



Designation: D6352 – 19^ε¹

Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 °C to 700 °C by Gas Chromatography¹

This standard is issued under the fixed designation D6352; 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.

^ε¹ NOTE—Editorially added research report information to Table 3 in May 2020.

1. Scope*

1.1 This test method covers the determination of the boiling range distribution of petroleum distillate fractions. The test method is applicable to petroleum distillate fractions having an initial boiling point greater than 174 °C (345 °F) and a final boiling point of less than 700 °C (1292 °F) (C10 to C90) at atmospheric pressure as measured by this test method.

1.2 The test method is not applicable for the analysis of petroleum or petroleum products containing low molecular weight components (for example naphthas, reformates, gasolines, crude oils). Materials containing heterogeneous components (for example alcohols, ethers, acids, or esters) or residue are not to be analyzed by this test method. See Test Methods [D3710](#), [D2887](#), or [D5307](#) for possible applicability to analysis of these types of materials.

1.3 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only and may be included as parenthetical values.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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. Referenced Documents

2.1 ASTM Standards:²

- [D86](#) Test Method for Distillation of Petroleum Products and Liquid Fuels 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
- [D5307](#) Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography (Withdrawn 2011)³
- [D6299](#) Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- [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

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](#).

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.

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

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 6.4.2), peak detection parameters are bypassed and the detector signal integral is recorded as area slices of consecutive, fixed duration time intervals.

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

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

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

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

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

3.2.7 *slice time, n*—the analysis time associated with each area slice throughout the chromatographic analysis. 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-C₁₀ for normal-decane, i-C₁₄ 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 medium 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.

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 control through the column 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 450 °C.

6.1.3 *Column Temperature Programmer*—The chromatograph shall be capable of linear programmed temperature operation up to 450 °C at selectable linear rates up to 20 °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. The flame jet should have an orifice of approximately 0.05 mm to 0.070 mm (0.020 in. to 0.030 in.).

6.1.4.1 *Operating Temperature*—100 °C to 450 °C.

6.1.4.2 *Sensitivity*—>0.005 C/g carbon.

6.1.4.3 *Minimum Detectability*—1 × 10⁻¹¹ g carbon/s.

6.1.4.4 *Linear Range*—>10⁶

6.1.4.5 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 7.6 and 8.2.2 may be used. Programmable temperature vaporization (PTV) and cool on-column injection systems have been used successfully.

6.2 *Microsyringe*—A microsyringe with a 23-gage or smaller stainless steel needle is used for on-column sample introduction. Syringes of 0.1 μL 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 (see Note 1). Glass, fused silica, 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 0.10 μm to 0.20 μm have been used. The column length and liquid phase film thickness shall allow the elution of at least C90 n-paraffin (BP = 700°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 8.2.1. The column shall provide a resolution between three (3) and ten (10) using the test method operating conditions.

NOTE 1—Based on recent information that suggests that true boiling points (atmospheric equivalent temperatures) versus retention times for all components do not fall on the same line, other column systems that can meet this criteria will be considered. These criteria will be specified after a round robin evaluation of the test method is completed.

6.4 *Data Acquisition System:*

6.4.1 *Recorder*—A 0 mV to 1 mV range recording potentiometer or equivalent with a full-scale response time of 2 s or less may be used. It is, however, not a necessity if an integrator/computer data system is used.

6.4.2 *Integrator*—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 detection mode). In addition, the system shall 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) shall be operated within the linear range of the detector/electrometer system used.

NOTE 2—Some gas chromatographs have an algorithm built into their operating software that allows a mathematical model of the baseline profile to be stored in memory. This profile is automatically subtracted from the detector signal on subsequent sample runs to compensate for the column bleed. Some integration systems also store and automatically subtract a blank analysis from subsequent analytical determinations.

7. Reagents and Materials

7.1 *Carrier Gas*—Helium, hydrogen, or nitrogen of high purity. The use of alternative carrier gases hydrogen and

nitrogen is described in Appendix X2. (**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 shall be sufficient to ensure a constant carrier gas flow rate.

7.2 *Hydrogen*—Hydrogen of high purity (for example, hydrocarbon free) is used as fuel for the FID. Hydrogen can also be used as the carrier gas. (**Warning**—Hydrogen is an extremely flammable gas under high pressure).

7.3 *Air*—High purity (for example, hydrocarbon free) compressed air is used as the oxidant for the FID. (**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.

7.4.1 *Carbon Disulfide* (CS_2)—(99+ % pure) is 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 asphaltic 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**— CS_2 is extremely flammable and toxic.)

7.4.2 *Cyclohexane* (C_6H_{12})—(99+ % pure) may be used in place of CS_2 for the preparation of the calibration mixture.

7.5 *Calibration Mixture*—A qualitative mixture of n-paraffins (nominally C10 to C100) dissolved in a suitable solvent. The final concentration should be approximately one part of n-paraffin mixture to 200 parts of solvent. At least one compound in the mixture shall have a boiling point lower than the initial boiling point and one shall have a boiling point higher than the final boiling point of the sample being analyzed, as defined in 1.1. The calibration mixture shall contain at least eleven known n-paraffins (for example C10, C12, C16, C20, C30, C40, C50, C60, C70, C80, and C90). Atmospheric equivalent boiling points of n-paraffins are listed in Table 1.

NOTE 3—A suitable calibration mixture can be obtained by dissolving a hydrogenated polyethylene wax (for example, Polywax 655 or Polywax 1000) in a volatile solvent (for example, CS_2 or C_6H_{12}). Solutions of 1 part Polywax to 200 parts solvent can be prepared. Lower boiling point paraffins will have to be added to ensure conformance with 7.5. Fig. 1 illustrates a typical calibration mixture chromatogram, and Fig. 2 illustrates an expanded scale of carbon numbers above 75.

⁴ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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.