Designation: D7500 – 14

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

This standard is issued under the fixed designation D7500; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the determination of the boiling range distribution of petroleum products by capillary gas chromatography using flame ionization detection. This standard test method has been developed through the harmonization of two test methods, Test Method D6352 and IP 480. As both of these methods cover the same scope and include very similar operating conditions, it was agreed that a single standard method would benefit the global simulated distillation community.

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

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

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

D1160 Test Method for Distillation of Petroleum Products at Reduced Pressure

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

D5307 Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography (Withdrawn 2011)[3]

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

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

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

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

E355 Practice for Gas Chromatography Terms and Relationships

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

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

2.2 *ISO Standard:*[4]

ISO 3170 Petroleum Liquids Manual Sampling

[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.

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

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

3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. For definitions of these terms used in this test method, refer to Practices E355, E594, and E1510.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *area slice, n*—the area resulting from the integration of the chromatographic detector signal within a specified retention time interval. In area slice mode (see 6.4.1), peak detection parameters are bypassed and the detector signal integral is recorded as area slices of consecutive, fixed duration time intervals.

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

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

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

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

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

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

3.2.8 *total sample area, n*—the cumulative corrected area, from the initial area point to the final area point, where the chromatographic signal has returned to baseline after complete sample elution.

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

4. Summary of Test Method

4.1 The boiling range distribution determination by distillation is simulated by the use of gas chromatography. A non-polar open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point.

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

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

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

5. Significance and Use

5.1 The boiling range distribution of medium and heavy petroleum distillate fractions provides an insight into the composition of feed stocks and products related to petroleum refining processes (for example, hydrocracking, hydrotreating, visbreaking, or deasphalting). The gas chromatographic simulation of this determination can be used to replace conventional distillation methods for control of refining operations. This test method can be used for product specification testing with the mutual agreement of interested parties.

5.2 This test method extends the scope of boiling range determination by gas chromatography to include distillates (IBP > 100 °C) and heavy petroleum distillate fractions beyond the scope of Test Method D2887 (538 °C).

5.3 Boiling range distributions obtained by this test method have not been analyzed for correlation to those obtained by low efficiency distillation, such as with Test Method D86 or D1160. This test method does not claim agreement between these physical distillations and simulated distillation. Efforts to resolve this question will continue. When successful resolutions of the questions are determined, this test method will be revised accordingly.

6. Apparatus

6.1 *Chromatograph*—The gas chromatographic system used shall have the following performance characteristics:

6.1.1 *Carrier Gas Flow Control*—The chromatograph shall be equipped with carrier gas pressure or flow control capable of maintaining constant carrier gas flow to ±1 % throughout the column temperature program cycle.

6.1.2 *Column Oven*—Capable of sustained and linear programmed temperature operation from near ambient (for example, 30 °C to 35 °C) up to 430 °C.

6.1.3 *Column Temperature Programmer*—The chromatograph shall be capable of linear programmed temperature operation up to 430 °C at selectable linear rates up to 10 °C/min. The programming rate shall be sufficiently reproducible to obtain the retention time repeatability of 0.1 min (6 s) for each component in the calibration mixture described in 7.5.

6.1.4 *Detector*—This test method requires the use of a flame ionization detector (FID). The detector shall meet or exceed the following specifications in accordance with Practice E594. Check the detector according the instrument manufacturers instructions.

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

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

6.1.5 *Sample Inlet System*—Any sample inlet system capable of meeting the performance specification in Annex A3 and execute the conditions of Table 2. Programmable temperature vaporization (PTV) and cool on-column (COC) injection systems have been used successfully.

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

6.2.1 Automatic syringe injection is recommended to achieve best precision.

6.3 *Column*—This test method is limited to the use of non-polar wall coated open tubular (WCOT) columns of high thermal stability. Fused silica (aluminum coated) and stainless steel columns with 0.53 mm to 0.75 mm internal diameter have been successfully used. Cross-linked or bonded 100 % dimethyl-polysiloxane stationary phases with film thickness of 0.09 µm to 0.17 µm have been used. The column length and liquid phase film thickness shall allow the elution of C_{110} *n*-paraffin (BP = 735 °C). The column and conditions shall provide separation of typical petroleum hydrocarbons in order of increasing boiling point and meet the column performance requirements of A3.2.1. The column shall provide a resolution not less than 2 and not higher than 4 using the test method operating conditions in Table 2.

6.4 *Data Acquisition System:*

6.4.1 *Integrator/Computer System*—Means shall be provided for determining the accumulated area under the chromatogram. This can be done by means of an electronic integrator or computer-based chromatography data system. The integrator/computer system shall have normal chromatographic software for measuring the retention time and areas of eluting peaks (peak processing mode). In addition, the system shall be capable of converting the continuously integrated detector signal into area slices of fixed duration (slice mode). These contiguous area slices, collected for the entire analysis, are stored for later processing. A similar collection of contiguous slices is also collected for the blank run. It is necessary that the number of slices collected for sample and blank analysis are the same. The electronic range of the integrator/computer (for example 1 V, 10 V) shall be operated within the linear range of the detector/electrometer system used.

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

TABLE 1 Reference Material 5010[A]

% Dist. m/m	°C	°F	r, °C	R, °C	r, °F	R, °F
IBP	421	789	3	9	5	16
5	476	888	2	4	4	8
10	491	916	2	4	3	7
20	510	950	2	5	3	9
30	524	975	2	5	3	9
40	536	998	2	5	3	9
50	548	1018	2	5	3	9
60	559	1039	2	5	3	9
70	572	1061	2	5	3	9
80	585	1085	2	5	3	9
90	602	1116	2	5	3	9
95	617	1142	2	5	3	9
FBP	661	1223	9	17	16	31

[A] Values obtained from including Reference Oil 5010 in the ILS sample set.

TABLE 2 Typical Operating Conditions for Gas Chromatograph

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

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

7. Reagents and Materials

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

7.2 *Carrier Gases*—Helium, of at least 99.999 % (v/v) purity. Any oxygen present is removed by a chemical resin filter. (**Warning—**Follow the safety instructions from the filter supplier.) Total impurities not to exceed 10 mL/m^3. Helium or Nitrogen (99.999 %) can also be used as detector makeup gas. The use of alternative carrier gases hydrogen and nitrogen is described in Appendix X1.

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

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

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

to be used with Polywax 655 or 1000.[5] A solution of these alkanes is prepared by adding 500 mg of each alkane into a 20 mL vial. Additionally *n*-tetracontane (C_{40}) can also be added to for ease of carbon counting. This solution is used to spike the Polywax[5] solution.

7.6 *Polywax 655 or 1000.*[5]

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

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

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

NOTE 3—Calibration mixtures are commercially available.

7.9 *Reference Oil 5010*—A reference sample that has been analyzed by laboratories participating in the test method cooperative study. Consensus values for the boiling range distribution of this sample are given Table 1.

NOTE 4—The 5010 reference oil is available commercially.

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

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

8. Sampling and Sample Preparation

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

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

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

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

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

9. Preparation of Apparatus

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

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

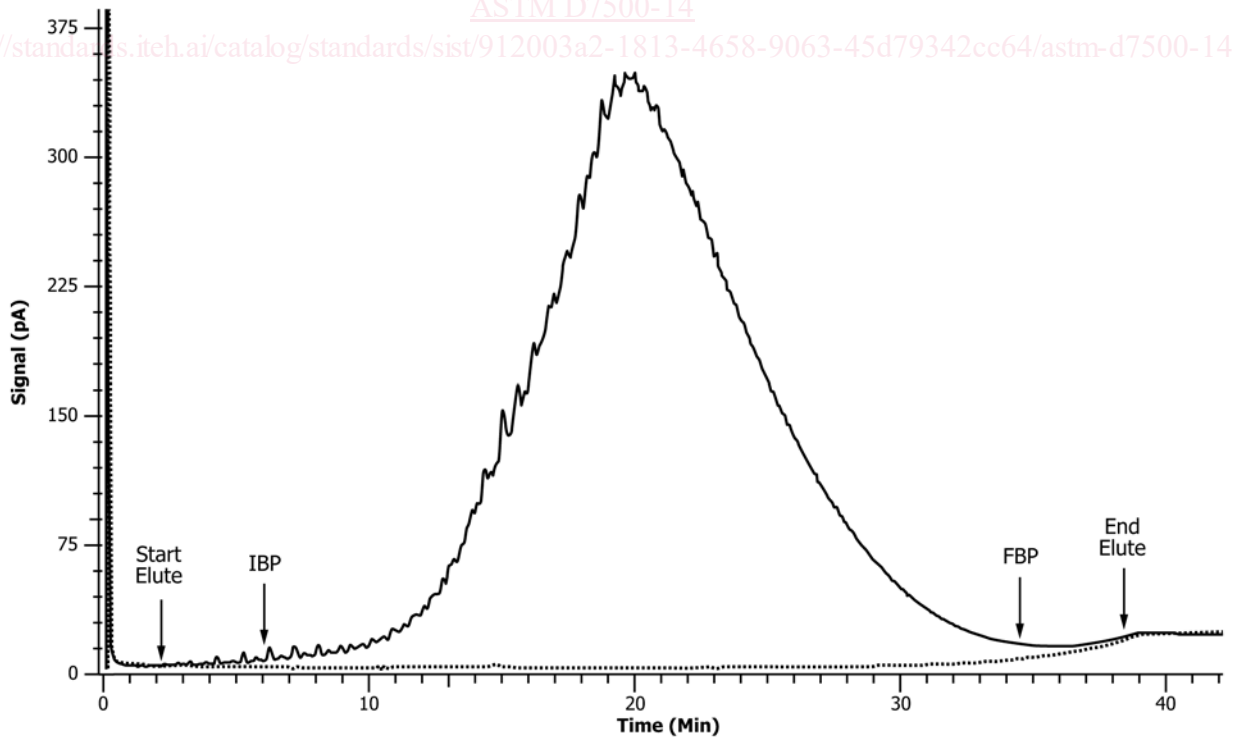

FIG. 1 Typical Sample Chromatogram which has a FBP of 700 ºC

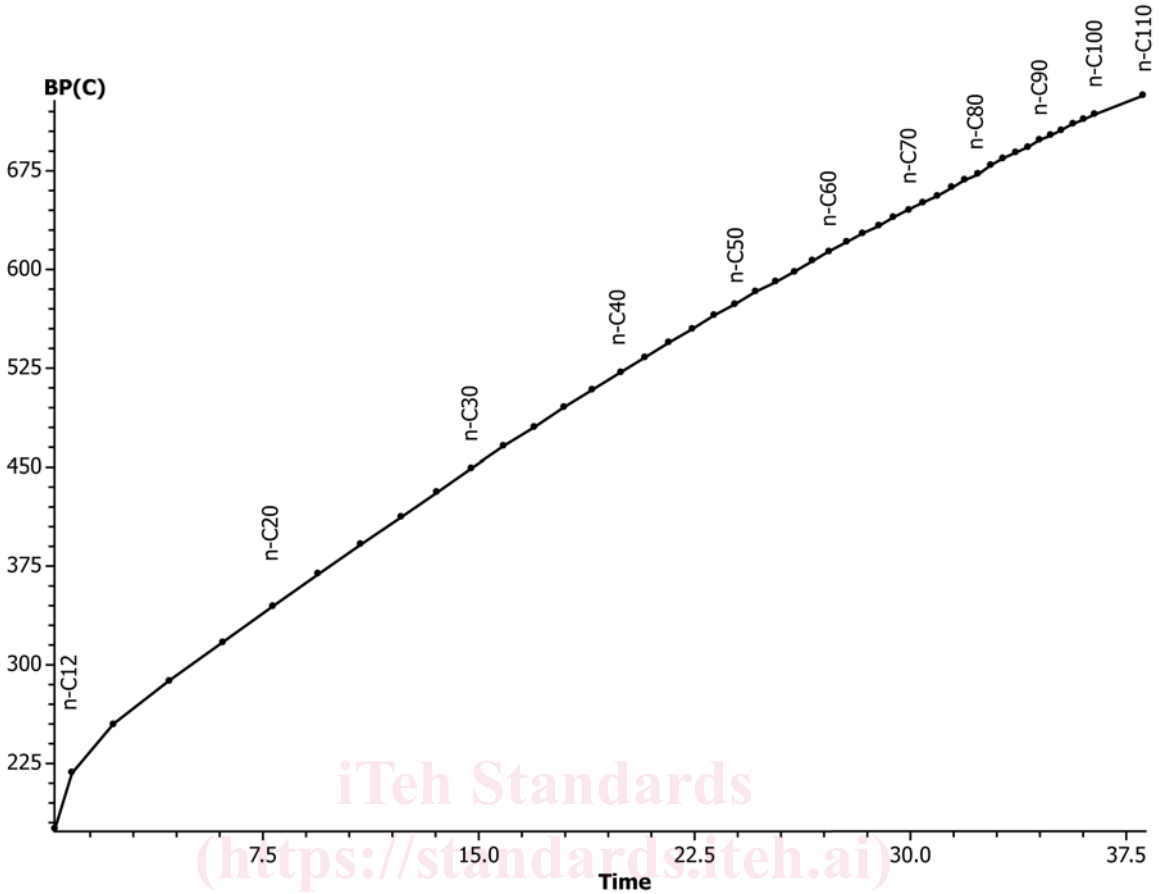

FIG. 2 Typical Calibration Curve of Retention Time versus Boiling Point

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

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

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

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

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

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

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

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

10. Calibration

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

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

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

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

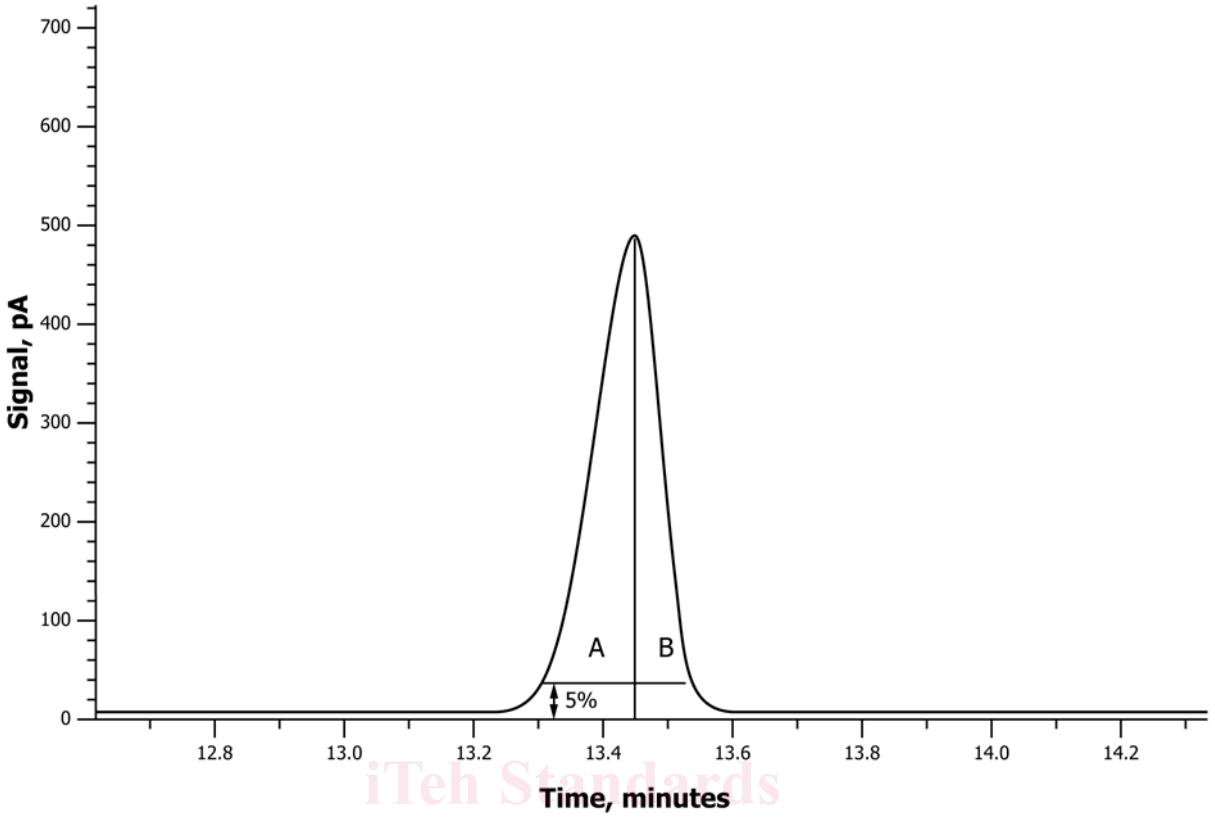

FIG. 3 Peak Skewness for Calibration Mix Peak C_{20}

columns with a film thickness ranging from 0.09 µm to 0.17 µm or less. (See A3.4.)

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

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

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

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

11. Sample Analyses Procedure

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

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

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

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

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

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

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

11.6 Visually inspect the chromatogram. Using the data system, load each sample chromatogram overlay the nearest blank baseline obtained after the sample as listed in the Sequence. Enlarge the section of the chromatogram at the end of sample elution and compare the relative magnitudes of the sample and blank baseline with the examples shown in Fig. 7. Insure that the end of the run merges with the sample