and meet the column resolution requirements of 8.2.1. The column shall provide a resolution of at least three (3) using the test method operating conditions. Table 2 gives some examples of columns used successfully.

6.4 *Data Acquisition System:*

6.4.1 *Computer*—Means shall be provided for determining the accumulated area under the chromatogram. This can be done by means of a computer based chromatography data system. The computer system shall have normal chromatographic software for measuring the retention time and areas of eluting peaks (peak detection mode). In addition, the system shall be capable of converting the continuously integrated detector signal into area slices of fixed duration (area slice mode). These contiguous area slices, collected for the entire analysis, are stored for later processing. Gas Chromatographs with analog to digital conversion of the detector signal, shall be operated within the linear range of the detector/electrometer system used. Since the chromatogram is developing in a very short time and since the peaks elute at a fast rate, it is necessary to acquire the signals at 50–100 hz.

7. Reagents and Materials

7.1 *Carrier Gas*—Helium, or hydrogen of high purity (99.999 %) have been used as shown in Table 2. (**Warning**—See Notes 1 and 2.) Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available pressure shall be sufficient to ensure a constant carrier gas flow rate.

TABLE 2 Examples of UFGC Operating Conditions and Column Assembly Heating Types

Parameters	Instrument A	Instrument B	Instrument C
	Resistively heated columns	Resistively heated columns	Resistively heated columns
Inlet Temperature	Programmable TPI; 100°C to 360°C @ 300°C/min-1.0 min	Split: Split ratio 50:1- 150:1 350°C	Split/Splitless 0.4 min purge delay
Auto sampler	required	required	required
Data collection	100 Hz	100 Hz	100 Hz
Column	4 m-0.25 mm-0.25 μ pdms	2 m-0.32 mm-0.20 μ pdms	5 m-0.53 mm-2.65 μ pdms
Inlet/FID Transfer Lines	360°C	350°C	340°C
Flow conditions	4 ml/min	1 ml/min	9 ml/min
Make-up gas	25 ml/min		25 ml/min
Detector	Flame Ionization 400°C	Flame Ionization 350°C	Flame Ionization 380°C
Column program	40° to 360° at 160°C/min-1min	40°C-375°C at 60°C/min	40° (0.5 min) to 240°C at 100°C/min then 340°C at 100°C/min-0.5 min
Equilibration time	2 min	1.5 min	2 min
Sample size	0.2 μl	0.3-0.08 μl	0.2 μl
Sample dilution	2 % in CS_2	2 % in CS_2 up to neat	neat
Calibration dilution	1 % total solids in CS_2	0.1 wt/w % each component in CS_2	1 % total solids in CS_2
Carrier	He	H_2	He

NOTE 1—**Warning:** Helium and Hydrogen are compressed gases under high pressure.

NOTE 2—**Warning:** Hydrogen is an extremely flammable gas.

7.2 *Hydrogen*—Hydrogen of high purity (99.999 %) is used as fuel for the flame ionization detector (FID). (**Warning—**See Note 2.)

7.3 *Air*—High purity (for example hydrocarbon free) compressed air is used as the oxidant for the flame ionization detector (FID). (**Warning—**See Note 3.)

NOTE 3—**Warning:** Compressed air is a gas under high pressure and supports combustion.

7.4 *Solvents*—Unless otherwise indicated, it is intended that all solvents conform to the specifications of the committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used provided it is first ascertained that the solvent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. The polar solvent used to dissolve the sample shall not interfere with any of the peaks of the sample components.

7.4.1 *Carbon Disulfide (CS_2)*—(99+ % pure) may be used as a viscosity reducing solvent and as a means of reducing mass of sample introduced onto the column to ensure linear detector response and reduced peak skewness. It is miscible with hydrocarbons and provides a relatively small response with the FID. The quality (hydrocarbon content) should be determined by this test method prior to use as a sample diluent. (**Warning—**See Note 4.)

NOTE 4—**Warning:** Carbon disulfide is extremely flammable and toxic.

7.5 *Cyclohexane (C_6H_{12})*—(99+ % pure) may be used as a viscosity reducing solvent. It is miscible with hydrocarbons; however, it has a high response to the FID. Use Cyclohexane for the retention time solvent only The quality (hydrocarbon content) should be determined by this test method prior to use as a sample diluent. (**Warning—**See Note 5.)

NOTE 5—**Warning:** Cyclohexane is flammable.

7.6 *Calibration Mixture*—A qualitative mixture of n-paraffins (nominally C_5 to C_{44}) dissolved in a suitable solvent. The concentration is adjusted for the injection technique used (for example, direct injection, PTV split etc). For direct injections approximately one part of n-paraffin mixture to one hundred parts of solvent may be satisfactory. At least one compound in the mixture shall have a boiling point lower than the initial boiling point of the sample being analyzed, as defined in the scope of this test method (1.1). 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.

7.7 *Response Linearity Mixture*—If the calibration mixture is prepared quantitatively it may be used to determine the linearity of the detector. Alternatively, response and injection discrimination over the boiling range of interest may be tested with a mixture of at least two petroleum oils which yield a baseline gap between the two to allow relative determination of concentration. The two fractions that constitute the blend should contain no aromatic components.

7.8 *Reference Material*—The Reference Gas Oil (RGO) whose values are listed in D2887 is used in this test method. Depending on the analyzer and the columns used, either a neat sample or a solution in CS_2 is used. Solutions of the RGO are made and chromatographed and it is a requirement that the reference Boiling Point values be obtained (see D2887 TableX) in order to proceed with sample analysis.

8. Preparation of Apparatus

8.1 *Gas Chromatograph Setup:*

8.1.1 Place the gas chromatograph and ancillary equipment into operation in accordance with the manufacturer's instructions. Recommended operating conditions for several approaches used for ultra fast gas chromatographs are shown in Table 2.

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[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 *Analar 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.

8.1.2 When attaching the column to the detector inlet, ensure that the end of the column terminates as close as possible to the FID jet. Follow the instructions in E1510 or as specified by the manufacturer.

8.1.3 The FID should be periodically inspected and, if necessary, remove any foreign deposits formed in the detector from combustion of silicone liquid phase or other materials. Such deposits will change the response characteristics of the detector.

8.1.4 The inlet liner and initial portion of the column shall be periodically inspected and replaced if necessary to remove extraneous deposits or sample residue.

8.1.5 *Column Conditioning*—A new column will require conditioning at the upper test method operating temperature to reduce or eliminate significant liquid phase bleed, resulting in a stable chromatographic baseline. Follow the guidelines outlined in E1510 or as suggested by manufacturer. Columns may also be conditioned by repeated blank cycles until the baseline as stabilized and quality control reference samples are within specifications.

8.2 *System Performance Specification:*

8.2.1 *Column Resolution*—The column resolution, influenced by both the column physical parameters and operating conditions, affects the overall determination of boiling range distribution. Resolution is therefore specified to maintain equivalence between different systems (laboratories) employing this test method. Resolution is determined using Eq 1 and the C_{16} and C_{18} n-paraffins from a calibration mixture analysis (see 7.6). Resolution (R) should be at least three (3) using the

identical conditions employed for sample analyses. An example illustrating the use of this calculation is shown in Fig. 4.

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

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.

8.2.2 *Detector Response Calibration*—This test method assumes that the FID response to petroleum hydrocarbons is proportional to the mass of individual components. This shall be verified when the system is put in service, and whenever any changes are made to the system or operational parameters. Analyze the response linearity mixture (7.7) using the identical procedure to be used for the analysis of samples (Section 9). Calculate the relative response factor for each n-paraffin (relative to n-eicosane, C_{20}) as per Practice D4626 and Eq 2:

$$F_n = (M_n\ \ /A_n)/(M_{20}\ \ /A_{20}) \tag{2}$$

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_{20} = mass of the n-eicosane in the mixture, and
A_{20} = peak area of the n-eicosane in the mixture.

The relative response factor (F_n) of each n-paraffin shall not deviate from unity by more than ±5 %.
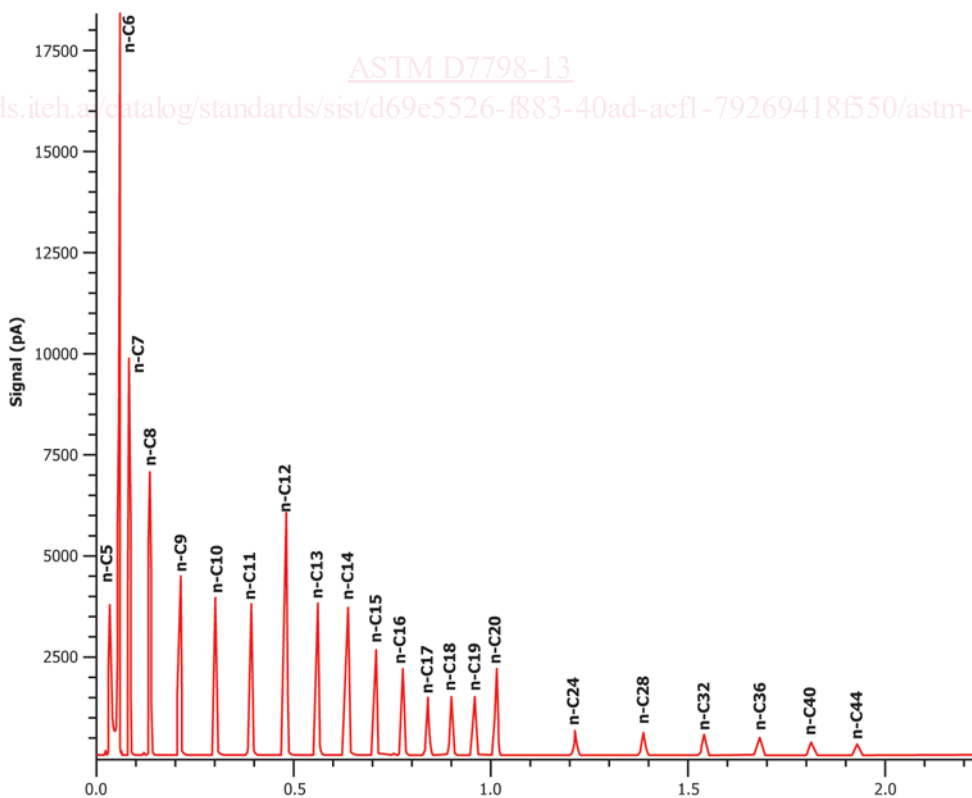

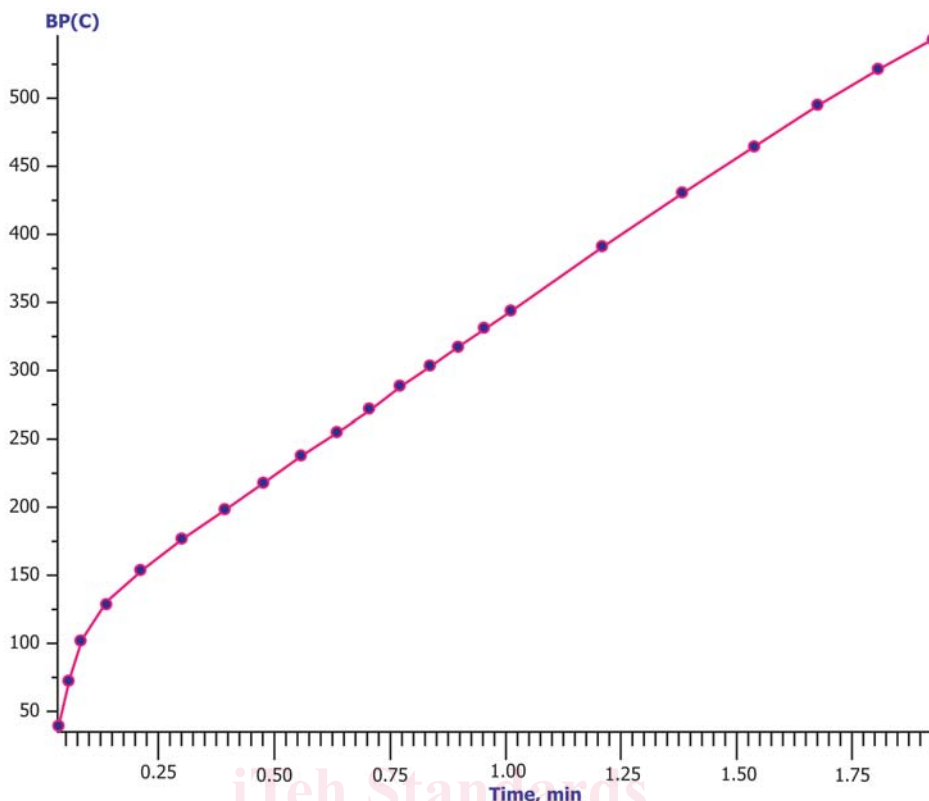FIG. 1 Calibration Chromatogram Obtained at 200°C/Min

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FIG. 2 Example Boiling Point Calibration Plot Obtained from an Ultra Fast Gas Chromatogram

$H_{10\%}$ PEAK HEIGHT AT 10% HEIGHT

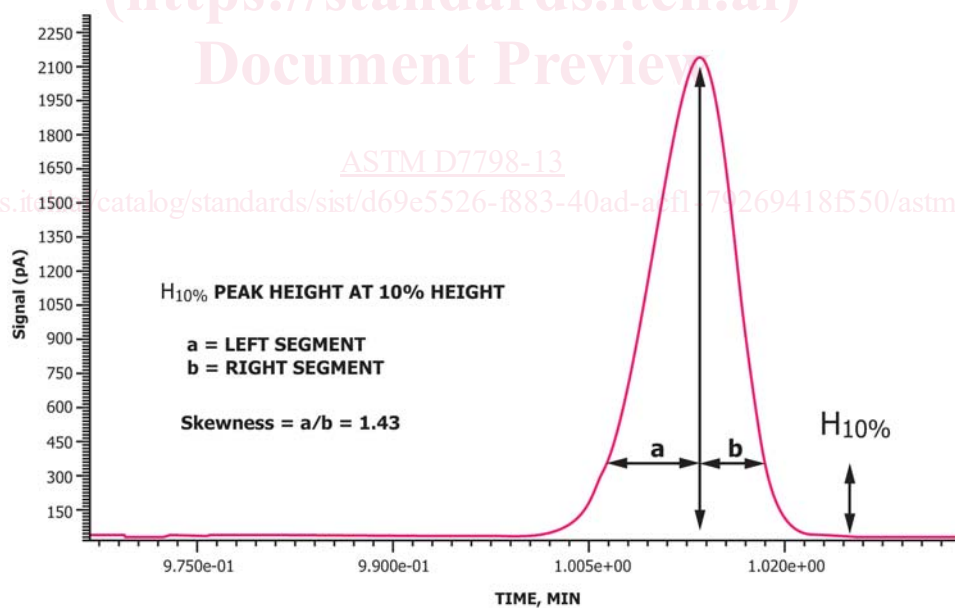a = LEFT SEGMENT
b = RIGHT SEGMENT

Skewness = a/b = 1.43

FIG. 3 Designation of Parameters for Calculation of Peak Skewness Obtained from an Ultra Fast Chromatogram

8.2.3 *Column Temperature*—The column temperature program profile is selected such that at least the C_5 peak can be differentiated from the solvent and that the maximum boiling point (545°C) n-paraffin (C_{44}) is eluted from the column before end of the run time. The actual program rate used will be influenced by other operating variables such as column dimensions, liquid phase film thickness, carrier gas and flow rate, and sample size.

8.2.4 *Column Elution Characteristics*—The column liquid phase is the non-polar phase 100 % dimethyl-polysiloxane.

9. Procedure

9.1 *Analysis Sequence Protocol*—Define and use a predetermined schedule of analysis events designed to achieve maximum reproducibility for these determinations. The schedule will include cooling the column oven and injector to the initial