Designation: D7169 – 11

Standard Test Method for
Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography[1]

1. Scope*

1.1 This test method covers the determination of the boiling point distribution and cut point intervals of crude oils and residues by using high temperature gas chromatography. The amount of residue (or sample recovery) is determined using an external standard.

1.2 This test method extends the applicability of simulated distillation to samples that do not elute completely from the chromatographic system. This test method is used to determine the boiling point distribution through a temperature of 720°C. This temperature corresponds to the elution of n-C_{100}.

1.3 This test method is used for the determination of boiling point distribution of crude oils. This test method uses capillary columns with thin films, which results in the incomplete separation of C_4-C_8 in the presence of large amounts of carbon disulfide, and thus yields an unreliable boiling point distribution corresponding to this elution interval. In addition, quenching of the response of the detector employed to hydrocarbons eluting during carbon disulfide elution, results in unreliable quantitative analysis of the boiling distribution in the C_4-C_8 region. Since the detector does not quantitatively measure the carbon disulfide, its subtraction from the sample using a solvent-only injection and corrections to this region via quenching factors, results in an approximate determination of the net chromatographic area. A separate, higher resolution gas chromatograph (GC) analysis of the light end portion of the sample may be necessary in order to obtain a more accurate description of the boiling point curve in the interval in question (see Appendix X1).

1.4 This test method is also designed to obtain the boiling point distribution of other incompletely eluting samples such as atmospheric residues, vacuum residues, etc., that are characterized by the fact that the sample components are resolved from the solvent.

1.5 This test method is not applicable for the analysis of materials containing a heterogeneous component such as polyesters and polyolefins.

1.6 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered standard.

1.7 *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 warning statements are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

D6729 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography

D6730 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100–Metre Capillary (with Precolumn) High-Resolution Gas Chromatography

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

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 of Terms Specific to This Standard:*

3.1.1 *cut point interval, n*—the mass % obtained between two selected temperatures of the interval.

3.1.2 *data acquisition rate, n*—the speed of conversion of the analog signal to a digital signal, expressed in Hz (cycles/second).

3.1.3 *final boiling point (FBP), n*—the temperature, for fully eluting samples (recovery = 100 %), at which 99.5 % of the sample is eluted.

3.1.4 *final elution time (FEt), n*—the retention time of the component of the reference time standard sample that elutes at the end of the temperature ramp of the oven.

3.1.5 *final elution temperature (FET), n*—the boiling point of the normal paraffin that elutes at the time when the oven reaches its final temperature.

3.1.6 *initial boiling point (IBP), n*—the temperature corresponding to an accumulated 0.5 % of the total area of the eluted sample after correcting for the percent of sample recovery.

3.1.7 *quenching factor (QF), n*—a number that corrects for the diminished response due to the solvent profile co-eluting with sample components.

3.1.7.1 *Discussion*—Data acquired during the quenching interval (QI) shall be corrected by applying the quenching factor.

3.1.8 *quenching interval (QI), n*—the time interval of the start and end of elution of the CS_2 used as a solvent.

3.1.8.1 *Discussion*—Sample components that elute during this time interval shall be corrected by a factor due to their diminished response resulting from the co-elution of the relatively large amount of solvent present in the sample with the light sample components.

3.1.9 *residue (R), n*—the mass % of the sample that has not eluted at the temperature of calculation.

3.1.9.1 *Discussion*—Residue is calculated from the %recovery.

3.1.10 *response factor (RF), n*—the factor used in order to calculate the %recovery of the sample.

3.1.10.1 *Discussion*—The response factor is determined from the net area of the standard (A_{STD}), mass of standard (M_{STD}), and mass of solvent (M_{SLSTD}) used in the solution of the standard. A fully eluting sample, such as Reference Oil 5010, is used in obtaining the response factor.

3.1.11 *sample area obtained (A_{SMP}), n*—the net chromatographic area (after baseline subtraction) obtained for the sample at the final elution time or temperature.

3.1.12 *slice, n*—the reciprocal of the data acquisition rate; the time interval used to accumulate data, expressed in seconds.

3.1.12.1 *Discussion*—Normally 0.1 s is used. In cases where sample elutes immediately after injection, 0.05 s is used.

3.1.13 *start elution temperature (SET), n*—the temperature at which the first amount of hydrocarbon is detected by the flame ionization detector above a predetermined threshold.

3.1.14 *%recovery (RC), n*—percentage of the sample eluted.

3.1.14.1 *Discussion*—%Recovery is calculated from the sample area (A_{SMP}), the response factor (RF), the sample mass, (M_{SMP}), and the solvent mass (M_{SLSMP}) used in sample dissolution.

3.1.15 *%recovery threshold (R_t), n*—if the %recovery falls above a preset limit, the sample is considered fully eluted and its recovery is assumed to be 100 %.

3.1.15.1 *Discussion*—If the %recovery values found for duplicate analyses of a nearly completely eluting sample are 99.6 and 101.2 %, the %recovery threshold (R_t) may be set to 99.6 % and thus either of these results may be considered as fully eluted and set to 100 %.

3.2 *Symbols*:

A_{SMP} = net area of the sample

A_{STD} = net area of the response factor standard

M_{SL} = mass of solvent used in preparing sample solution

M_{SLSTD} = mass of solvent used in preparing the response factor standard solution

M_{SMP} = sample mass used in sample preparation

M_{STD} = mass of the standard used in preparing the response factor solution

4. Summary of Test Method

4.1 This is a gas chromatographic method utilizing an inlet and a capillary column, both of which are subject to a temperature program. A flame ionization detector is used as a transducer that converts mass to an electrical signal A data acquisition system operating in the slice mode and chromatography software is used to accumulate the electronic signal. A retention time calibration mixture is used to develop a retention time versus boiling point curve. A solution of the Reference Oil 5010, which fully elutes from the column under the conditions of the test method and whose boiling point distribution has been characterized in Test Method D6352, is used to determine the detector response factor. Solvent injections are made, and the resulting signal is subtracted from both the response factor standard and the sample chromatogram. Finally, the sample solution is injected and with the use of the response factor, the amount of sample recovered is calculated. After converting the retention times of the sample slices to temperature, the boiling point distribution can be calculated up to the recovered amount.

5. Significance and Use

5.1 The determination of the boiling point distribution of crude oils and vacuum residues, as well as other petroleum fractions, yields important information for refinery operation. These boiling point distributions provide information as to the potential mass percent yield of products. This test method may provide useful information that can aid in establishing operational conditions in the refinery. Knowledge of the amount of residue produced is important in determining the economics of the refining process.

6. Apparatus

6.1 *Gas Chromatograph*—A gas chromatograph provided with a cryogenic valve for cooling the oven to sub ambient

TABLE 1 Gas Chromatographic Conditions[A]

Initial Oven Temperature	–20°C
Initial Oven Time	0 min
Oven Temperature Program	15°C/min
Final Oven Temperature	425 to 435°C[B]
Final Hold Time	10 min
Inlet Initial Temperature[C]	50°C
Inlet Temperature Program	15°C/min
Inlet Final Temperature	425°C
Column	5 m × 0.53 mm × 0.09[B]-0.15 µm PDMS
Column Flow	20 mL/min
Carrier Control	Constant Flow
Detector[D]	FID
Detector Temperature	435°C
Detector Gases:	
Hydrogen	40 mL/min
Air	450 mL/min
Make-Up (N_2, He)	15 mL/min
Volume Injected	0.2 µL-0.5 µL-1.0 µL[B]
Sample Concentration	2.0 % (m/m)
Data Acquisition Rate	10 Hz
Total Acquisition Time	40 to 50 min

[A] Conditions used for the interlaboratory study.
[B] Several participants used these conditions also.
[C] Use lowest temperature recommended by manufacturer.
[D] Use GC manufacturer's recommendations.

temperatures is required. The conditions of operating the Gas Chromatograph are given in Table 1. It shall also have the following components:

6.1.1 *Flame Ionization Detector (FID)*—A flame ionization detector capable of maintaining a temperature 5 to 10°C higher than the highest column temperature. The flame ionization detector should possess a jet orifice of about 0.018 in. (0.45 mm) in order to delay the plugging of the orifice due to column bleed. The FID should possess a sensitivity of 0.005 coulombs/g (see Practice E594) and should have a linear range of 10^6.

6.1.2 *Inlet*—Either a temperature programmable inlet with a glass liner or a cool-on-column inlet can be used. The inlet shall be capable of operating in a temperature-programmed mode from 50°C to the final temperature of the oven. It is important that the temperature of the inlet, at any time during the analysis, be either equal to or greater than the oven temperature. With the use of either inlet, frequent replacement of the liner or removal of a section of the column may be required due to accumulation of non-volatile sample components. It is important that a leak free seal be reestablished after replacement of the liner or the removal of a small section of the column.

6.2 *Carrier Gas Purification System*—Gas purifiers are used in order to remove traces of oxygen as well as moisture and other impurities present in the carrier gas. The purification system should contain a hydrocarbon trap and an oxygen trap. The latter should preferably have a visible indicator in order to assess the remaining capacity of the oxygen trap.

6.3 *Data System*—A data system composed of a computer and software for data acquisition, which digitizes the detector signal, is recommended. Some instrumentation digitizes the signal at the electrometer board in order to reduce noise. The data system is used at acquisition rates of about 10 Hz, which

correspond to slices of 0.1 s. This rate of data acquisition is necessary to obtain a minimum number of slices void of sample or solvent elution immediately after injection. Data acquisition systems facilitate the inspection of the baseline under high magnification and allow the inspection of the retention time calibration mixture chromatogram. Retention time shifts can be measured. Overlaying chromatograms is also possible to ascertain similar signal amplitude.

6.4 *Integrator*—An integrator that digitizes the signal can also be used to acquire chromatograms of the retention time calibration mixture, the sample, the solvent and the reference oil standard.

6.5 *Automatic Sample Injector*—It is mandatory to use an auto sampler since the external standard technique used in this analysis requires identical volumes for all injections. Additionally, small volumes (0.1 to 0.2 µL) shall be injected in a reproducible manner. Syringes of 5 to 10 µL having needle gauges of size 23 to 26 are to be used.

6.6 *Carrier Gas Control*—The gas chromatograph shall be operated under constant flow conditions. The flow rate at the beginning of the oven temperature program shall not differ by more than 1 % from the flow measured at the final oven temperature. Electronic pneumatic control is highly recommended.

7. Column and Column Performance Criteria

7.1 A 100 % bonded polydimethylsiloxane column having a nominal inside diameter of 0.5 mm and a film thickness of 0.09 to 0.17 µm is used.

7.2 The column used should be capable of sustaining temperatures of 435°C under temperature programming. Aluminum covered fused silica and metal columns have been successfully used.

7.3 The column should be capable of eluting carbon number 100 at its highest temperature. It is important that C_{100} be eluted during the temperature program cycle of the oven.

7.4 Column resolution is determined from the separation of carbons 50 and 52 in the retention time calibration mixture chromatogram. The resolution should be between 1.8 to 4.0. See Eq 1 in 13.1.

7.5 The column shall be capable of allowing the start of the elution of n-C_5 prior to the solvent elution, which is CS_2, at –20°C. The descending edge of the n-C_5 peak co-elutes with the solvent. It is to be noted that at these low temperatures liquid phases may turn solid, and retention shifts may be observed during the elution of compounds at these low oven temperatures.

7.6 *Column Overloading*—The prevention of column overloading is carried out by determining the skewness of a selected peak among the components of the retention time calibration mixture chromatogram. Any paraffin with a carbon number between C_{12} and C_{24} may be chosen. The skewness should be between 0.8 to 1.2. See Eq 2 in 13.2.

7.7 *Column Flow*—Helium is used as carrier. Column flow rate is set to 20 mL/min.