Designation: D7807 – 12

Standard Test Method for Determination of Boiling Range Distribution of Hydrocarbon and Sulfur Components of Petroleum Distillates by Gas Chromatography and Chemiluminescence Detection[1]

This standard is issued under the fixed designation D7807; 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. The test method is applicable to petroleum products and fractions having a final boiling point of 538°C (1000°F) or lower at atmospheric pressure as measured by this test method. This test method is limited to samples having a boiling range greater than 55°C (100°F), and having a vapor pressure sufficiently low to permit sampling at ambient temperature.

1.1.1 The applicable sulfur concentration range will vary to some extent depending on the boiling point distribution of the sample and the instrumentation used; however, in most cases, the test method is applicable to samples containing levels of sulfur above 10 mg/kg.

1.2 This test method requires the use of both FID and SCD for detection. The hydrocarbon simulated distillation data obtained from the FID signal should be performed according to Test Method D2887.

1.3 The test method is not applicable for analysis of petroleum distillates 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, D7096, D5307, D7169, or D7500.

1.4 This test method does not purport to identify all sulfur species in a sample. The detector response to sulfur is equimolar for all sulfur compounds within the scope (1.1) of this test method. Thus, unidentified sulfur compounds are determined with equal precision to that of identified substances. Total sulfur content is determined from the total area of the sulfur detector.

1.4.1 This test method uses the principles of simulated distillation methodology.

1.5 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.6 *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

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

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)

D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

D3710 Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography (Withdrawn 2014)[3]

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

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]

[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.

D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence
D5623 Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
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
D7500 Test 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
E178 Practice for Dealing With Outlying Observations
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. Detailed definitions of these can be found in 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. 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 equal to 0.5 % of the total sample area under the chromatogram is obtained.

3.2.6 *response factor (RF), n*—the factor used in order to calculate the mg/kg Sulfur recovery of the sample.

3.2.7 *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).

3.2.8 *slice time, n*—the cumulative slice rate (analysis time) associated with each area slice throughout the chromatographic analysis. The slice rate is the time at the end of each contiguous area slice.

3.2.9 *total sample area, n*—the cumulative corrected area from the initial point to the final area point.

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, normal decane n-C10, iso-tetradecane = i-C14).

4. Summary of Test Method

4.1 The boiling range distribution determination by distillation is simulated by the use of gas chromatography. A nonpolar open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. The column temperature is raised at a reproducible linear rate and the area under the chromatogram is recorded throughout the analysis. Boiling points are assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analyzing a known mixture of hydrocarbons covering the boiling range expected in the sample. A quantitative standard is used to determine the SCD detector response factor. 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. From these data, the boiling range distribution can be obtained.

4.1.1 By splitting the column effluent to FID and Sulfur Chemiluminescence Detector, simultaneous detection for Hydrocarbon (FID) and Sulfur (SCD) components boiling range distribution is obtained. The Hydrocarbon simulated distillation data should be calculated according to Test Method D2887.

4.1.2 Alternatively, the FID may be used with the SCD detector superimposed over the FID and thus avoiding splitting the sample through the column exit. This type of arrangement will lower the sensitivity of the detector in the sulfur mode.

4.2 A sample aliquot is 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 reproducible linear rate to effect separation of the sample components in

order of increasing boiling point. The elution of sample components is quantitatively determined using a flame ionization detector and a sulfur chemiluminescence detector. The detector signal integral 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 this test method (C5- C44) are determined and correlated to their theoretical 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.

4.5 *Sulfur Chemiluminescence Detection*—As sulfur compounds elute from the gas chromatographic column, they are processed in a heated combustion zone. The products are collected and transferred to a sulfur chemiluminescence detector (SCD). This technique provides a sensitive, selective, linear response to volatile sulfur compounds and is used for the selective sulfur detection, while collecting hydrocarbon data from the FID.

4.6 *Alternative Detectors*—This test method is written for the sulfur chemiluminescence detector but other sulfur specific detectors can be used provided they have sufficient linearity, sensitivity and have equimolar response to all eluted sulfur compounds, do not suffer from interferences, and satisfy quality assurance criteria. Regulatory agencies may require demonstration of equivalency of alternative detection systems to the SCD.

5. Significance and Use

5.1 The boiling range distribution of light and medium petroleum distillate fractions provides an insight into the composition of feed stocks and products related to petroleum refining processes. This gas chromatographic determination of boiling range 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 Test Method D2887 (538°C) boiling range determination by gas chromatography to include sulfur boiling range distribution in the petroleum distillate fractions. Knowledge of the amount of sulfur and its distribution in hydrocarbons is economically important in determining product value and in determining how best to process or refine intermediate products. Sulfur compounds are known to affect numerous properties of petroleum and petrochemical products. The corrosion of metals and poisoning of catalysts is of particular concern. In addition, the content of sulfur in various refined products may be subject to governmental regulations. Test Methods, such as, D2622, D3120, D5504 and D5623, are available to determine total sulfur content or content of individual sulfur compounds in petroleum and petroleum products. Test Methods, such as, D86, D1160, D2887, D3710, D2892, are also available to determine the hydrocarbon boiling ranges of such samples. The gas chromatographic determination of the sulfur boiling range assists in process development, in treatment and control of refining operations and is useful for assessing product quality. This determination produces detailed information about the sulfur distribution in a sample that cannot be obtained by either total sulfur analysis or analysis of sulfur in discreet distillation cuts.

5.2.1 The hydrocarbon boiling range distributions obtained by Test Method D2887 are theoretically equivalent to those obtained by true boiling point (TBP) distillation (see Test Method D2892). They are not equivalent to results from low efficiency distillation such as those obtained with Test Method D86 or D1160.

6. Apparatus

6.1 *Chromatograph*—Any gas chromatograph, with hardware necessary for interfacing to a chemiluminescence detector and containing all features necessary for the intended application(s) can be used. The gas chromatographic system used shall have the following performance characteristics:

6.2 *Column Temperature Programmer*—The chromatograph must be capable of linear programmed temperature operation over a range sufficient to elute compounds up to a boiling temperature of 538°C (1000°F) before reaching the upper end of the temperature program. The programming rate must be sufficiently reproducible to obtain retention time repeatability of 0.01 min (0.6 s, corresponding to approximately 0.5°C) for each component in the calibration mixture described in 7.7.

6.3 *Detectors*—This test method requires a Flame Ionization Detector (FID) and a Sulfur Chemiluminescence Detector (SCD).

6.3.1 *FID*—The FID shall meet or exceed the following specifications in accordance with Practice E594. Check the detector according the instrument manufacturer's instructions.

6.3.2 *SCD*—The sulfur chemiluminescence detector shall meet or exceed the following specifications: *(1)* greater than 10^3 linearity, *(2)* less than 1 pg S/s sensitivity, *(3)* greater than 10^6 selectivity for sulfur compounds over hydrocarbons, *(4)* no quenching of sulfur compound response from co-eluting hydrocarbons when the same volume of sample is injected as for regular analysis, and *(5)* equimolar response ($<\pm 10$ %) on a sulfur basis.

6.3.2.1 For the purpose of boiling point calibration, the system must be capable of measuring sulfur compounds and hydrocarbons simultaneously from a single column and injection, for example, flame ionization detector with splitting the column effluent prior to the sulfur chemiluminescence detector. Alternatively, a combined FID/SCD can also be used in order to obtain simultaneous sulfur and FID chromatogram.

6.3.2.2 Sulfur compounds eluting from the chromatographic column are processed in a heated hydrogen rich combustion zone fitted to the end of the column. Products are transferred under reduced pressure to the reaction chamber of the chemiluminescence detector. An excess of ozone present in the chamber reacts with the sulfur combustion product(s) to liberate blue (480 nm) and ultraviolet light (260 nm).

6.3.3 *Detector Split Requirements*—To ensure the low levels of sulfur are detected properly, the system must be capable to detect the components in the system sulfur test mixture (see

8.9) with signal to noise (peak-to-peak) ratio of at least 100. Connections of the column to the detector shall be such that no temperature below the column temperature exists. Refer to Practice E1510 for proper installation and conditioning of the capillary column.

6.4 *Sample Inlet System*—Any sample inlet system capable of meeting the performance specification in 8.7 may be used. Programmed temperature vaporization (PTV) and programmable cool on-column injection systems have been used successfully.

6.5 *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.

6.6 *Micro syringe*—A micro syringe with a 23 gauge or smaller stainless steel needle is used for sample introduction. Syringes of 0.1 to 10 µL capacity are commercially available. Automatic syringe injection is recommended.

6.7 *Column*—This test method is limited to the use of non-polar wall coated open tubular (WCOT) columns.

6.7.1 Any column and conditions may be used that provide separation of typical petroleum hydrocarbons in order of increasing boiling point and meet the column performance requirements of 8.7.1 and 9.3.1.1.

6.7.2 Glass, fused silica, and stainless steel columns, with a 0.53 mm diameter have been successfully used. Cross-linked and bonded 100 % dimethyl-polysiloxane stationary phases with film thickness of 0.5 to 2.65 µm have been used. The column length and liquid phase film thickness shall allow the elution of at least C44 n-paraffin (BP = 545°C).

6.8 *Data Acquisition System*—Use of an electronic integrating device or computer is mandatory for determining the detector response and for boiling point calibration. The device must have the following capabilities: *(1)* graphic presentation of the chromatogram, *(2)* digital display of chromatographic peak areas, *(3)* measurement of area and time intervals, *(4)* calculation and use of response factors in accordance with Practice D4626, for example, external standardization, and *(5)* the maximum area measured must be within the linear range of the measuring 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 Typical Gas Chromatographic Conditions

Instrument	A gas chromatograph equipped with an on-column or temperature programmable vaporizing injector (PTV)
Column	Capillary 10 m, 0.53 mm ID, 0.88 µm 100 % dimethyl-polysiloxane stationary phase
Flow Conditions	25 mL/min He carrier (constant flow)
Inlet	Temperature: Programmed 100°C to 350°C at 25°C/min
Detector	Split FID – SCD or SCD with FID Adapter
FID	Temperature: 350°C 35 mL/min H2, 350 mL/min Air
SCD	Temperature: 950°C 10 mL/min O_2, 90 mL/min H_2 100 – 150 mL/min He or N_2 make-up
Oven	35°C to 350°C at 25°C/min
Sample Injection	0.1 µL neat

7. Reagents and Materials

7.1 *Carrier Gas*—Helium, of at least 99.999 % (v/v) purity (**Warning—**Helium is a compressed gas under high pressure). Any oxygen present is removed by a chemical resin filter (**Warning—**Follow the safety instructions from the filter supplier.) The total amount of impurities should not exceed 10 mL/m3. Helium or Nitrogen (at least 99.999 % (v/v)) can also be used as detector make-up gas.

7.1.1 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 at least 99.999 % (v/v) purity (suitable for the flame ionization detector (FID). (**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 flame ionization detector (FID). (**Warning—**Compressed air is a gas under high pressure and supports combustion.)

7.4 *Oxygen*—High purity (for example, hydrocarbon-free) compressed oxygen is used as the oxidant for the sulfur chemiluminescence detector (SCD). (**Warning—**compressed oxygen is a gas under high pressure and supports combustion.)

NOTE 2—Some SCD detectors allow the use of air instead of oxygen, contact the SCD manufacturer for information on the use of air as oxidant.

7.5 *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.

7.5.1 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.

7.6 *Cyclohexane (C_6H_{12})*—(99+ % pure) may be used as a viscosity reducing solvent. It is miscible with asphaltic hydrocarbons, however, it responds well to the FID. The quality (hydrocarbon content) should be determined by this test method prior to use as a sample diluent. (**Warning—**Cyclohexane is flammable.)

7.7 *Calibration Mixture*—An accurately weighed mixture of approximately equal mass quantities of nhydrocarbons dissolved in a suitable solvent. The mixture shall cover the boiling range from n-C5 to n-C44, but does not need to include every carbon number, but at least sufficient number of points to generate a reliable calibration curve and the C16 and C18.

7.7.1 At least one compound in the mixture must have a boiling point lower than the IBP of the sample and at least one

compound in the mixture must have a boiling point higher than the FBP of the sample. Boiling points of n-paraffin's are listed in Table 2.

7.7.2 If necessary, for the calibration mixture to have a compound with a boiling point below the IBP of the sample, propane or butane can be added to the calibration mixture, non-quantitatively, by bubbling the gaseous compound into the calibration mixture in a septum sealed vial using a gas syringe.

7.7.3 *Reference Material*—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 being determined.

8. Preparation of Apparatus

8.1 *Gas Chromatograph Setup:*

8.2 Place the gas chromatograph and ancillary equipment into operation in accordance with the manufacturer's instructions. Recommended operating conditions are shown in Table 1.

8.3 When attaching the column to the detector inlet, ensure that the end of the column terminates as close as possible to the FID jet. Follow the instructions in Practice E1510.

8.4 The FID should be periodically inspected and, if necessary, remove any foreign deposits formed in the detector from combustion of silicone liquid phase or other materials. Such deposits will change the response characteristics of the detector.

8.5 *SCD*—Place in service in accordance with the manufacturer's instructions. Optimization of the oxidant/fuel ratio is critical for ensuring complete combustion of hydrocarbon components in a sample. A flame or combustion zone that is too hydrogen rich will result in incomplete combustion. Matrix interference is occasionally observed when changing sample size. When matrix interference is indicated, samples may be analyzed by dilution or application of other mitigation efforts.

8.5.1 The typical flameless/combustion zone interface contains ceramic tubes in its construction. The performance of these tubes is critical to performance of the SCD system. Compromised ceramic tubes are susceptible to matrix effects. Compromised tubes may allow for reproducible duplicate sample analysis but will fail QA procedures such as matrix dilution and spike analyses. Poorly functioning tubes can also result in severe instrument drift, loss of equimolar response and general response instability. Compromised tubes must be replaced to restore nominal instrument function.

8.6 *Column Conditioning*—A new column will require conditioning at the upper test method operating temperature to reduce or eliminate significant liquid phase bleed, resulting in a stable chromatographic baseline. Follow the guidelines outlined in Practice E1510.

8.7 *System Performance Specification:*

8.7.1 *Column Resolution*—The column resolution, influenced by both the column physical parameters and operating conditions, affects the overall determination of boiling range distribution. Resolution is therefore specified to maintain equivalence between different systems (laboratories) employing this test method. Resolution is determined using Eq 1 and the C16 and C18 paraffins from the calibration mixture analysis

TABLE 2 Boiling Points of Normal Paraffins[A,B]

Carbon No.	Boiling Point, °C	Boiling Point, °F	Carbon No.	Boiling Point, °C	Boiling Point, °F
1	–162	–259	23	380	716
2	–89	–127	24	391	736
3	–42	–44	25	402	755
4	0	31	26	412	774
5	36	97	27	422	791
6	69	156	28	431	808
7	98	209	29	440	825
8	126	258	30	449	840
9	151	303	31	458	856
10	174	345	32	466	870
11	196	385	33	474	885
12	216	421	34	481	898
13	235	456	35	489	912
14	254	488	36	496	925
15	271	519	37	503	937
16	287	548	38	509	948
17	302	576	39	516	961
18	316	601	40	522	972
19	330	626	41	528	982
20	344	651	42	534	993
21	356	674	43	540	1004
22	369	695	44	545	1013

[A] API Project 44, October 31, 1972 is believed to have provided the original normal paraffin boiling point data that are listed in Table 1. However, over the years some of the data contained in both API Project 44 (Thermodynamics Research Center Hydrocarbon Project) and Test Method D6352 have changed and they are no longer equivalent. Table 1 represents the current normal paraffin boiling point values accepted by Subcommittee D02.04 and found in all test methods under the jurisdiction of Section D02.04.0H.

[B] Used *n*-paraffin boiling points are traditionally rounded to the nearest whole degree for calibration. The boiling points listed in Table 1 are correct to the nearest whole number in both degrees Celsius and degrees Fahrenheit. However, if a conversion is made from one unit to the other and then rounded to a whole number, the results will not agree with the table values for a few carbon numbers. For example, the boiling point of n-heptane is 98.425°C, which is correctly rounded to 98°C in the table. However, converting 98.425°C gives 209.165°F, which rounds to 209°F, while converting 98°C gives 208.4°F, which rounds to 208°F. Carbon numbers 2, 4, 7, 8, 9, 13, 14, 15, 16, 25, 27, and 32 are affected by rounding.

(see 7.7), and is illustrated in Fig. 1. Resolution (R) should be at least three, using the identical conditions employed for sample analyses:

$$R = 2(t_2 - t_1) / (1.699\ (w_2 + w_1)) \quad (1)$$

where:

R = resolution,
t_1 = time(s) fro the *n*-C16 peak maximum,
t_2 = time(s) for the *n*-C18 peak maximum,
w_1 = peak width(s), at half height, of the *n*-C16 peak, and
w_2 = peak width(s), at half height, of the *n*-C18 peak.

8.7.2 *Column Elution Characteristics*—The recommended column liquid phase is a non-polar phase such as 100 % dimethyl-polysiloxane.

8.8 *Sulfur Compound Standards*—99 + % purity (if available). Obtain pure standard material of all sulfur compounds of interest (**Warning—**Sulfur compounds can be flammable and harmful or fatal when ingested or inhaled.). If purity is unknown or questionable, analyze the individual standard material by any appropriate means and use the result to provide accurate standard quantities.

8.9 *System Sulfur Test Mixture*—Gravimetrically prepare a solution of sulfur compounds at approximately 20 mg/kg sulfur in ultra-low sulfur Diesel in accordance with Practice D4307. The test mixture should cover a broad boiling point range and should be within the range of the hydrocarbon distribution.

8.9.1 For example, Benzothiophene, DiBenzothiophene, and 2,2'-dithiopyridine.

Name	Formula	Mol wt	m/m%, S	Boiling Point, °C
Benzothiophene	C_8H_6S	134.2	23.89 %	221
Dibenzothiophene	$C_{12}H_8S$	184.26	17.40 %	332
2,2'-dithiopyridine	$C_{10}H_8N_2S_2$	220.31	29.10 %	348

8.10 *Sulfur Equimolarity*—The SCD is an equimolar detector. Therefore, response factors for all sulfur components should be within 10 %. Failure to satisfy this criterion indicates either system test mixture degradation or failure of the SCD heated combustion zone or in other parts of the analysis system.

8.10.1 Calculate the relative response factor for each sulfur compound in the System Sulfur test mixture (see 8.9):

8.10.2 Inject and analyze a suitable amount of the system sulfur test mixture (8.9). Relative response factors should be calculated for each sulfur compound in the test mixture (relative to a referenced component) in accordance with Practice D4626 or Eq 2.

$$R_m = \frac{C_n \times A_r}{C_r \times A_n} \quad (2)$$

where:

R_m = relative response factor for a given sulfur compound,
C_n = concentration of the sulfur compound as sulfur,
A_n = peak area of sulfur compound,
C_r = concentration of referenced sulfur standard as sulfur, and
A_r = peak area of the referenced sulfur standard.

8.10.2.1 The relative response factor (R_m) for each sulfur compound should not deviate from the average response factor by more than 10 %. Deviation of response by more than 10 % or severe peak asymmetry indicates a chromatography or detector problem that must be corrected to ensure proper selectivity, sensitivity, linearity, and integrity of the system. If necessary, optimize the system according to instructions from the manufacturer.

8.11 *Recovery Check*—To check the stability of the analysis system, a QC-sample analysis should be made at least every 10 analyses. The total area for the sulphur components should not deviate more than 10 % from the value obtained in the previous calibration run.

9. Procedure

9.1 *Analysis Sequence Protocol*—Define and use a predetermined schedule of analysis events designed to achieve maximum reproducibility for these determinations. The schedule will include cooling the column oven and injector to the initial

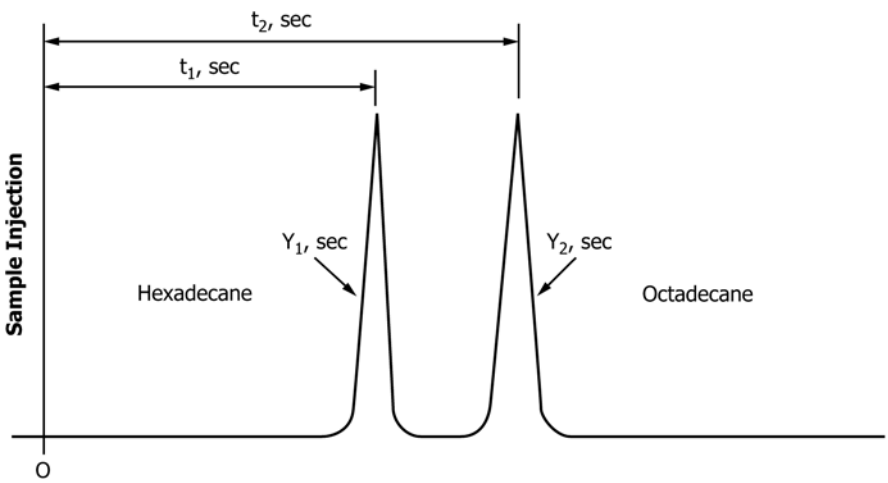

FIG. 1 Column Resolution Parameters

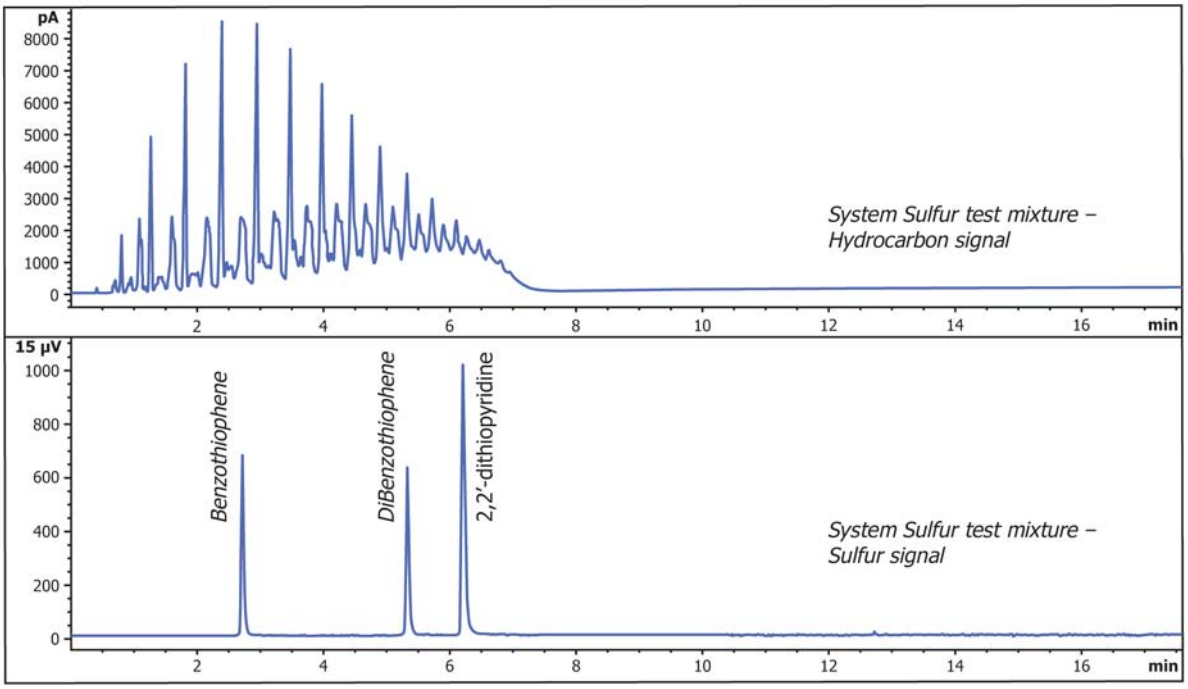

FIG. 2 System Sulfur Test Mixture

starting temperature, equilibration time, sample injection and system start, analysis, and final temperature hold time.

9.1.1 After chromatographic conditions have been set to meet performance requirements, program the column temperature upward to the maximum temperature to be used and hold that temperature for the selected time. Following the analysis sequence protocol, cool the column to the initial starting temperature.

9.1.2 Inject either the calibration mixture, solvent, or sample into the chromatograph; or make no injection (baseline blank). At the time of injection, start the chromatograph time cycle and the integrator/computer data acquisition. Follow the analysis protocol for all subsequent repetitive analyses or calibrations. Since complete resolution of sample peaks is not expected, do not change the sensitivity setting during the analysis.

9.2 *Baseline Blank*—Perform a blank analysis (baseline blank) at least once per day. The blank analysis may be without injection or by injection of an equivalent solvent volume as used with sample injections, depending upon the subsequent data handling capabilities for baseline/solvent compensation. The blank analysis is typically performed prior to sample analyses, but may be useful if determined between samples or at the end of a sample sequence to provide additional data regarding instrument operation or residual sample carryover from previous sample analyses.

NOTE 3—If automatic baseline correction (see Note 1) is provided by the gas chromatograph, further correction of area slices may not be required. However, if an electronic offset is added to the signal after baseline compensation, additional area slice correction may be required in the form of offset subtraction. Consult the specific instrumentation instructions to determine if an offset is applied to the signal. If the algorithm used is unclear, the slice area data can be examined to determine if further correction is necessary. Determine if any offset has been added to the compensated signal by examining the corrected area slices of those time slices which precede the elution of any chromatographic unretained substance. If these corrected area slices (representing the true baseline) deviate from zero, subtract the average of these corrected area slices from each corrected area slice in the analysis.

9.3 *Retention Time versus Boiling Point Calibration*—If this is the first time that an analysis is carried out, prepare the sequence to include the retention time calibration standard, the Reference Gas Oil and a blank which is necessary to calculate the Boiling Point Distribution of the Reference Gas Oil as well as for subsequent samples analysis. Calibration should be performed weeky when the instrument is in use, or whenever maintenance is performed and as dictated by the lab on-site precision and or Quality Control protocol. Inject an appropriate aliquot of the calibration mixture (see 7.7) into the chromatograph, using the analysis sequence protocol. Obtain a normal (peak detection) data record in order to determine the peak retention times and the peak areas for each component. Collect a time slice area record if a boiling range distribution report is desired. Fig. 3 illustrates a graphical plot of a calibration analysis.

9.3.1 Inspect the chromatogram of the calibration mixture for evidence of skewed (non-Gaussian shaped) peaks. Skewness is often an indication of overloading the sample capacity of the column, which will result in displacement of the peak apex relative to non-overloaded peaks. Distortion in retention time measurement and hence errors in boiling point temperature calibration will be likely if column overloading occurs. The column liquid phase loading has a direct bearing on acceptable sample size. Reanalyze the calibration mixture using a smaller sample size or a more dilute solution to avoid peak distortion.

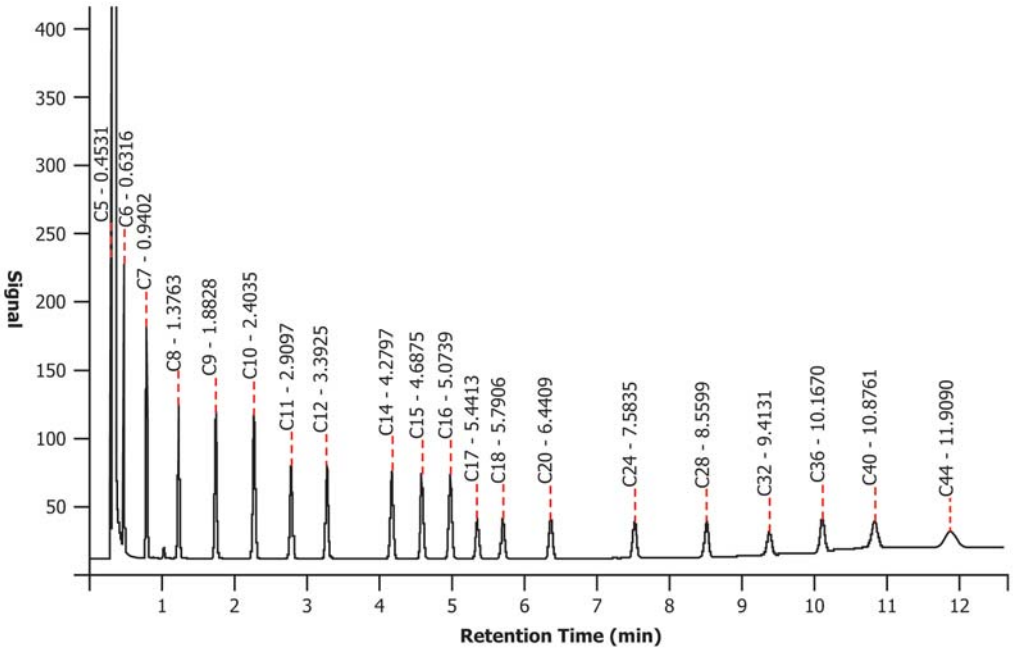

FIG. 3 Chromatogram of D_5 to C_{44} diluted in Cyclohexane

9.3.1.1 *Skewness Calculation*—Calculate the ratio A/B on specified peaks in the calibration mixture as indicated by the designations in Fig. 4. A is the width in seconds of the portion of the peak eluting prior to the time of the peak apex and measured at 10 % of peak height (0.10-H), and B is the width in seconds of the portion of the peak eluting after the time of the peak apex at 10 % of peak height (0.10-H). The skewness of all peaks shall be shall not be less than 0.5 nor more than 2.

9.3.2 Prepare a calibration table based upon the results of the analysis of the calibration mixture by recording the time of each peak maximum and the boiling point temperature in degrees Celsius (or Fahrenheit) for every component in the mixture. Normal paraffin boiling point temperatures (atmospheric equivalent temperatures) are listed in Table 2.

9.4 *Sample Preparation*—The amount of sample injected must not overload the column stationary phase capacity nor exceed the detector linear range. A narrow boiling range sample will require a smaller amount injected than a wider boiling range sample. Samples that are of low enough viscosity to be sampled with a syringe at ambient temperature may be injected neat. This type of sample may also be diluted with an appropriate solvent (for example, cyclohexane) to control the amount of sample injected.

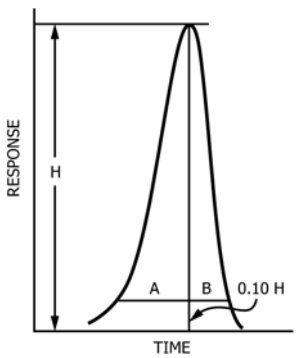

FIG. 4 Designation of Parameters for Calculation of Peak Skewness

9.4.1 Samples that are too viscous or waxy to sample with a syringe may be diluted with an appropriate solvent.

9.5 *Reference Gas Oil Analysis*—Perform an analysis of the gas oil following the analysis sequence protocol. Collect the area slice data and provide a boiling point distribution report as in Sections 10 and 11.

9.5.1 The results of this reference analysis must agree with the values given in Table 3 within the range specified by the test method reproducibility (see Section 12). If it does not meet the criteria in Table 3, 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 9.3.

9.5.2 Perform this reference gas oil confirmation test at least once per day or as often as required to establish confidence in consistent compliance with 9.5.1.

9.6 *Sample Analysis*—Using the analysis sequence protocol inject a sample aliquot into the gas chromatograph. Collect a contiguous time slice record of the entire analysis.

10. Calculations

10.1 Two signals are collected, one for the Hydrocarbons on the FID and one for the Sulfur on the SCD. For the Hydrocarbons on the FID the calculations should be performed according to Test Method D2887, for Sulfur on the SCD follow the calculations as described in 10.2 to 10.16.

10.2 Load the sample chromatograms slices into a table.

10.3 The number of slices required at the beginning of Data acquisition depends on chromatographic variables such as the

TABLE 3 Repeatability and Standard Deviation for the ASTM Reference Gas Oil in °C or °F Analyzed in the Sulfur Mode[A]

m/m %	BP (°C)	BP (°C)	BP (°C)	BP (°C)	BP (°C)	Average	ASTM Repeatability Std. Dev.
IBP	179.4	181.3	180.6	182.1	180.3	180.7	4.2
5	251.0	252.4	252.4	252.3	252.3	252.1	1.8
10	272.1	273.3	273.5	273.5	273.5	273.2	1.5
15	288.6	290.9	290.4	290.2	289.9	290	3.1
20	301.8	304.0	302.7	302.6	302.5	302.7	2.8
25	312.1	314.9	313.6	313.4	313.0	313.4	3.7
30	320.3	322.6	321.3	321.1	321.0	321.3	3.1
35	328.7	330.8	329.9	329.6	329.3	329.7	2.9
40	335.6	337.2	336.5	336.1	336.0	336.3	2.5
45	342.2	344.0	343.5	342.9	342.7	343.1	2.9
50	349.8	351.2	350.8	350.4	350.2	350.5	2.2
55	356.5	358.0	357.7	357.1	357.0	357.3	2.6
60	364.6	365.9	365.8	365.1	365.1	365.3	2.5
65	372.9	374.0	374.0	373.2	373.2	373.5	2.3
70	381.8	382.5	382.6	381.9	381.9	382.1	1.7
75	391.2	391.9	392.1	391.5	391.4	391.6	1.6
80	400.9	401.6	402.0	401.3	401.2	401.4	1.7
85	411.9	412.6	413.1	412.3	412.4	412.5	1.8
90	425.3	426.0	426.6	425.6	425.7	425.8	2.1
95	444.4	445.3	446.2	444.8	444.7	445.1	2.8
FBP	494.6	498.1	501.2	497.4	495.2	497.3	9.0
m/m %	BP (°F)	BP (°F)	BP (°F)	BP (°F)	BP (°F)	Average	ASTM Repeatability Std. Dev
IBP	354.9	358.3	357.1	359.8	356.5	357.3	7.5
5	483.8	486.3	486.3	486.1	486.1	485.8	3.3
10	521.8	523.9	524.3	524.3	524.3	523.8	2.7
15	551.5	555.6	554.7	554.4	553.8	554.0	5.5
20	575.2	579.2	576.9	576.7	576.5	576.9	5.1
25	593.8	598.8	596.5	596.1	595.4	596.1	6.6
30	608.5	612.7	610.3	610.0	609.8	610.3	5.5
35	623.7	627.4	625.8	625.3	624.7	625.5	5.3
40	636.1	639.0	637.7	637.0	636.8	637.3	4.4
45	648.0	651.2	650.3	649.2	648.9	649.6	5.3
50	661.6	664.2	663.4	662.7	662.4	662.9	4.0
55	673.7	676.4	675.9	674.8	674.6	675.1	4.6
60	688.3	690.6	690.4	689.2	689.2	689.5	4.4
65	703.2	705.2	705.2	703.8	703.8	704.3	4.2
70	719.2	720.5	720.7	719.4	719.4	719.8	3.1
75	736.2	737.4	737.8	736.7	736.5	736.9	2.9
80	753.6	754.9	755.6	754.3	754.2	754.5	3.1
85	773.4	774.7	775.6	774.1	774.3	774.5	3.3
90	797.5	798.8	799.9	798.1	798.3	798.4	3.8
95	831.9	833.5	835.2	832.6	832.5	833.2	5.1
FBP	922.3	928.6	934.2	927.3	923.4	927.1	16.1

[A] This data set is from one laboratory only.

column flow, column film thickness, initial column temperature and column length. In addition, the detector signal level has to be as low as possible at the initial temperature of the analysis. The detector signal level for both the sample signal and the blank at the beginning of the run must be within 10 % for proper zeroing of the signals. Thus, the sampling frequency has to be adjusted so that at least a significant number of slices are acquired prior to the start of elution of sample or solvent. Adjust the sampling frequency to obtain a minimum of 5 slices. These slices should not contain area counts due to either sample or solvent elution.

10.4 Calculate the average slice offset at start of chromatogram as follows:

10.4.1 Verify the presence of large positive or negative slices by comparing the areas of each slice. These anomalies are indication of an instrumental or chromatographic problem. These slices if used will cause erroneous results in the boiling point distribution calculation.

10.4.2 Noisy signals and or signals presenting spurious events may require the use of such techniques as Data Smoothing or outliers determination as outlined in Practice E178. However, if good chromatographic principles are used, the occurrence of these large negative or positive signals is rare. They will manifest themselves in the resulting chromatogram and are therefore easily corrected.

10.5 Subtract the average slice offset from all the slices of the sample chromatogram. This will zero the chromatogram.

10.6 Load the blank run chromatogram slices into a table.

NOTE 4—For instruments that compensate the baseline directly at the detector producing an electronically corrected baseline, either process the sample chromatogram directly or do a baseline subtraction. If the compensation is made by the instrument, 10.6 up to 10.10 may be

eliminated and proceed to 10.11.

10.7 Repeat 10.2 using the blank run table.

10.8 Verify that the slice width used to acquire the sample chromatogram is the same used to acquire the blank run chromatogram.

10.9 Subtract from each slice in the sample chromatogram table with its correspondent slice in the blank run chromatogram table.

10.10 Offset the corrected slices of the sample chromatogram by taking the smallest slice and subtracting it from all the slices. This will zero the chromatogram.

10.11 Determine the Start of Sample Elution Time:

10.11.1 *Calculate the Total Area*—Add all the corrected slices in the table. If the sample to be analyzed has a solvent peak, start counting area from the point at which the solvent peak has eluted completely. Otherwise, start at the first corrected slice.

10.11.2 *Calculate the Rate of Change between each Two Consecutive Area Slices*—Begin at the slice set in 10.11.1 and work forward. The rate of change is obtained by subtracting the area of a slice from the area of the immediately preceding slice and dividing by the slice width. The time where the rate of change first exceeds 0.0001 % per second of the total area (see 10.11.1) is defined as the start of the sample elution time.

10.11.3 To reduce the possibility of noise or an electronic spike falsely indicating the start of sample elution time, a 3 s slice average can be used instead of a single slice. For noisier baselines, a slice average larger than 3 s may be required.

10.12 *Calculate the Sample Total Area*—Add all the corrected slices in the table starting from the slice corresponding to the start of sample elution time.

10.12.1 *Calculate the Rate of Change between each Two Consecutive Area Slices*—Begin at the end of run and work backward. The rate of change is obtained by subtracting the area of a slice from the area of the immediately preceding slice and dividing by the slice width. The time where the rate of change first exceeds 0.0001 % per second of the total area (see 10.11.1) is defined as the end of sample elution time.

10.12.2 To reduce the possibility of noise or an electronic spike falsely indicating the end of sample elution a 3 s slice average can be used instead of a single slice. For noisier baselines a slice average larger than 3 s may be required.

10.13 *Calculate the Sample Total Area*—Add all the slices from the slice corresponding to the start of sample elution time to the slice corresponding to the end of sample elution time.

10.14 *Normalize to Area Percent*—Divide each slice in the sample chromatogram table by the total area (see 10.11.1) and multiply it by 100.

10.15 *Calculate the Boiling Point Distribution Table:*

10.15.1 *Initial Boiling Point*—Add slices in the sample chromatogram until the sum is equal to or greater than 0.5 %. If the sum is greater than 0.5 %, interpolate (refer to the algorithm in 10.17) to determine the time that will generate the exact 0.5 % of the area. Calculate the boiling point temperature corresponding to this slice time using the calibration table. Use interpolation when required (refer to the algorithm in 10.17).

10.15.2 *Final Boiling Point*—Add slices in the sample chromatogram until the sum is equal to or greater than 99.5 %. If the sum is greater than 99.5 %, interpolate (refer to the algorithm in 10.17) to determine the time that will generate the exact 99.5 % of the area. Calculate the boiling point temperature corresponding to this slice time using the calibration table. Use interpolation when required (refer to the algorithm in 10.17).

10.15.3 *Intermediate Boiling Point*—For each point between 1 and 99 %, find the time where the accumulative sum is equal to or greater than the area percent being analyzed. As in 10.15.1 and 10.15.2, use interpolation when the accumulated sum exceeds the area percent to be estimated (refer to the algorithm in 10.17). Use the calibration table to assign the boiling point.

10.16 *Report Results*—Print the boiling point distribution table.

10.17 *Calculation Algorithms:*

10.17.1 Calculations to determine the exact point in time that will generate the X percent of total area, where X = 0.5, 1, 2, ..., 99.5 %.

10.17.1.1 Record the time of the slice just prior to the slice that will generate an accumulative slice area larger than the X percent of the total area. Let us call this time, T_s and the accumulative area at this point, A_c.

10.17.1.2 Calculate the fraction of the slice required to produce the exact X percent of the total area:

$$A_x = \frac{A_{c+1} - A_c}{X - A_c} \tag{3}$$

10.17.1.3 Calculate the time required to generate the fraction of area A_x:

$$T_f = A_x \times W \tag{4}$$

where:

W = the slice width.

10.17.1.4 Record the exact time where the accumulative area is equal to the X percent of the total area:

$$T_t = T_s \times T_f \tag{5}$$

10.17.2 Interpolate to determine the exact boiling point given the retention time corresponding to the cumulative slice area.

10.17.2.1 Compare the given time against each retention time in the calibration table. Select the nearest standard having a retention time equal to or larger than the interpolation time.

10.17.2.2 If the interpolation time is equal to the retention time of the standard, record the corresponding boiling point.

10.17.2.3 If the retention time is not equal to a retention time of the standards (see 7.7), interpolate the boiling point temperature as follows:

10.17.2.4 If the interpolation time is less than the first retention time in the calibration table, then extrapolate using the first two components in the table:

$$BP_x = m_1 \times (RT_x - RT_1) + BP_1 \tag{6}$$

where:

m_1 = $(BP_2 - BP_1) / (RT_2 - RT_1)$,
BP_x = boiling point extrapolated,
RT_x = retention time to be extrapolated,
RT_1 = retention time of the first component in the calibration table,
BP_1 = boiling point of the first component in the calibration table,
RT_2 = retention time of the second component in the calibration table, and
BP_2 = boiling point of the second component in the calibration table.

10.17.2.5 If the interpolation time is between two retention times in the calibration table, then interpolate using the upper and lower standard components:

$$BP_x = m_u \times (RT_x - RT_1) + BP_1 \quad (7)$$

where:

m_u = $(BP_u - BP_1) / (RT_u - RT_1)$,
BP_x = boiling point extrapolated,
RT_x = retention time to be extrapolated,
RT_1 = retention time of the first component in the calibration table,
BP_1 = boiling point of the first component in the calibration table,
RT_u = retention time of the second component in the calibration table, and
BP_u = boiling point of the second component in the calibration table.

10.17.2.6 If the interpolation time is larger than the last retention time in the calibration table, then extrapolate using the last two standard components in the table:

$$BP_x = m_n \times (RT_x - RT_{n-1}) + BP_{n-1} \quad (8)$$

where:

m_n = $(BP_n - BP_{n-1}) / (RT_n - RT_{n-1})$,
BP_x = boiling point extrapolated,
RT_x = retention time to be extrapolated,
RT_{n-1} = retention time of the standard component eluting prior to the last component in the calibration table,
BP_{n-1} = boiling point of the standard component eluting prior to the last component in the calibration table,
RT_n = retention time of the last component in the calibration table, and
BP_n = boiling point of the standard component in the calibration table.

10.18 *Mass Concentration of Sulfur*—Total sulfur in the sample is obtained by the method of external standardization. The total area of the sample is related to the total area of the standard by the system response factor. Calculate the total concentration of sulfur according to Eq 9 as follows:

$$C_s = C_e \left(\frac{A_s}{A_e} \times \frac{D_e}{D_{sx}} \right) \quad (9)$$

where:

C_s = concentration (mg/kg) of sulfur in the sample,
C_e = concentration (mg/kg) of external standard calculated as sulfur,
A_s = total area of sulfur in the sample,
A_e = total area of sulfur in the external standard,
D_e = density of external standard matrix, and
D_{sx} = density of sample matrix.

This equation assumes that equivalent volumes of sample and standard are injected.

10.19 *Sulfur Content of Individual Boiling Point Cuts*—The content of sulfur in individual cuts of the sample of interest is calculated by Eq 10 as follows:

$$C_s = C_s \left(\frac{A_c}{A_s} \right) \quad (10)$$

and

$$C_s = \Sigma_{i=1}^{n} C_{ci} \quad (11)$$

where:

C_c = concentration (mg/kg) of sulfur in an individual boiling point cut,
C_s = concentration (mg/kg) of total sulfur in the sample,
A_c = area of sulfur in an individual cut,
A_s = total area of sulfur in the sample, and
C_{ci} = concentration (mg/kg) of sulfur in the *i*-th individual boiling point cut and n = the total number of individual cuts.

11. Report

11.1 For the Hydrocarbon and Sulfur Distribution, report the temperature to the nearest 0.1°C (or 0.1°F) at 1 % intervals between 1 and 99 % and at the IBP (0.5 %) and the FBP (99.5 %). Other report formats based upon users' needs may be employed.

11.1.1 Total sulfur in the sample can be reported to the nearest 0.1 mg/kg S.

12. Precision and Bias

12.1 The temporary precision is determined according to Section A21.2.3 of the ASTM "Form and Style for ASTM Standards. The repeatability standard deviation is shown in Table 3, Table 4 and Table 5. The full precision will be determined within five years.

NOTE 5—Users of other sulfur-specific detectors are requested to participate in the development of the final precision statement.

13. Keywords

13.1 boiling range distribution; distillation; gas chromatography; petroleum ; simulated distillation; sulfur chemiluminescence detection; sulfur distribution

TABLE 4 Repeatability Standard Deviation for Selected Fractions[A]

Cut in (°C) or (°F)								
°(C)	(°F)	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	Average	ASTM Repeatability Std. Dev
SET, EET[B]	SET, EET	12431.1	12338.5	12342.3	11986.7	11640.9	12147.9	550.4
SET, 120.0	SET, 248.0	39.2	38.0	38.7	38.3	36.3	38.1	2
SET, 220.0	SET, 428.0	249.9	227.6	229.2	220.4	219.7	229.4	38.2
SET, 320.0	SET, 608.0	3695.5	3469.4	3576.4	3486.4	3399.1	3525.4	388.1
SET, 420.0	SET, 788.0	10954.4	10840.9	10820.2	10548.1	10235.8	10679.8	473.5

[A] This data set is from one laboratory only.
[B] SET = Start Elution Time, EET = End Elution Time

TABLE 5 Reference Gas Oil Values in the Carbon Mode in °C or °F

% Off	BP (°C)	BP (°C)	BP (°C)	BP (°C)	BP (°C)	Average	ASTM Repeatability Std. Dev.
IBP	115.7	115.8	115.8	115.7	115.9	115.8	0.2
5	152.3	152.3	152.3	152.3	152.4	152.3	0.0
10	178.1	178.2	178.3	178.2	178.4	178.2	0.2
20	227.2	227.3	227.3	227.3	227.5	227.3	0.1
30	262.4	262.5	262.5	262.5	262.9	262.5	0.1
40	291.6	293.3	291.7	291.7	292.3	292.1	2.1
50	314.1	315.1	314.1	314.1	314.4	314.4	1.7
60	332.8	333.3	332.8	332.8	332.9	332.9	0.6
70	354.8	355.1	354.8	354.8	354.9	354.9	0.4
80	379.5	379.2	379.1	379.1	379.1	379.2	0.4
90	407.8	407.7	407.8	407.8	407.7	407.8	0.1
95	429.2	429.1	429.2	429.2	429.1	429.1	0.1
FBP	474.8	475.2	474.9	475.2	475.1	475	0.9
% Off	BP (°F)	BP (°F)	BP (°F)	BP (°F)	BP (°F)	Average	ASTM Repeatability Std. Dev
IBP	240.3	240.4	240.4	240.3	240.6	240.4	0.4
5	306.1	306.1	306.1	306.1	306.3	306.1	0.0
10	352.6	352.8	352.9	352.8	353.1	352.8	0.4
20	441.0	441.1	441.1	441.1	441.5	441.1	0.2
30	504.3	504.5	504.5	504.5	505.2	504.5	0.2
40	556.9	559.9	557.1	557.1	558.1	557.8	3.8
50	597.4	599.9	597.4	597.4	597.9	597.9	3.1
60	631.0	631.9	631.0	631.0	631.2	631.2	1.1
70	670.6	671.2	670.6	670.6	670.8	670.8	0.7
80	715.1	714.6	714.4	714.4	714.4	714.6	0.7
90	766.0	765.9	766.0	766.0	765.9	766.0	0.2
95	804.6	804.4	804.6	804.6	804.4	804.4	0.2
FBP	886.6	887.4	886.8	887.4	887.2	887.0	1.5

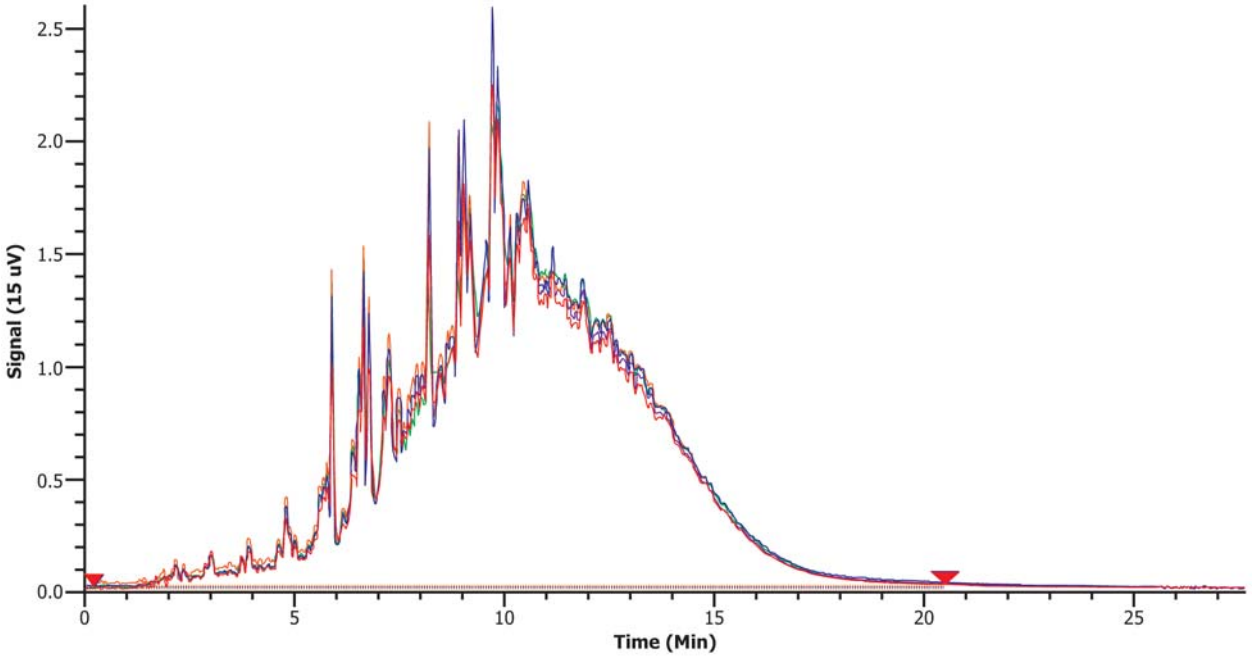

FIG. 5 Repeatability Study of the ASTM Reference Gas Oil with the SCD Detector

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Practice D6299 and ASTM MNL 7[4]).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice D6299 and ASTM MNL 7).1 Any out-of-control data should trigger an investigation for root cause(s).

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions. See Practice D6299 and ASTM MNL 7 for further guidance on QC and control charting techniques.

[4] *Manual on Presentation of Data and Control Chart Analysis*, Dean V. Neubauer, Ed., 8th Edition, 2010.