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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]

This standard is issued under the fixed designation D7169; 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.

~~ε[1] NOTE—Editorially corrected Table 2 in August 2020.~~

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 as described in Test Method D7900 (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 A correlation between boiling range distribution results from Test Method D2892, and the weight percentage data determined via this method, is presented in Appendix X2.

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

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

1.7 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.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements are given in Section 8.

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

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 °C to 700 °C by Gas Chromatography
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
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
D7900 Test Method for Determination of Light Hydrocarbons in Stabilized Crude Oils by Gas Chromatography
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 *cut specific density (CSD), n*—the ratio of the relative weight and the relative volume of a crude oil specimen distillate fraction (cut), defined by an upper and lower temperature, T_1 and T_2.

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

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

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 *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.~~

3.1.7 *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.

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

[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.

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

3.1.9 *quenching interval (QI), n*—the time interval of the start and end of elution of the CS_2 used as a solvent.
3.1.9.1 *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.

3.1.10 *residue (R), n*—the mass % of the sample that has not eluted at the temperature of calculation.
3.1.10.1 *Discussion—*
Residue is calculated from the %recovery.

3.1.11 *response factor (RF), n*—the factor used in order to calculate the %recovery of the sample.
3.1.11.1 *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 or Gravimetric Blend No. 1, is used in obtaining the response factor.

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

3.1.13 *simulated distillation, n*—the procedure of the determination of boiling ranges distribution by gas chromatography.

3.1.14 *slice, n*—the reciprocal of the data acquisition rate; the time interval used to accumulate data, expressed in seconds.
3.1.14.1 *Discussion—*
Normally 0.1 s is used. In cases where sample elutes immediately after injection, 0.05 s is used.

3.1.15 *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.

3.1.16 *volume percentage (Vol%), n*—relative volume percentage of the cut defined by a temperature range between T_1 and T_2.

3.1.17 *weight percentage (Wt%), n*—relative weight percentage of the cut defined by a temperature range between T_1 and T_2.

3.1.18 *%recovery (RC), n*—percentage of the sample eluted.
3.1.18.1 *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.

3.1.19 *%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 %.
3.1.19.1 *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:*

3.2.1 A_{SMP}—net area of the sample

3.2.2 A_{STD}—net area of the response factor standard

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

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

3.2.5 M_{SMP}—sample mass used in sample preparation

3.2.6 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 or Gravimetric Blend No. 1, which fully elutes from the column under the conditions of the test method and whose boiling point distribution have been characterized in Test Method D6352 or D7500, is used to determine the detector response factor. In addition, the composition of Gravimetric Blend No. 1 can be determined by two cut points; correct cut point values for Gravimetric Blend No. 1 ensure correct detector response. 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 temperatures is required. Typical conditions of operating the Gas Chromatograph are given in Table 1. It shall also have the following components:

TABLE 1 Typical Gas Chromatographic Conditions[A]

Initial Oven Temperature	–20 °C
Initial Oven Time	0 min
Oven Temperature Program	15 °C ⁄ min
Final Oven Temperature	425 °C 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 min to 50 min

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

6.1.1 *Flame Ionization Detector (FID)*—A flame ionization detector capable of maintaining a temperature 5 °C 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 *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 µL to 0.2 µL) shall be injected in a reproducible manner. Syringes of 5 µL to 10 µL having needle gauges of size 23 to 26 are to be used.

6.5 *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 µm 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 and 2.0. See Eq 2 in 13.2.

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

8. Reagents and Materials

8.1 *Carbon Disulfide (CS_2),* 99+ % pure. (**Warning—**Extremely flammable and toxic liquid.) Used as a solvent to dilute the sample and standards as well. Use gloves and safety glasses when handling the CS_2 in a well-ventilated area or fume hood. It is recommended to use adjustable-volume bottle dispensers and/or pipettors to minimize direct handling and avoid cross-contamination of CS_2. Wash vials containing CS_2 should be capped with a solvent resistant septa.

8.2 *Polywax 655 or Polywax 1000*—Used as a component of the retention time calibration mixture. Since these Polywaxes have carbon 22 as the first component, it shall be complemented with the mixture of paraffins described in 8.4.1 and 8.4.3 so that the entire range of carbon numbers (C_5-C_{100}) is present in the sample.

8.3 *Paraffins*—The following normal paraffins are used in the preparation of the retention time calibration mixture:

pentane	undecane	heptadecane
hexane	dodecane	octadecane
heptane	tridecane	nonadecane
octane	tetradecane	eicosane
nonane	pentadecane	tetracontane
decane	hexadecane	

8.3.1 The purities of these compounds should be 99 % or greater.

8.4 *Retention Time Calibration Standard*—This standard can be obtained from chromatography supply companies. This standard is composed of a mixture of Polywax (either P655 or P1000) as well as a mixture of paraffins. The addition of the paraffin mixture is necessary to cover the range of C_5-C_{20} since these paraffins are absent in the Polywax. Furthermore the amounts of the paraffins are chosen so as to facilitate identifying the carbons in the retention time calibration mixture chromatogram. Alternatively, a successful mixture that has been used may be prepared by the procedure described in 8.4.1 – 8.4.3 which requires the preparation first of the *n*-paraffin mixture (see 8.3) and then spiking an aliquot of this mix to a weighed amount of Polywax 655 or 1000.

8.4.1 Place approximately 20 mL of CS_2 into a round bottom 50 mL flask. Transfer with care.

8.4.2 Prepare a mixture of the paraffins listed in 8.3 as follows. Weigh 500 mg of each component into a 20 mL vial. Add an additional 500 mg for dodecane and about 20 mg of tetracontane. Store this mixture at 4 °C and use it as a spiking mixture in the preparation of the Polywax 655 retention time calibration mixture. These additional quantities are spiked to ease the identification of the n-paraffins; other n-paraffins may be chosen as peak markers.

8.4.3 Weigh about 25 mg of the Polywax 655 and add it to the vessel prepared in 8.4.1. Add approximately 10 mg of the paraffin spiking mixture prepared in 8.4.2. Stir the solution under a fume hood and heat with an infrared lamp (about 200 W) placed at a safe distance (about 15 cm to 20 cm) from the mixture for a period of 20 min or until the solution is clear. Other precautionary methods of dissolution are acceptable. Careful attention should be given to avoid the ignition of the CS_2 (see 8.1).

8.4.4 Transfer a 2 mL aliquot of the final mixture obtained in 8.4.3 into a 2 mL auto sampler vial and seal it firmly. This solution can be used for about one week if stored at 4 °C. The contents of this vial are injected in order to obtain the retention time–boiling point curve.

NOTE 1—Polywax is a trademark of the Baker Petrolite Corporation (Barnsdall, OK). This retention time calibration mixture is commercially available from chromatographic supply houses as well as from companies that build simulated distillation analyzers. The retention time calibration mixture may differ among supply houses in that docosane, tetracosane and hexacosane are also added to the Polywax 655 or Polywax 1000 in order to enhance the concentration of these hydrocarbons in the polywaxes.

8.5 *Detector Relative Response Test Mixture*—It is necessary to initially validate the response of the entire gas chromatographic system. Since this test method assumes that all hydrocarbons have the same relative response regardless of their retention time, a solution shall be prepared in order to determine the relative response factors. An alternative procedure is to use a gravimetric blend as specified in Test Method D7500.

8.5.1 Prepare a solution containing the following normal paraffins:

decane	octacosane
tetradecane	dotriacontane
octadecane	tetracontane
eicosane	pentacontane

8.5.2 Weigh about 100 mg of each paraffin to the nearest 0.1 mg into a 50 mL volumetric flask. Mix well and add CS_2 to the mark. Ensure that the paraffins are completely dissolved. Record the masses of the paraffins, which will be used in Eq 3 in order to calculate the relative response factor of each of the paraffins.

8.5.3 Record the assayed purity of each paraffin for use in Eq 3.

8.5.4 Transfer an aliquot of the mixture prepared in 8.5.2 to a 2 mL injection vial. Ensure that the components are in solution prior to the transfer. Warm the vial if necessary. Inject 0.1 µL to 0.2 µL.

8.6 *QC Materials*—This method requires the use of QC materials in order to validate the boiling point distribution and detector response factor and to determine the sample recovery. New QC materials are required to have their accepted reference values (ARV) validated according to Practice D6299. A minimum of 16 laboratories are required to participate in the evaluation of the QC material. In addition, the existing QC material must be analyzed during the evaluation of the new QC reference material whenever possible.

8.6.1 *Reference Oil 5010*—The 5010 Reference Oil has been used as a QC material since the inception of this method, and therefore, there are limited supplies of this material remaining.

8.6.2 *Gravimetric Blend No. 1*—This gravimetric blend was prepared from two different fractions that were mixed gravimetrically in equal weight proportions. The use of a gravimetric blend is described in Test Method D7500. The consensus boiling point distribution and cut point values for Gravimetric Blend No. 1 obtained from an ILS (RR:D02-1926[3]) are shown in Table 2. Gravimetric Blend No. 1 can be used as a QC material in all sections of this method where Reference Oil 5010 is used.

8.7 *Gases*—The following compressed gases are utilized for the operation of the gas chromatograph:

8.7.1 *Nitrogen,* 99.999 %. (**Warning—**Compressed gas under high pressure.) Total impurities should not exceed 10 mL/m^3. This gas is used as detector makeup. Helium has also been used as makeup gas.

8.7.2 *Hydrogen,* 99.999 %. (**Warning—**Extremely flammable gas under high pressure.) Total impurities should not exceed 10 mL/m^3. This gas is used as fuel for the operation of the detector.

8.7.3 *Air,* 99.999 %. (**Warning—**Compressed gas under high pressure and supports combustion.) Total impurities should not exceed 10 mL/m^3. This gas is used to sustain combustion in the FID detector.

8.7.4 *Helium,* 99.999 %. (**Warning—**Compressed gas under high pressure.) This gas is used as carrier gas and should not contain more than 5 mL/m^3 of O_2. The total amount of impurities should not exceed 10 mL/m^3.

9. Preparation of the Gas Chromatograph

9.1 A summary of the conditions used for developing the precision statement is given in Table 1.

9.2 *Column Installation*—The column is installed using graphite ferrules and an electronic leak detector is used to ascertain the absence of leaks. Follow the instructions given in Test Method D2887 and Practice E1510 for the installation of silica or aluminum clad silica columns. Metal columns require slightly different techniques in cutting and installation. Follow the recommendations of the column supplier.

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1926. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Boiling Point Values and Cut Points for Gravimetric Blend No. 1[A,B]

% Off	BP, °C	Allowed Deviation, °C	BP, °F	Allowed Deviation, °F
IBP	186.6	1.9	367.9	3.4
5	206.2	2.2	403.1	4.0
10	215.6	1.9	420.1	3.3
15	219.3	2.0	426.8	3.5
20	226.0	2.0	438.8	3.6
25	230.5	2.2	447.0	4.0
30	236.3	2.3	457.4	4.1
35	239.2	2.7	462.6	4.9
~~40~~	~~247.3~~	~~2.6~~	~~477.1†~~	~~4.7~~
40	247.3	2.6	477.1	4.7
45	255.0	2.6	491.1	4.8
55	495.0	5.6	923.0	10.1
60	510.9	4.2	951.5	7.6
65	523.0	4.0	973.4	7.1
70	533.6	3.4	992.4	6.2
75	542.9	3.3	1009.3	6.0
80	552.7	3.5	1026.8	6.3
85	562.6	3.6	1044.6	6.5
90	573.3	3.6	1064.0	6.4
95	588.2	3.6	1090.7	6.5
FBP	629.0	7.9	1164.2	14.3
Cut Point 1	SET - 330 °C (626 °F)		49.43 %	± 0.58 %
Cut Point 2	330 °C (626 °F) - EET		50.57 %	± 0.58 %

[A] The data is interpreted using the 95 % / 95 % tolerance margin where a user can be 95 % confident that at least 95 % of all future measurements at any of the listed distillation or cut points (for example, 20 % Off), by multiple labs, will fall within their corresponding allowed deviations (for example, 2.0 °C of 226.0 °C).

[B] ILS results for Gravimetric Blend No. 1 are detailed in RR:D02-1926.[3]

† Editorially corrected.

9.3 *Detector Temperature*—Select a detector temperature that is at least 5 °C to 10 °C higher than the highest oven temperature.

9.4 *Initial Oven Temperature*—The initial temperature of the oven is chosen according to the sample type to be analyzed as follows:

9.4.1 *Crude Oil Samples*—Crude oil samples may contain hydrocarbons starting from methane, C_2, C_3, and C_4 which probably co-eleute with C_5. Therefore, even at an initial temperature of −20 °C, C_5 and C_6 are partially resolved from the CS_2. Further decreases in oven temperature do not increase the separation of C_5 from C_1-C_4 hydrocarbons which co-elute with *n*-C_5.

9.4.2 *Residues and Samples Having Higher IBP*—For samples that have an initial boiling point of 100 °C or greater, such as vacuum residues or atmospheric residues, the initial oven temperature can be set to between 35 °C and 40 °C. Ensure that the sample is resolved from the solvent peak at the initial oven temperature selected. If the light ends cannot be separated from the solvent, then proceed as in 9.4.1. If the user does not know the type of sample to be analyzed, all samples can be analyzed with an initial temperature of −20 °C.

10. Sample Preparation

10.1 Ensure that the sample is a representative sample. Follow the guidelines established in Practice D4057. Samples should be handled according to their content of volatile components. If the sample is submitted for other analyses, remove a small aliquot (~10 mL) early in the testing sequence in order to avoid loss of volatile components. Allow sample to warm to room temperature prior to weighing.

10.2 Samples that are solid or semi-solid at room temperature may require heating up to as high as 60 °C in order to pour them into a weighed container. Only samples that are soluble in carbon disulfide (CS_2) can be analyzed by this test method.

10.3 Weigh 0.2 g to 0.25 g of the sample to the nearest 0.1 mg. Add 10 mL of CS_2. Record this weight also to the nearest 0.1 mg. Enter these values in the data acquisition system if appropriate.

10.4 Store all prepared solutions at a temperature of 4 °C. Care should be taken that the solution is prepared a short time prior to running the analysis. Samples can be stored in the auto sampler vials.

10.5 Prepare as many vials of a sample as are necessary to carry out multiple analyses of that sample. Do not use the same vial to run duplicates; use separate vials containing the same solution.

11. Preparation of the Response Factor Standard

11.1 Weigh 0.2 g to 0.25 g of Reference Oil 5010 or Gravimetric Blend No. 1 to the nearest 0.1 mg. Add 10 mL of CS_2 and record the weight of the solvent to the nearest 0.1 mg. Store this solution at 4 °C, if not used immediately.

12. Preparation of the Apparatus and Data System

12.1 After the column is installed and checked for leaks, prepare the gas chromatograph to analyze the sample according to the typical conditions given in Table 1.

12.2 Set the acquisition system to digitize the data at 10 Hz. This will result in a slice width of 0.1 s. This data acquisition rate is kept constant for all samples, standards, and the solvent blank in order to acquire the same number of slices. The baseline chromatogram may contain the same or larger number of slices than the sample chromatograms, depending on when the data acquisition stops. Thus, various chromatograms taken in a sequence may differ by 5 to 10 slices. This fact is of no consequence with regard to the calculations.

12.3 Arrange to save the acquired data files. Build the sequence of samples to be injected by the gas chromatograph.

13. Verification of System Performance

13.1 *Column Resolution*—Prepare the gas chromatograph for injection of the retention time calibration mixture prepared in 8.4. Inject 0.1 µL to 0.2 µL of this sample. Determine the column resolution as follows:

$$R = 2(t_2 - t_1)/(1.699)\,(W_2 + W_1) \quad (1)$$

where:

R = resolution,
t_2 = retention time (s) for the n-C_{50} paraffin,
t_1 = retention time (s) for the n-C_{52} paraffin,
W_1 = peak width (s) at half height of the n-C_{50} peak, and
W_2 = peak width (s) at half height for the n-C_{52}.

13.1.1 Ensure that the resolution, R, is between 1.8 to 4.0.

13.2 *Skewness Test for Column Overloading*—Select a component between C_{12}-C_{24} of the previous chromatogram or of the chromatogram of the retention time calibration mixture prepared in 8.4. For the component selected, determine the skewness as follows. The skewness, s, is calculated by Eq 2: ILS participants reported skewness of 0.8 to 2.0 for peaks C_7 to C_{100}.

$$s = (a + b)/2a \quad (2)$$

where:

s = skewness of the peak,
a = left time segment measured at 10 % of the peak height and that intersects the perpendicular from the apex of the peak to the retention time axis, and
b = right time segment measured at 10 % of the peak height and that intersects the perpendicular from the peak apex to the retention time axis. Ensure that the skewness is between 0.8 and 2.0. Data acquisition systems can calculate this parameter.

13.3 *Determination of Detector Relative Response Factors*—Prepare the gas chromatograph for the injection of the detector test mixture prepared in 8.5. Inject 0.1 µL to 0.2 µL of this sample. Calculate the relative response factor, F_i, of each paraffin relative to eicosane as follows:

$$F_i = \frac{M_i \times P_i \times Ac_{20}}{A_i \times Mc_{20} \times Pc_{20}} \quad (3)$$

where:

M_i = mass of the paraffin in mg,
Mc_{20} = mass of the eicosane in mg,
A_i = peak area of the paraffin,
Ac_{20} = peak area of the eicosane,
P_i = % purity of the paraffin as recorded in 8.5.3, and
Pc_{20} = % purity of eicosane.

13.3.1 The relative response factor, F_i, should have a value of between 0.9 and 1.10. Failure to achieve this range may be due to inlet problems, lack of constant flow, or partial blockage of the flame tip orifice, or a combination thereof.

14. Analytical Sequence

14.1 Set up a sequence of the samples to be analyzed. The sequence will contain the order of the samples to be injected into the column. This schedule should be designed to achieve maximum reproducibility. A suggested order of the samples to be analyzed is described in 14.2 – 14.6. If time constraints require a shorter sequence, the user shall ensure that there is no carryover between samples and sample types.

14.2 *Blank Run*—At the beginning of each sequence, after any column maintenance is performed, make a blank run. It may take more than 2 blanks to show a stable plateau with no indication of residual elution. A blank run constitutes an identical solvent injection having the same volume as the sample injection. An acceptable blank run should show a stable plateau at the highest temperature of the oven (see 15.3). Furthermore, it should not show any indication of carryover or residual sample elution. It should also not contain any ghost peaks. A typical blank sample run is shown in Fig. A1.1. Several blanks may be necessary after column installation or after an idle period of the gas chromatograph. Verification of acceptable blanks is obtained by analyzing the Reference Oil 5010 or a gravimetric blend and a QC material.

14.3 *Retention Time Calibration Mixture*—Insert the retention time calibration mixture vial prepared in 8.4 into the auto sampler for injection. A typical chromatogram of the retention time calibration mixture is shown in Fig. A1.2. The insert in the Fig. A1.2 shows the best separation possible for the C_5, CS_2, C_6, and C_7 and shows good peak shape for the C_6 and C_7 hydrocarbons. Identify all carbons up to C_{100}.

14.4 *Response Factor Standard*—Insert the vial containing Reference Oil 5010 prepared in 8.5, which is used as a response factor standard. Inject this standard in duplicate. Gravimetric Blend No. 1 can also be used in order to obtain the response factor. A typical chromatogram of the reference oil analyzed at an initial oven temperature of –20 °C is shown in Fig. A1.3. A typical chromatogram of Gravimetric Blend No. 1 obtained at –20 °C is shown in Fig. A1.9. Verify that the response factor calculated by Eq 4 does not vary by more than 2 % for either of the two reference materials.

14.5 *Sample Analysis*—Insert the sample vials prepared in 10.3. Inject samples. Analyzing a QC material with acceptable results before the analysis of unknown samples is strongly recommended.

14.6 *Additional Blank Runs*—Insert a vial containing CS_2 in order to obtain a second blank run. Carry out a blank run after each sample injection, and verify the absence of carryover from the previous samples. An ambient temperature version of the method with faster oven ramping can be employed for these clean-out runs in between samples to reduce run time and use of cryogenic fluids.

15. Verification of Acquired Data

15.1 Inspect all chromatograms by loading the data files in the data acquisition system. Observe that the signal magnitude for each sample injected is approximately the same as that for the retention time calibration mixture and the Reference Oil 5010 or Gravimetric Blend No. 1 chromatograms.

15.2 *Verification of the Retention Time Calibration Mixture Chromatogram*—Inspect the chromatograms acquired during a

sequence run. Do not use a chromatogram where the peaks do not meet the criteria of skewness as defined in 13.2. Inspect the chromatogram for the components C_5-C_7 and the solvent peak as shown in the insert of Fig. A1.2. The peaks should not present peak splitting nor peak tailing.

15.3 *Sample Chromatograms*—Inspect the sample chromatograms and verify that the chromatograms can be overlaid to a duplicate chromatogram and show that the profile is reproducible. Fig. A1.4 shows a chromatogram of a 30°API crude oil where the solvent peak is not resolved from the sample components. Fig. A1.5 shows a typical chromatogram of an atmospheric residue where the solvent peak is resolved from the sample components.

15.3.1 It is recommended that a QC material be analyzed at the beginning and end of every sequence. The QC sample should have the same matrix as the samples analyzed.

15.4 *Baseline or Blank Runs*—Inspect, in the data system, the chromatograms of the blank solvent injections to verify that the blank signal obtained does not differ substantially from that obtained during the sample analysis. Check that the baseline exhibits a gradual rise up to the isothermal section of the chromatogram and ensure that there is a gradual transition back to the plateau of the baseline. Disregard any baseline that shows material eluting near the highest temperature of the column. Also disregard any baseline that shows ghost peaks. Overlay the baseline signal with the sample signal as shown in Fig. A1.6. Use only those sample signals that asymptotically approach the baseline signals. Reject any sample run where the baseline signal at the end of the run exceeds in value the sample run. Reject any sample run at which at the end of the run the signal exceeds the baseline signal by 10 %. It is recommended that a new full blank analysis be performed at regular intervals (for example, after every 4 to 5 samples) in a sequence of samples to ensure good baseline data for subsequent samples.

15.4.1 *Determine the Quenching Interval*—Select the time that the solvent peak starts to elute. Determine when the solvent peak has eluted. Note the times of this interval in minutes. An expanded time scale chromatogram of the solvent peak is shown in Fig. A1.7.

15.4.2 *Determine the Magnitude of Solvent Response*—Using the data system, overlay the solvent chromatograms and verify that the profiles are similar. Verify that the total areas do not differ by more than 3 % from each other.

15.5 *External Standard Response Factor Chromatogram*—Inspect the external standard chromatogram obtained from the injection of Reference Oil 5010 or Gravimetric Blend No. 1. For Reference Oil 5010, verify that the boiling point distribution is within the consensus values as indicated in Test Method D6352. Typical boiling point distribution values for Reference Oil 5010, obtained with this test method, are shown in Table 3. For Gravimetric Blend No. 1, the boiling point values should fall within the allowed deviations listed in Table 2. Correct any chromatography errors if the consensus values are not obtained (see 16.1.7).

TABLE 3 Consensus Values Obtained for the Boiling Point Distribution of Reference Oil 5010 Used as External Standard[A]

%BP	avg °C	Allowable Differences, °C	avg °F	Allowable Differences, °F
IBP	428	9	801	16
5	477	3	891	5
10	493	3	918	5
15	502	3	936	5
20	510	3	950	6
25	518	4	963	6
30	524	4	975	7
35	531	4	987	7
40	537	4	998	8
45	543	4	1008	8
50	548	4	1019	8
55	554	4	1030	8
60	560	4	1040	8
65	566	4	1051	8
70	572	4	1062	8
75	578	5	1073	9
80	585	4	1086	8
85	593	4	1099	7
90	602	4	1116	8
95	616	4	1140	7
FBP	655	18	1213	32

[A] As reported in Test Method D6352.

16. Calculations

NOTE 2—The calculations are listed in this section. The chromatogram for the Reference Oil 5010, Gravimetric Blend No. 1, the sample, and the baseline shall be zeroed as given in 16.1.2.

NOTE 3—The baseline chromatogram is subtracted from the Reference Oil 5010 or Gravimetric Blend No. 1 and from the sample chromatogram in order to obtain the net area as shown in 16.1.4.

16.1 *Zeroing of the Reference Oil or the Gravimetric Blend Chromatogram:*

16.1.1 Examine the chromatogram obtained for Reference Oil 5010 (external standard) or Gravimetric Blend No. 1, and ensure, by visual inspection of the chromatogram in the data system, that the first 5 slices contain neither sample nor solvent elution.

16.1.2 Set up an array that contains slices obtained from the Reference Oil 5010 or Gravimetric Blend No. 1 chromatogram. Calculate the average of the first five area slices. Subtract the average slice area from each slice in the Reference Oil 5010 or Gravimetric Blend No. 1 chromatogram. Set negative numbers to zero.

16.1.3 Zero the blank baseline chromatogram by carrying out an analogous calculation as in 16.1.2.

16.1.4 *Blank Baseline Subtraction from the Reference Oil 5010 or Gravimetric Blend No. 1 Chromatogram*—Subtract each zeroed blank baseline slice from the corresponding zeroed Reference Oil 5010 or Gravimetric Blend No. 1 slice. If there are negative slices, set the slice values to zero.

16.1.5 *Determination of the End of Elution Time of Reference Oil 5010 or Gravimetric Blend No. 1*—Since it is a requirement that the sample chosen to obtain a response factor shall fully elute prior to the *FEt* time, the end of sample elution for this chromatogram is to be determined as described in Test Method D6352, using the algorithm to determine the time the signal of the completely eluted sample returns to baseline.

16.1.6 *Determination of the Area of the Chromatogram for Reference Oil 5010 or Gravimetric Blend No. 1*—Determine the end time of solvent elution. Sum all of the slices from the end of solvent elution to the end of sample elution. This is the area of the standard, A_{STD}.

16.1.7 *Calculation of the Boiling Point Distribution of Reference Oil 5010 or Gravimetric Blend No. 1*—The resulting corrected slices obtained for Reference Oil 5010 or Gravimetric Blend No. 1 are submitted to a Test Method D6352 calculation for boiling point distribution. A comparison of the values obtained with the consensus values listed in Table 3 or Table 2 shall be made and all the boiling point values shall fall within the specified windows. If this requirement is not met, correct any chromatographic problems prior to proceeding with sample analysis. Typical problems found in this step are: contaminated solvent; problems in sample preparation; sample residue in the inlet or column, or both; quality of the baseline used, a partially blocked detector jet, or a combination thereof.

16.1.8 *Calculation of the Gravimetric Blend No. 1 Cut Points*—Gravimetric Blend No. 1 consists of two cuts with an approximately 50:50 stoichiometric composition. The actual percentage of each cut, as shown in Table 2, was determined by means of an ILS (RR:D02-1926[3]). Verifying the achievement of the gravimetric composition within the allowed deviation shown in Table 2 is indicative of the correct operation of the detector and the gas chromatographic system.

16.2 *Zeroing of Sample Chromatograms:*

16.2.1 In the case of crude oil analysis or samples in which the solvent peak is not resolved from the sample components, ensure, by visual inspection of the chromatogram in the data system, that the first 5 slices contain neither sample nor solvent elution. If there is sample elution, decrease the number of slices for the averaging to 3 or increase the digitization rate given in 12.2.

16.2.2 *Zeroing the Sample Chromatogram*—Proceed in a manner analogous to that described in 16.1.2.

16.2.3 *Zeroing the Blank Baseline Chromatogram*—Carry out an analogous calculation as in 16.1.3.

16.3 *Blank Baseline Subtraction from the Sample Chromatogram*—Carry out an analogous calculation as in 16.1.4.

16.4 *Quenching Correction*—For crude oil samples, a quenching factor is used to correct for the diminished FID response when