



# Standard Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 5307; 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 ( $\epsilon$ ) 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 water-free crude petroleum through 538°C (1000°F). Material boiling above 538°C is reported as residue. This test method is applicable to whole crude samples, that can be solubilized in a solvent to permit sampling by means of a microsyringe.

1.2 The values stated in SI units are to be regarded as the standard. The values stated in inch-pound units are for information only.

1.3 *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.* Specific precautionary statements are given in 7.2, 7.5, 7.6, 7.7, and 7.9.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

D 2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

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

3.1.1.1 *Discussion*—In area slice mode (see 6.2.2), peak detection parameters are bypassed and the detector signal integral is recorded as area slices of consecutive, fixed duration time intervals.

3.1.2 *corrected area slice, n*—an area slice corrected for baseline drift, by subtraction of the exactly corresponding area slice in a previously recorded blank (nonsample) analysis; correction for signal offset may also be required.

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

3.1.4 *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 theoretical total area is obtained.

3.1.5 *residue, RES n*—the amount of sample boiling above 538°C (1000°F).

3.1.6 *theoretical total area, T n*—the area that would have been obtained if the entire sample had been eluted from the column.

3.1.6.1 *Discussion*—This is determined in 12.3.

### 3.2 Abbreviations: 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, normal decane =  $n\text{-C}_{10}$ ; isotetradecane =  $i\text{-C}_{14}$ ).

## 4. Summary of Test Method

4.1 The crude oil sample is diluted with carbon disulfide, and the resulting solution is injected into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible, linear rate, and the area under the chromatogram is recorded throughout the run. Boiling points are assigned to the time axis by comparison to a calibration curve obtained under the same chromatographic conditions by running a mixture of  $n$ -paraffins of known boiling point through a temperature of 538°C (1000°F). The amount of sample boiling above 538°C is estimated by means of a second analysis of the crude oil to which an internal standard has been added. From these data, the boiling range distribution of the water-free sample is calculated.

<sup>1</sup> 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.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

## 5. Significance and Use

5.1 The determination of the boiling range distribution is an essential requirement in crude oil assay. This information can be used to estimate refinery yields and, along with other information, to evaluate the economics of using one particular crude as opposed to another.

5.2 Results obtained by this test method are equivalent to those obtained from Test Method **D 2892**. (See **Appendix X1**.)

5.3 This test method is faster than Test Method **D 2892** and can be used when only small volumes of samples are available. Also, this test method gives results up to 538°C while Test Method **D 2892** is limited to 400°C.

## 6. Apparatus

6.1 *Gas Chromatograph*—Any gas chromatograph may be used that has the capabilities described below and meets the performance requirements in Section 10.

6.1.1 *Detector*—This test method is limited to the use of the flame ionization detector (FID). The detector must be capable of operating continuously at a temperature equal to or greater than the maximum column temperature employed, and it must be connected to the column so as to avoid cold spots.

6.1.2 *Column Temperature Programmer*—The chromatograph must be capable of reproducible, 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 with boiling points of 538°C (1000°F) before the end of the temperature ramp.

6.1.3 *Cryogenic Column Oven*—If the IBP of the crude oil is below 90°C (194°F), an initial column temperature below ambient will be required. This necessitates a cryogenic cooling option on the gas chromatograph. Typical initial column temperatures are listed in **Table 1**.

6.1.4 *Sample Inlet System*—Either of the following two types of sample inlet systems may be used.

6.1.4.1 *Flash Vaporization*—A vaporizing sample inlet system must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed. The sample inlet system also must be connected to the chromatographic column so as to avoid any cold spots.

6.1.4.2 *On-Column*—Capable of introducing a liquid sample directly onto the head of the column. Means must be

provided for programming the entire column, including the point of sample introduction, up to the maximum column temperature employed.

6.1.5 *Flow Controller*—The chromatograph must be equipped with a flow controller capable of maintaining carrier gas flow constant to  $\pm 1\%$  over the full operating temperature range of the column. The inlet pressure of the carrier gas, supplied to the chromatograph, must be sufficiently high to compensate for the increase of backpressure in the column as the temperature is programmed upward. An inlet pressure of 550 kPa gage (80 psig) has been found satisfactory with the columns described in **Table 1**.

### 6.2 Data Retrieval System:

6.2.1 *Recorder*—A 0–1 mV range recording potentiometer or equivalent, with a full-scale response time of 2 s or less may be used for graphic presentation of the FID signal.

6.2.2 *Integrator*—Electronic integrator or computer-based chromatography data system must be used for detector signal integration and accumulation. The integrator/computer system must have normal chromatographic software for measuring 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 representing contiguous fixed duration time intervals (area slice mode). The recommended time interval is 1 s. No time interval shall be greater than 12 s. The system must be capable of subtracting the area slice of a blank run from the corresponding area slice of a sample run. Alternatively, the baseline chromatogram can be subtracted from the sample chromatogram and the net resulting chromatogram can be processed in the slice mode. A computer program that performs the slice calculation as a post-run calculation is also used.

6.3 *Column*—Any gas chromatographic column that provides separation in order of boiling points and meets the performance requirements of Section 10 can be used. Columns and conditions, which have been used successfully, are shown in **Table 1**.

6.4 *Microsyringe*—A 5 or 10  $\mu\text{L}$  syringe is used for sample introduction. The use of an automated liquid sampling device is highly recommended.

## 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.<sup>3</sup> 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.

**TABLE 1 Typical Operating Conditions**

	1	2	3
Column length, mm (in.)	457 (18)	610 (24)	457 (18)
Column diameter, mm (in.)	3.17 (1/8)	3.17 (1/8)	3.17 (1/8)
Liquid phase	10 % UCV-982	3 % OV-1	10 % SE-30
Support material	Chromosorb P <sup>A</sup> -AW	Chromosorb W <sup>A</sup> -HP	Chromosorb P <sup>A</sup> -AW
Column temperature initial value, °C	–30	–30	–40
Column temperature final value, °C	380	350	360
Programming rate, °C/min	10	10	10
Carrier gas type	N <sub>2</sub>	He	N <sub>2</sub>
Carrier gas flow, mL/min	25	20	28
Detector temperature, °C	400	380	400
Injection port temperature, °C	380	375	400

<sup>A</sup>See Footnote 5.

<sup>3</sup> *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.

7.2 *Air*—Zero grade (hydrocarbon free) for use with the FID. (**Warning**—Air is a compressed gas under high pressure and supports combustion.)

7.3 *Calcium Chloride, Anhydrous (CaCl<sub>2</sub>)*.

7.4 *Calibration Mixture*—A mixture of *n*-paraffins dissolved in carbon disulfide (**Warning**—see 7.5) covering the boiling range of the sample through 538°C (1000°F). At least one compound in the mixture must have a boiling point equal to or lower than the IBP of the sample. Methane, ethane, propane, or butane can be added to the calibration mixture, if necessary, by injecting about 1 mL of the pure gaseous compound into a septum-capped, sealed vial containing the rest of the calibration mixture, using a gas syringe. If *n*-paraffin peaks can be unambiguously identified in the sample chromatogram, their retention times can be used for calibration.

7.5 *Carbon Disulfide (CS<sub>2</sub>)*—Carbon disulfide (99 % minimum purity) is used as a viscosity reducing solvent because it is miscible with crude oils and has only a slight response with the FID. (**Warning**—Carbon disulfide is extremely volatile, flammable, and toxic.)

7.6 *Carrier Gas*—Nitrogen or helium of high purity that has been dried over molecular sieves or similar suitable drying agents. (**Warning**—Helium and nitrogen are compressed gases under high pressure.)

7.7 *Column Resolution Test Mixture*—A mixture of 1 % each of *n*-C<sub>16</sub> and *n*-C<sub>18</sub> 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.)

7.8 *Detector Response Test Mixture*—An accurately weighed mixture of approximately equal masses of at least six *n*-paraffins covering the carbon number range from 10 to 44. Dissolve one part of this mixture with approximately five parts of CS<sub>2</sub> (or sufficient CS<sub>2</sub> to ensure a stable solution at room temperature).

7.9 *Hydrogen*—Hydrogen of high quality (hydrocarbon free) is used as fuel gas for the FID. (**Warning**—Hydrogen is an extremely flammable gas under high pressure.)

7.10 *Internal Standard*—A mixture of approximately equal amounts of four *n*-paraffins, *n*-C<sub>14</sub> through *n*-C<sub>17</sub>. Concentrations of the individual components need not be known but must be within the linear range of the detector/electronics system used.

7.11 *Liquid Phase*—A nonreactive, nonpolar liquid or gum of low volatility. Silicone gum rubbers are typically used. In general, liquid phase loadings of 3 to 10 % have been found most satisfactory.

7.12 *Solid Support*—A diatomaceous earth or equivalent nonreactive particulate material. Typical particle size ranges are 60/80 or 80/100 mesh.

## 8. Sampling

8.1 Obtain samples for analysis by this test method in accordance with instructions given in Practice D 4057.

8.1.1 Ensure that samples are received in sealed containers and show no evidence of leakage.

## 9. Preparation of Apparatus

9.1 *Column Preparation*—Any satisfactory method used in the practice of the art, that will produce a column meeting the requirements of Section 10, may be used.

9.2 *Column Conditioning*—The column must be conditioned at the maximum operating temperature to reduce baseline shifts due to bleeding of the column substrate. The column can be conditioned rapidly and effectively using the following procedure:

9.2.1 Connect the column to the inlet system but leave the detector end free.

9.2.2 Purge the column at ambient temperature with carrier gas.

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

9.2.4 Seal off the open end of the column with an appropriate fitting.

9.2.5 Raise the column to the maximum operating temperature and hold at this temperature 4 to 6 h, with no flow through the column.

9.2.6 Cool the column to ambient temperature.

9.2.7 Remove the cap from the column and connect the column to the detector. Re-establish carrier flow.

9.2.8 Program the column temperature to the maximum several times with normal carrier gas flow rate.

9.3 An alternate method of column conditioning, that has been found effective with columns with an initial loading of 5 % liquid phase, consists of purging the column (disconnected from the detector) with normal carrier gas flow rate for 12 to 16 h, while holding the column at the maximum operating temperature.

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

9.4.1 Excessively low initial column temperature must be avoided to ensure that the column phase functions as gas-liquid chromatographic column. Consult the stationary phase manufacturer's literature for minimum operating temperature. The initial temperature of the column should be only low enough to obtain a calibration curve meeting the specifications under 6.1.3.

9.4.2 Silica from combustion of column material deposits on the FID parts. This deposit must be removed regularly, by brushing, because it changes response characteristics of the detector.

9.4.3 Silica deposits also can plug the end of the flame jet. This problem can be alleviated greatly by utilizing a flame jet with an inside diameter of at least 0.76 mm (0.030 in.)

## 10. System Performance

10.1 *Resolution*—Analyze an aliquot of the column resolution test mixture (see 7.7) utilizing identical conditions as used in the analysis of samples. The resolution of *n*-C<sub>16</sub> and *n*-C<sub>18</sub> *n*-paraffin peaks must be between three and ten when calculated in accordance with the following equation (refer to Fig. 1):

$$R = [2(t_2 - t_1)]/[1.699(Y_2 + Y_1)] \quad (1)$$