Designation: D 5399 – 95

Standard Test Method for Boiling Point Distribution of Hydrocarbon Solvents by Gas Chromatography[1]

This standard is issued under the fixed designation D 5399; 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 point distribution of hydrocarbon solvents by capillary gas chromatography. This test method is limited to samples having a minimum initial boiling point of 37°C (99°F), a maximum final boiling point of 285°C (545°F), and a boiling range of 5 to 150°C (9 to 270°F) as measured by this test method.

1.2 The values stated in SI units are standard. The values given in parentheses are for information purposes 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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 86 Test Method for Distillation of Petroleum Products[2]

D 850 Test Method for Distillation of Industrial Aromatic Hydrocarbons and Related Materials[3]

D 1078 Test Method for Distillation Range of Volatile Organic Liquids[3]

D 2887 Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography[4]

D 2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)[4]

D 3710 Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography[4]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *initial boiling point (IBP)*—the point at which a cumulative area count equal to 0.5 % of the total area under the chromatogram is obtained.

3.1.2 *final boiling point (FBP)*—the point at which a cumulative area count equal to 99.5 % of the total area under the chromatogram is obtained.

4. Summary of Test Method

4.1 The sample is introduced into a capillary gas chromatographic column that separates hydrocarbons in the order of increasing boiling point. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout the run. Boiling points are assigned from a calibration curve obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling point distribution of the sample is obtained.

5. Significance and Use

5.1 The gas chromatographic determination of the boiling point distribution of hydrocarbon solvents can be used as an alternative to conventional distillation methods for control of solvents quality during manufacture, and specification testing.

5.2 Boiling point distribution data can be used to monitor the presence of product contaminants and compositional variation during the manufacture of hydrocarbon solvents.

5.3 Boiling point distribution data obtained by this test method are not equivalent to those obtained by Test Methods D 86, D 850, D 1078, D 2887, D 2892, and D 3710.

6. Apparatus

6.1 *Chromatograph*—Any gas chromatograph that can handle capillary column and has the following characteristics:

6.1.1 *Detector*—A flame ionization detector (FID) capable of continuous operation at a temperature equivalent to the maximum column temperature employed.

6.1.2 *Column Temperature Programmer*—The chromatograph must be capable of reproducible linear temperature programming over a range sufficient to establish a retention time of 1 min for *n*-pentane and to allow elution of entire sample within a reasonable time period.

6.1.3 *Sample Inlet System*—The sample inlet system must be capable of operating continuously at a temperature up to the maximum column temperature employed, or provide on-column injection.

NOTE 1—The use of cool, on-column injection using an automatic

[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 06.04.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

injector or sampler has been shown to provide better precision relative to manual injection.

6.1.4 *Column*—A 10 to 30 m by 0.53 mm inside diameter by 3-µm bonded methyl silicone, fused silica, or equivalent column that elutes components in order of boiling points, and meets the resolution criteria specified in 8.2 must be used (see 8.4).

6.1.5 *Integrator*—Means must be provided for determining the accumulated area under the chromatogram. This can be done by means of a computer or electronic integrator. A timing device can be used to record the area at set time intervals. The same basis for measuring time must be used to determine the retention times in the calibration, and the sample. The maximum signal measured must be within the linear range of the measuring system used.

6.1.6 *Flow Controller*—The chromatograph must be equipped with a constant-flow device capable of maintaining the carrier gas at a constant flow rate throughout the temperature program.

6.1.7 *Sample Introduction*—A microsyringe is required for the introduction of the sample to the gas chromatograph (see Note 1).

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in the preparation of the calibration mixture.

7.2 *Calibration Mixture*—A synthetic blend of pure liquid hydrocarbons of known boiling points. The components of the calibration mixture are listed in Table 1 and prepared by mixing equivolume quantities of the components. At least one component in the mixture must have a boiling point equal to or lower than the initial boiling point of the sample, and one component must have a retention time greater than any component in the sample.

7.3 *Carrier Gas*, helium (high purity)—Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons.

NOTE 2—**Warning:** Helium is a compressed gas under high pressure.

7.4 *Detector Gases*, air, hydrogen (high purity)—Additional purification for air and hydrogen is recommended by the use of molecular sieves, activated carbons, or other suitable agents to remove water and organics.

TABLE 1 Calibration Mixture

Peak Number	Compound Identification	Normal Boiling Point, °C
1	*n*-Pentane	36.1
2	2-Methyl Pentane	60.0
3	*n*-Hexane	68.9
4	2,4-Dimethyl Pentane	80.6
5	*n*-Heptane	98.3
6	Toluene	110.6
7	*n*-Octane	125.6
8	*p*-Xylene	138.3
9	*n*-Propyl Benzene	159.4
10	*n*-Decane	173.9
11	*n*-Butyl Benzene	183.3
12	*n*-Dodecane	216.1
13	*n*-Tridecane	235.6
14	*n*-Tetradecane	253.9
15	*n*-Pentadecane	270.6
16	*n*-Hexadecane	287.2

NOTE 3—**Warning:** Air and hydrogen are compressed gases under high pressure. Hydrogen is an extremely flammable gas.

8. Preparation of Apparatus

8.1 *Column Preparation*—The column must be conditioned at the maximum operating temperature to reduce baseline shifts due to bleeding of column substrate.

NOTE 4—The column can be conditioned using the following procedure:

(*a*) Disconnect the column from the detector,

(*b*) Purge the column at ambient temperature with carrier gas for at least 30 min,

(*c*) With carrier gas flowing through the column, raise the column temperature to the maximum operating temperature and maintain the temperature at this level for 12 to 16 h,

(*d*) Cool the column to ambient temperature,

(*e*) Reconnect the column to the detector,

(*f*) Set the detector temperature to at least 5°C higher than the maximum column temperature, and

(*g*) Program the column temperature up to the maximum several times with normal carrier flow until a stable, flat baseline is obtained.

8.2 *Column Resolution*—To test column resolution, inject the same volume of the calibration mixture as used during normal sample analysis and obtain the chromatogram by the procedure described in Section 9. Using the *n*-dodecane (C_{12}) and *n*-tridecane (C_{13}) peaks, and Fig. 1, calculate the resolution, *R*, as calculated from the equation:

$$R = 2D/(Y_1 + Y_2) \quad (1)$$

where:

D = time, s, between *n*-C_{12} and *n*-C_{13} apexes,
Y_1 = peak width of *n*-C_{12}, s, and
Y_2 = peak width of *n*-C_{13}, s.

The resolution, *R*, thus calculated must be between eight and twelve to be acceptable.

8.3 *Skewing of Peaks*—Calculate the ratio *A/B* on peaks in the calibration mixture as shown in Fig. 2. Call the width in seconds of the part of the peak ahead of the time of the apex at 5 % of peak height *A*, and call *B* to equal the width in seconds of the part of the peak after the time of the apex at 5 % of peak height. This ratio must not be less than 0.5 nor more than 2.0

8.4 Typical instrument parameters are as follows:

8.4.1 Column length equals 10 to 30 m,

8.4.2 Column material and size equal fused silica or glass, 0.53 to 0.75 mm inside diameter,

8.4.3 Liquid phase equals bonded methyl silicone or equivalent,

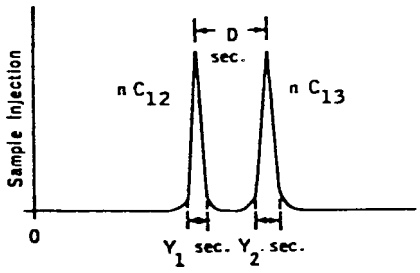

FIG. 1 Column Resolution

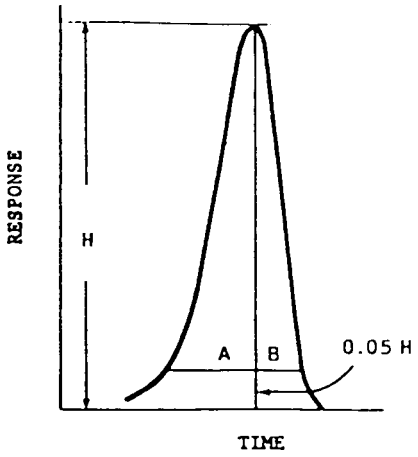

FIG. 2 Peak Skewness

8.4.4 Column film thickness equals 3 to 5 µm,
8.4.5 Initial column temperature equals 35°C (95°F),
8.4.6 Initial hold equals 2 min,
8.4.7 Program rate equals 10 to 20°C (18 to 36°F)/min,
8.4.8 Final temperature equals 225°C (437°F) to 280°C (536°F),
8.4.9 Final time equals 2 min,
8.4.10 Injector temperature equals cool, on-column,
8.4.11 Detector temperature equals 250°C (482°F),
8.4.12 Detector range (HP) equals 6 to 8,
8.4.13 Carrier gas flow rate equals 8 to 10 mL/min, and
8.4.14 Sample size equals 0.1 to 0.5 µL.

9. Procedure

9.1 *Calibration*—After preparing the apparatus as in Section 8, inject the calibration mixture into the gas chromatograph. Record the data in such a manner that the retention times of peak maxima and the peak areas for each component are obtained.

9.1.1 The sample size of the calibration mixture must be chosen as to avoid distortion of the individual component peak shape caused by overloading the sample capacity of the column. Distortion in retention time measurement and hence errors in boiling point distribution will be likely with column overloading. Sample size of 0.1 to 0.5 µL have been shown to give good results.

9.1.2 This test method requires the use of commercially available "Simulated Distillation" softwares[6] to process the chromatographic data in order to obtain good precision of results. Calibration of the gas chromatographic method can be done by inputting the retention times, and the normal boiling points of each of the components of the calibration mixture. The equation for the temperature versus retention time calibration curve is automatically generated by the software.

9.1.3 Insure a rigorous syringe cleaning step between samples where multiple volumes of the next sample are flushed through the syringe and deposited to waste prior to actual injection. If an autosampler or injector is used, the syringe flushing feature has to be programmed so that syringe carryover is minimized. If injections are made manually, insure that the syringe needle is thoroughly wiped clean before injection.

9.1.4 A typical calibration curve using a 30-m column is shown in Fig. 3.

9.1.5 For best precision, make sure that the calibration curve is essentially a linear plot of boiling point versus retention time. It is essential that at least one point on the calibration curve be at a lower boiling point than the IBP of the sample. Extrapolation of the curve at the upper end is more accurate, but for best accuracy, make sure that calibration points bracket the boiling range of the sample at both the low and high ends.

[6] Beckman CALS Simulated Distillation software was used in developing this test method. There are other Simulated Distillation softwares available in the market. Such softwares are marketted by Hewlett Packard, Perkin Elmer-Nelson, Analytical Controls, VG, Separation Systems, and others.

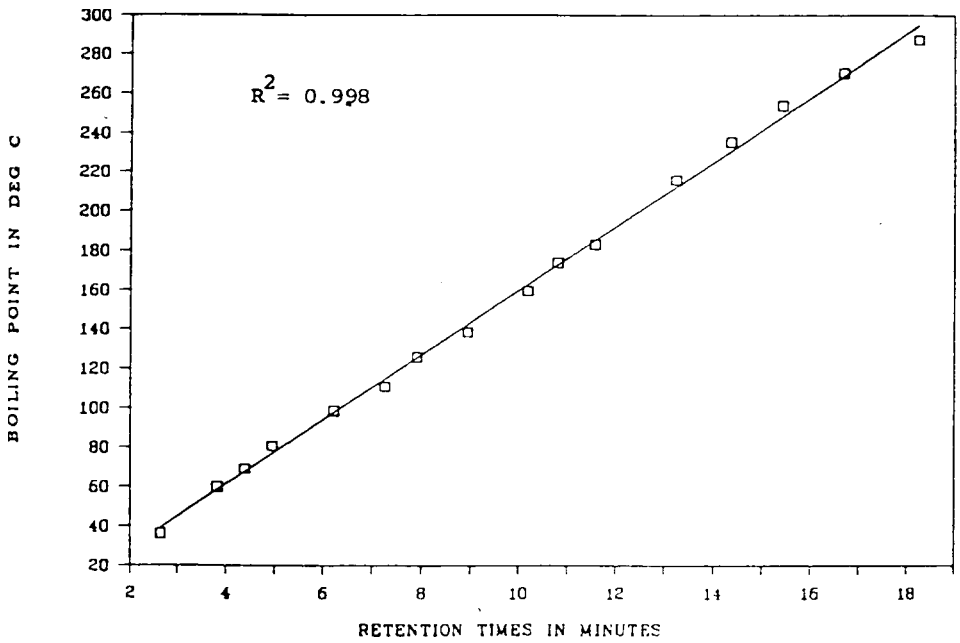

FIG. 3 Calibration Curve

9.1.6 The calibration must be checked at least once a day.

9.2 *Sample Analysis*—Using identical instrument parameters and conditions used in the calibration run, inject the sample into the gas chromatograph. Record the data in such a manner that the retention times and areas of chromatographic peaks are obtained.

9.2.1 The same software used to process the calibration run must be used to process the sample gas chromatographic data. The software must be able to process the data and report IBP, and FBP, as well as boiling point data for any percent recovered (at 1 % interval) between the initial and the final boiling point.

9.2.2 Care must be taken that the sample size chosen does not allow some peaks to exceed the linear range of the detector. Choose the detector range and the sample size such that all peaks are fully integrated.

9.2.3 Baseline stability is generally not a problem for these types of samples. If problems with baseline is encountered, constant attention must be given to all factors that influence baseline stability such as column bleed, septum bleed, detector temperature control, carrier gas flow, leaks, etc. Baseline correction is generally not required for these types of samples.

9.2.4 Make periodic blank runs in the normal manner without injection of sample to insure that the system is free from contamination. If the blank run shows sample carryover contamination, steps must be taken to eliminate the source of contamination.

10. Calculation

10.1 The gas chromatographic data is processed by a data processor or computer using commercially available "Simulated Distillation" software.

10.2 The total area of all the peaks in the chromatogram is calculated.

10.3 The retention time at which the cumulative area count is equal to 0.5 % of the total area is translated to a boiling point value from the calibration equation obtained in the calibration procedure (see 9.1) and is reported as the initial boiling point (IBP) of the sample.

10.4 The retention time at which the cumulative area count is equal to 99.5 % of the total area is translated to a boiling point value from the calibration equation obtained in the calibration procedure (see 9.1) and is reported as the final boiling point (FBP) of the sample.

10.5 The cumulative area at each interval between the initial and final boiling points is divided by the total area and multiplied by 100 to give the cumulative percent of the sample recovered at each time interval. The retention time associated with each percent between 1 and 99 is translated to a boiling point temperature from the calibration equation obtained in the calibration procedure (see 9.1).

11. Report

11.1 Report the temperature to the nearest 0.1°C (0.2°F) at 1 % intervals between 1 and 99 %, at the IBP (0.5 %), and at the FBP (99.5 %). Other report formats based upon the user's needs can be employed.

12. Precision and Bias

12.1 *Precision*—The precision of this test method was determined by the statistical examination of interlaboratory test results.[7]

12.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty:

Percent Off	Repeatability
IBP to 50 %	0.7°C (1.3°F)
51 % to FBP	0.7°C (1.3°F)

12.1.2 *Reproducibility*—The difference between two single independent results obtained by two different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty:

Percent Off	Reproducibility
IBP to 50 %	2.0°C (3.6°F)
51 % to FBP	3.0°C (5.4°F)

12.2 The interlaboratory testing was conducted and results analyzed according to Practice E 691. Eight laboratories and six samples were involved.

12.3 *Bias*—Bias cannot be determined since there is no acceptable reference material suitable for determining the bias for the procedure in this test method.

13. Keywords

13.1 boiling point distribution; distillation; gas chromatography; simulated distillation

[7] Supporting data are available from ASTM headquarters. Request RR:D01-1081.