



Designation: D7157 – 22

Standard Test Method for Determination of Intrinsic Stability of Asphaltene-Containing Residues, Heavy Fuel Oils, and Crude Oils (*n*-Heptane Phase Separation; Optical Detection)¹

This standard is issued under the fixed designation D7157; 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 a procedure for quantifying the intrinsic stability of the asphaltenes in an oil by an automatic instrument using an optical device.

1.2 This test method is applicable to residual products from thermal and hydrocracking processes, to products typical of Specifications D396 Grades No. 5L, 5H, and 6, and D2880 Grades No. 3-GT and 4-GT, and to crude oils, providing these products contain 0.5 % by mass or greater concentration of asphaltenes (see Test Method D6560).

1.3 This test method quantifies asphaltene stability in terms of state of peptization of the asphaltenes (S -value), intrinsic stability of the oily medium (S_o) and the solvency requirements of the peptized asphaltenes (S_a).

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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.*

1.6 *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.*

¹ This test method is under the jurisdiction of Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.14 on Stability, Cleanliness and Compatibility of Liquid Fuels.

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2. Referenced Documents

2.1 ASTM Standards:²

D396 Specification for Fuel Oils

D2880 Specification for Gas Turbine Fuel Oils

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4870 Test Method for Determination of Total Sediment in Residual Fuels

D6560 Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products

D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories

3. Terminology

3.1 Definitions:

3.1.1 For definitions of some terms used in this test method, refer to Terminology D4175.

3.1.2 *asphaltenes, n*—(rarely used in the singular), *in petroleum technology*, represent an oil fraction that is soluble in a specified aromatic solvent but separates upon addition of an excess of a specified paraffinic solvent.

3.1.2.1 *Discussion*—In this test method, the aromatic solvent is toluene and the paraffinic solvent is *n*-heptane.

3.1.3 *compatibility, n*—*of crude oils or of heavy fuel oils*, the ability of two or more crude oils or fuel oils to blend together within certain concentration ranges without evidence of separation, such as the formation of multiple phases.

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.

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

3.1.3.1 *Discussion*—Incompatible heavy fuel oils or crude oils, when mixed or blended, result in the flocculation or precipitation of asphaltenes. Some oils may be compatible within certain concentration ranges in specific mixtures, but incompatible outside those ranges.

3.1.4 *flocculation, n—of asphaltenes from crude oils or heavy fuel oils*, the aggregation of colloiddally dispersed asphaltenes into visible larger masses which may or may not settle.

3.1.5 *peptization, n—of asphaltenes in crude oils or heavy oils*, the dispersion of asphaltenes to produce a colloidal dispersion.

3.1.6 *stability reserve, n—in petroleum technology*, the property of an oil to maintain asphaltenes in a peptized state and prevent flocculation of asphaltenes.

3.1.6.1 *Discussion*—An oil with a low stability reserve is likely to undergo flocculation of asphaltenes when stressed (for example, extended heated storage) or blended with a range of other oils. Two oils each with a high stability reserve are likely to maintain asphaltenes in a peptized state and not lead to flocculation when blended together.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *intrinsic stability (S-value), n—of refinery residual streams, residual fuel oils and crude oils*, an indication of the stability or available solvency power of an oil with respect to precipitation of asphaltenes.

3.2.1.1 *Discussion*—Since the equation defining *S*-value is $S = (1 + X_{min})$, where X_{min} is the minimum volume (in mL) of paraffinic solvent, *n*-heptane, to be added to 1 g of oil to result in flocculation of asphaltenes, the smallest *S*-value is 1, which means the oil is unstable and can precipitate asphaltenes without addition of any paraffinic solvent. A higher *S*-value indicates that an oil is more stable with respect to flocculation of asphaltenes. *S*-value by this test method relates specifically to toluene and *n*-heptane as the aromatic and paraffinic solvents, respectively.

3.2.2 *inversion point, n—point in the n-heptane titration curve*, where the onset of asphaltene flocculation leads to inversion of the light intensity.

3.2.2.1 *Discussion*—At the first stage of the addition of *n*-heptane to a dilution of specimen and toluene, light intensity increases through dilution. When asphaltenes start to flocculate, there will be a point where the increase in light intensity through dilution matches the light intensity decrease (inversion) as a result of coagulated asphaltenes obstructing the light beam.

3.2.3 *S_a, n—the S-value of an asphaltene*, which is the peptizability or ability of an asphaltene to remain in a colloidal dispersion.

3.2.3.1 *Discussion*—*S_a* can also be described as one minus the ratio of *S_o* to *S*. *S_a* is linked to the length and number of aromatic chains within the asphaltenes.

3.2.4 *S_o, n—the S-value of an oil*.

3.2.4.1 *Discussion*—*S_o* can also be described as the aromatic equivalent of the oil expressed as the ratio of the

aromatic solvent to the aromatic plus paraffinic solvent mixture having the same peptizing power as the oil.

3.2.5 *solvent aromaticity, n—of a binary mixture of a paraffinic and an aromatic solvent*, the solvency power of the binary mixture.

3.2.5.1 *Discussion*—For the purpose of this test method, solvent aromaticity is defined as a ratio by volume of the aromatic solvent (toluene) to the paraffinic solvent (*n*-heptane).

3.3 Symbols:

3.3.1 *FR*—flocculation ratio

3.3.2 *FR_{max}*—maximum flocculation ratio

3.3.3 *S*—the intrinsic stability of an oil

3.3.4 *S_a*—the peptizability of an asphaltene

3.3.5 *S_o*—the peptizing power of an oil

3.3.6 *X_{min}*—paraffinic solvent consumption of undiluted oil, in mL/g of oil

4. Summary of Test Method

4.1 This test method uses an integrated automated analytical measurement system with an optical probe or cell for the detection of asphaltene precipitation from a toluene solution of the sample.

4.2 Three test specimens are dissolved in three different quantities of toluene. The three specimen/toluene solutions are automatically and simultaneously titrated with *n*-heptane to cause precipitation of the asphaltenes. The optical probe or cell monitors the formation of flocculated asphaltenes during the titration. Flocculated asphaltenes will alter the detected light intensity. Start of flocculation is interpreted when the optical probe or cell detects a significant and sustained decrease in rate-of-change of the light intensity.

4.3 A computer routine calculates stability parameters and subsequently the intrinsic stability of the oil from the added *n*-heptane at the inversion point, the mass of specimen, and the volume of toluene, for the three specimen/toluene solutions.

5. Significance and Use

5.1 This test method describes a sensitive method for estimating the intrinsic stability of an oil. The intrinsic stability is expressed as *S*-value. An oil with a low *S*-value is likely to undergo flocculation of asphaltenes when stressed (for example, extended heated storage) or blended with a range of other oils. Two oils each with a high *S*-value are likely to maintain asphaltenes in a peptized state and not lead to asphaltene flocculation when blended together.

5.2 This test method can be used by petroleum refiners to control and optimize the refinery processes and by blenders and marketers to assess the intrinsic stability of blended asphaltene-containing heavy fuel oils.

6. Interferences

6.1 High content of insoluble inorganic matter (sediment) has some interference in this test method. In this case, the insoluble matter shall be removed by filtration according to Test Method [D4870](#).

6.2 Free water present in the oil can cause difficulties with the optical detector and should be removed by any suitable means (for example, centrifugation) prior to testing.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1 *Toluene*. (**Warning**—Flammable. Health hazard. Vapor may cause flash fire.) (See [Annex A1](#).)

7.1.2 *n-Heptane*. (**Warning**—Flammable. Vapor harmful. Vapor may cause flash fire.) (See [Annex A1](#).)

7.2 *Quality Control Sample*—A stable and homogeneous residual fuel oil having physical and chemical properties similar to those of typical sample fuels routinely tested.

8. Apparatus and Procedure

8.1 Two procedures exist and are mainly differentiated by the method of dilution of the sample with toluene: Procedure A—Manual Dilution (Rofa apparatus) and Procedure B—Automatic Dilution (AD Systems apparatus).

8.2 Both procedures use the same dilution table (see [Table 1](#)).

TABLE 1 Specimen and Toluene Dilutions

Product Type		Dilution 1	Dilution 2	Dilution 3
1: Liquid at <30 °C	Mass sample, g	9	5.5	3
	Volume toluene, mL	2	5.5	8
2: Liquid between 30 °C – 100 °C	Mass sample, g	7	5.5	3
	Volume toluene, mL	4	5.5	8
3: Liquid at >100 °C	Mass sample, g	4	3	2
	Volume toluene, mL	7	8	9
Very stable products	Mass sample, g	3	2	1
	Volume toluene, mL	1	2	3

8.3 These dilutions are the dilutions usually used, but it is possible to use other dilutions in certain circumstances.

9. Procedure A (Manual Dilution)

9.1 Apparatus:

9.1.1 *General*—(See [Fig. X1.1](#)) This procedure uses an integrated automated analytical measurement system^{4,5} comprised of a PC-based computer and three titration stations.

³ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

⁴ The sole source of supply of the Procedure A apparatus (Automated Stability Analyzer) known to the committee at this time is Rofa France, 6 Rue Raymond Poincaré, F-25300, Les Allées, France. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

9.1.2 *Computer*, PC-based computer with associated software, capable of controlling up to three independent titration stations, controlling test sequencing, and acquisition of optical probe signal data. The associated software also provides for processing calculations and automatically produces a report of important test parameters.

9.1.3 Titration Stations:

9.1.3.1 *Titration Unit*, automatic computer controlled, adjustable motor-driven ceramic piston pump, capable of delivering solvent at a rate of 0.01 mL/s to 0.5 mL/s, with a volume dispensing accuracy of ± 0.01 mL.

9.1.3.2 *Magnetic Stirrer*, adjustable from 200 r/min to 400 r/min.

9.1.3.3 *Optical Probe*, consisting of a system of three areas of light emitters (880 nm) and three areas of light receivers. The analytical measurement system will automatically select the optimum area, based on the level of translucency of the sample.

9.1.3.4 *Titration Cell*, of borosilicate glass, flat bottom, outside diameter 30 mm \pm 2 mm, volume 95 mL \pm 15 mL, fitted with a tapered ground glass joint (female).

9.1.4 *Balance*, capable of reading to 0.1 mg or better.

9.1.5 *Dispenser*, capable of delivering up to 10 mL of toluene with an accuracy of ± 0.1 mL.

9.1.6 *Condenser*, double surface with a tapered ground-glass joint (male) at the bottom to fit the top of the titration cell.

9.1.7 *Magnetic Stirrer/Hotplate*, stirrer speed adjustable from 100 r/min to 1000 r/min.

9.1.8 *Stirring Bar*, magnetic, PFTE-coated, 20 mm in length.

9.2 Sampling and Test Specimens:

9.2.1 Sampling:

9.2.1.1 Obtain representative samples in accordance with recognized sampling procedures such as Practices [D4057](#) or [D4177](#).

9.2.1.2 Samples of very viscous materials may be warmed until they are reasonably fluid before they are sampled.

9.2.1.3 Store samples prior to taking test specimens at ambient temperatures.

9.2.2 Test Specimen Preparation:

9.2.2.1 *Sample Temperature*—If necessary, warm viscous samples until they can be mixed readily before opening the storage container. For fuels with a high wax content (high pour point) the temperature must be at least 15 °C above the pour point.

9.2.2.2 Manually shake the sample thoroughly. If the sample contains high content of insoluble inorganic matter, filter the sample through a 47 mm diameter glass fiber filter medium (such as Whatman Grade GF/A), using the Test Method [D4870](#) filtration apparatus. Specimen should be representative of the whole sample.

9.2.3 *Preparation of Specimen Dilutions*—Prepare three dilutions of specimen in toluene in different ratios (see [Table 1](#)) as follows:

9.2.3.1 Place a magnetic stirrer bar into a clean titration cell.

⁵ The Rofa stability analyzer is covered by a patent owned by Total Raffinage France; INPI, date 18/05/04, registration number 04.05406.

9.2.3.2 Add the required amount of specimen to the titration cell and obtain the mass of the specimen to the nearest 0.001 g (M_{oil}).

9.2.3.3 Add the appropriate volume of toluene to the nearest 0.1 mL to the titration cell.

9.2.3.4 Stir dilutions of sample Type 1, without heating, for at least two minutes. Obtain the mass of the specimen plus toluene to the nearest 0.001 g (M_1). Proceed with Section 9.4.

9.2.3.5 For specimen dilutions of Type 2 and 3, place a condenser on the titration cell, place on the hot plate, and boil under reflux, while stirring, for a minimum of 10 min for specimens of Type 2 and for a minimum of 15 min for specimens of Type 3.

9.2.3.6 Discontinue heating and while stirring, allow the dilutions to cool to ambient temperature. Disconnect the condenser and obtain the mass of specimen plus toluene to the nearest 0.001 g (M_1). Proceed with Section 9.4.

NOTE 1—In this context, “liquid” means the minimum temperature at which the product has sufficient fluidity to be handled as a liquid.

9.3 Preparation of Apparatus:

9.3.1 Prepare and set up the instrument for operation according to the manufacturer’s manual. (Refer to Fig. X1.1.)

9.3.2 Plug the optical probes into their connectors and place them in their stand by position.

9.3.3 Ensure that the reagent vessel contains sufficient *n*-heptane to run the tests (minimum 200 mL).

9.3.4 *Cleaning Instructions*—Perform the following cleaning procedure after the test procedure (see 9.4.8).

9.3.4.1 Carefully remove the dosing tube and the optical probe from the titration cell. Clean the optical probe with an appropriate solvent (toluene) (see 7.1.1).

9.3.4.2 Remove the stirrer bar. Empty the titration cell. Clean the reactor cell and stirrer bar with an appropriate solvent (toluene) (see 7.1.1).

9.4 Test Procedure:

9.4.1 Place the titration cells containing the specimen solutions (9.2.3.4 and 9.2.3.6) into their slot positions in the measurement system.

9.4.2 Position the optical probes in the titration cells.

9.4.3 Place the dosing tubes of the titration apparatus into the titration cell. The position of the tube is such that droplets fall directly into the sample vortex so that mixing is optimal.

9.4.4 Switch on the magnetic stirrer and adjust the speed so that agitation is just visible on the surface of the sample.

9.4.5 Initiate the automatic test procedure according to the manufacturer’s instruction manual. For further details, refer to Appendix X1.

9.4.6 *n*-heptane is added in steps of 0.05 mL at a rate of 0.05 mL/s. Addition of *n*-heptane is discontinued for 2 s between each step.

9.4.7 For dilutions of very stable samples (see Table 1), it is needed to pre-add an accurately known quantity of 7 mL of *n*-heptane by the automatic titration unit to ensure that the probe is fully immersed.

NOTE 2—The addition of 7 mL of *n*-heptane is automatically performed by the apparatus when “pre-dilution” mode is selected by the operator.

9.4.8 The test is completed when either an inversion point is encountered (V_{para}) or when the total liquid content of the titration cell reaches a maximum of 50 mL. A report is displayed automatically at that time or earlier if requested by the operator.

NOTE 3—The apparatus will stop automatically when the maximum limit of 50 mL liquid has been reached.

9.4.9 Draw a straight line through the three points (see Fig. 1) using the least squares fit equation. For a valid result the measure of goodness of fit (R-squared) should be ≥ 0.98 . If R-squared < 0.98 , discard the result and repeat the test with fresh dilutions from 9.2.3 onwards.

NOTE 4—See Appendix X1 for detailed automatic test program and examples of the titration curve and regression report.

9.4.10 When, for any of the three dilutions, *n*-heptane has been added up to a total of 50 mL liquids in the titration cell without encountering an inversion, the sample is considered to be very stable. In such a case, the test shall be repeated from 9.2.3 onwards, using fresh dilutions as given in Table 1 under “Very stable samples.”

10. Procedure B (Manual Dilution)

10.1 Apparatus⁶:

10.1.1 *General*—(See Fig. X2.1). This procedure uses an integrated automated analytical measurement system comprising a user interface and three fully automated titration stations.

10.1.2 *User Interface*, capable of controlling up to three independent titration stations, controlling test sequencing, and acquisition of optical signal data. This also provides data for processing calculations and automatically produces a test report and important test parameters.

10.1.3 Titration Stations:

10.1.3.1 *Dilution Unit*, automatically controlled, adjustable motor-driven piston pump, capable of delivering solvent (toluene), with a volume dispensing accuracy of ± 0.01 mL.

10.1.3.2 *Titration Unit*, automatically controlled, adjustable motor-driven ceramic piston pump, capable of delivering solvent at a rate of 0.01 mL/s to 0.3 mL/s, with a volume dispensing accuracy of ± 0.01 mL.

10.1.3.3 *Magnetic Stirrer*, adjustable from 0 r/min to 600 r/min.

10.1.3.4 *Optical Cell*, consisting of an infrared light emitter and receiver system. This infrared light beam crosses the sample, and the analytical measurement system will automatically select the optimum settings, based on the level of translucency of the sample.

10.1.3.5 *Titration Cell*, made of borosilicate glass, flat bottom, volume 95 mL \pm 15 mL.

10.1.3.6 *Heating Crucible*, titration cell receptacle, with adjustable temperature from ambient to 100 °C.

⁶ The sole source of supply of the Procedure B apparatus (Automated Stability Analyzer) known to the committee at this time is AD Systems, Allée de Cindais, F-14320, Saint André Sur Orne, France. The apparatus is manufactured under a license of TOTALEnergies. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

10.1.4 *Condenser*, double surface with suitable shape to fit the top of the titration cell. Cooled by a system fully integrated into the device. The temperature is adjustable from 0 °C to 50 °C

10.1.5 *Balance*, capable of reading to 0.1 mg or better.

10.1.6 *Stirring Bar*, magnetic, PTFE-coated, 20 mm in length.

10.1.7 *Cleaning Cell*, made of borosilicate glass, flat bottom, volume 300 mL ± 15 mL.

10.2 Sampling and Test Specimens:

10.2.1 Sampling:

10.2.1.1 Obtain representative samples in accordance with recognized sampling procedures such as Practices [D4057](#) or [D4177](#).

10.2.1.2 Samples of very viscous materials may be warmed until they are reasonably fluid before they are sampled.

10.2.1.3 Store samples prior to taking test specimens at ambient temperatures.

10.2.2 Test Specimen Preparation:

10.2.2.1 *Sample Temperature*—If necessary, warm viscous samples until they can be mixed readily before opening the storage container. For fuels with a high wax content (high pour point) the temperature must be at least 15 °C above the pour point.

10.2.2.2 Manually shake the sample thoroughly. If the sample contains high content of insoluble inorganic matter, filter the sample through a 47 mm diameter glass fiber filter medium (such as Whatman Grade GF/A), using the Test Method [D4870](#) filtration apparatus. Specimen should be representative of the whole sample.

10.2.3 *Preparation of Specimen*—Prepare three specimens in different mass (see [Table 1](#), Section 8) as follows:

10.2.3.1 Place a magnetic stirrer bar into a clean titration cell.

10.2.3.2 Add the required amount of specimen to the titration cell and obtain the mass of the specimen to the nearest 0.001 g (M_{oil}). Proceed with [10.4](#).

NOTE 5—In this context, “liquid” means the minimum temperature at which the product has sufficient fluidity to be handled as a liquid.

10.3 Preparation of Apparatus:

10.3.1 Prepare and set up the instrument for operation according to the manufacturer’s manual. (Refer to [Fig. X2.1](#).)

10.3.2 Ensure that the reagent vessels contain sufficient amount of *n*-heptane and toluene to run the tests (minimum 200 mL).

10.3.3 *Cleaning Instructions*—Perform the following cleaning procedure after the test procedure (see [10.4.10](#)).

10.3.3.1 Replace the titration cell by the cleaning cell. Launch the automatic cleaning program that will rinse the entire circuit. At the end, remove the cleaning cell containing the solvent and use a tissue to dry the circulation and dosing tubes.

10.3.3.2 Remove the stirrer bar. Empty the titration cell. Clean the titration cell and stirrer bar with an appropriate solvent (toluene) (see [7.1.1](#)).

10.4 Test Procedure:

10.4.1 Place the titration cells containing the specimen samples ([10.2.3.2](#)) into their slot positions in the measurement system.

10.4.2 Install the cover equipped with the circulation and dosing tubes.

10.4.3 Enter the mass of the specimen and then launch the test.

10.4.4 The appropriate volume of toluene will be automatically added to the nearest 0.01 mL.

10.4.5 For sample Type 1, dilutions are stirred without heating, for at least two minutes.

10.4.6 For sample dilutions of Type 2 and 3, the sample is heated until it becomes liquid. When the sample is liquid, the stirring is starting, for a minimum of 10 min for a sample of Type 2 and for a minimum of 15 min for a sample of Type 3. Heating is then discontinued, and the sample temperature is allowed to decrease to ambient temperature.

10.4.7 At the end of the dilution, the solution will start to circulate, and titration will start automatically. For samples of Type 2 or 3, titration will start when the sample is back to ambient temperature.

10.4.8 *n*-heptane is added continuously at a rate of 1 mL/min while the solution is circulating through the optical cell.

10.4.9 For dilutions of very stable samples (see [Table 1](#), Section 8), it is needed to pre-add an accurately known quantity of 7 mL of *n*-heptane by the automatic titration unit to ensure that the dosing tube is fully immersed.

NOTE 6—The addition of 7 mL of *n*-heptane is automatically performed by the apparatus when “pre-dilution” mode is selected by the operator.

10.4.10 The test is completed when either an inversion point is encountered (V_{para}) or when the total liquid content of the titration cell reaches a maximum of 50 mL. A report is displayed automatically at that time or earlier if requested by the operator.

NOTE 7—The apparatus will stop automatically when the maximum limit of 50 mL liquid has been reached.

10.4.11 Draw a straight line through the three points (see [Fig. X2.2](#)) using the least squares fit equation. For a valid result, the measure of goodness of fit (R-squared) should be ≥0.98. If R-squared <0.98, discard the result and repeat the test with fresh dilutions from [10.2.3](#) onwards.

NOTE 8—See [Appendix X2](#) for detailed automatic test program and examples of the titration curve and regression report.

10.4.12 When, for any of the three dilutions, *n*-heptane has been added up to a total of 50 mL liquids in the titration cell without encountering an inversion, the sample is considered to be very stable. In such a case, the test shall be repeated from [10.2.3](#) onwards, using fresh dilutions as given in [Table 1](#), Section 8 under “Very stable products.”

11. Quality Control Monitoring

11.1 Confirm the performance of the instrument and test procedure by analyzing quality control (QC) samples.

11.1.1 When quality control/quality assurance (QC/QA) protocols are already established in the testing facility, these can be used when they confirm the reliability of the test result.

11.1.2 When there is no QC/QA protocol established in the testing facility, Guide D6792 can be used for guidance.

12. Calculation of Results

12.1 The instrument automatically calculates the stability parameters, using the following equations:

$$M_{tol} = M_1 - M_{oil} \quad (1)$$

$$V_{arom} = (M_{tol})/D_{tol} \quad (2)$$

$$FR = (V_{arom})/(V_{arom} + V_{para}) \quad (3)$$

$$1/X = (M_{oil})/(V_{arom} + V_{para}) \quad (4)$$

where:

- M_{oil} = mass of oil, g (see 9.2.3.2 and 10.2.3.2),
- M_1 = mass of specimen plus toluene, g (see 9.2.3.4 or 9.2.3.6),
- M_{tol} = mass of toluene in the mixture, g,
- V_{arom} = volume of toluene in the mixture, mL,
- D_{tol} = density of toluene at 20 °C = 0.8669 kg/L,
- FR = flocculation ratio,
- V_{para} = volume of *n*-heptane in the mixture at inflection point, mL (see 9.4.8 and 10.4.10), and
- $1/X$ = oil to solution ratio, g/mL.

12.2 From linear regression and extrapolation of FR versus $1/X$ (see Fig. 1), using the expressions given below, the following stability parameters are calculated:

$$S = 1 + X_{min} \quad (5)$$

$$Sa = 1 - FR_{max} \quad (6)$$

$$So = (FR_{max})S \text{ or } So = (FR_{max})(1 + X_{min}) \quad (7)$$

where:

- S = *S*-value of an oil,
- X_{min} = paraffinic solvent consumption of undiluted oil, mL/g of oil (at $FR = 0$),
- Sa = peptizability of an asphaltene,
- FR_{max} = maximum flocculation ratio (at $1/X = 0$), and
- So = peptizing power of the oil matrix.

The R-squared of the regression provides a measure for the validity of the test. The test results are acceptable if R-squared is equal to or greater than 0.98 (see 9.4.9 and 10.4.11).

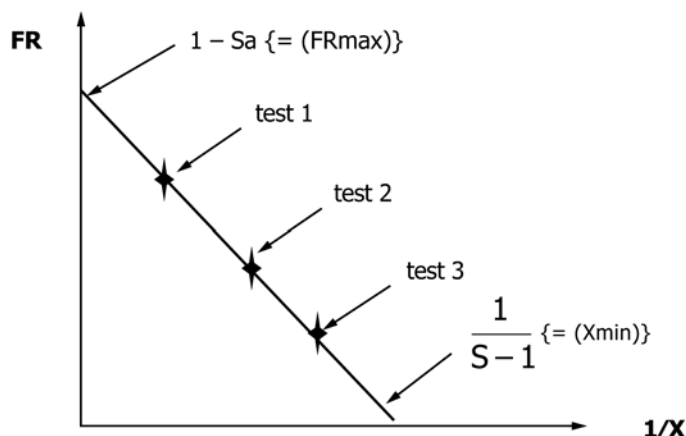


FIG. 1 Derivation of Maximum Flocculation Ratio (FR_{max}) and Reciprocal Critical Heptane Dilution ($1/X_{min}$)

13. Report

13.1 Report the following information:

13.1.1 A reference to this test method and the procedure used. If Procedure B was used, then it should be stated that the method only has preliminary precision data.

13.1.2 The sample identification.

13.1.3 The date of the test.

13.1.4 The stability parameters: *S*, *Sa*, and *So*, to the nearest 0.01.

13.1.5 The goodness of fit, R-squared.

13.1.6 Any deviation, by agreement or otherwise, from the specified procedures.

13.2 For an example of the output report of the analyzer system and the intermediate calculations given in equations Eq 1-4 (see 12.1), refer to Fig. X1.2, Fig. X1.3, Fig. X2.2, and Fig. X2.3.

NOTE 9—Users of this test method would normally use stability and compatibility parameters to determine stability reserve of residual products, fuel blends, and crude oils. However, the interpretation of stability, stability reserve, and compatibility is beyond the scope of this test method.

14. Precision and Bias

14.1 *Precision Procedure A*⁷—The precision statements for *S*, *Sa*, and *So* were obtained by statistical analysis of results from an interlaboratory study involving 11 laboratories using 5 residual fuel oils, 2 thermally cracked residues, 1 atmospheric distillation residue, and 3 crude oils. The study covered the *S* nominal range from 1.29 to 4.23, the *Sa* nominal range from 0.4 to 0.85, and the *So* nominal range from 0.46 to 1.36.

NOTE 10—Nominal ranges are determined by (min. sample mean – Reproducibility) to (max. sample mean + Reproducibility).

14.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus, under constant operating conditions, on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 2 only in one case in twenty.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values in Table 2 only in one case in twenty.

14.1.3 *Bias*—This test method has no bias because the results of the test are defined only in terms of this test method.

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: RR:D02-1662. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Repeatability (*r*) and Reproducibility (*R*) for *S*, *Sa*, and *So*

	<i>S</i>	<i>Sa</i>	<i>So</i>
Repeatability (<i>r</i>)	0.064*(<i>X</i> + 1.2)	0.03	0.15* <i>X</i>
Reproducibility (<i>R</i>)	0.1*(<i>X</i> + 1.2)	0.04	0.22* <i>X</i>

where:
X = the average of two results

14.2 Precision Procedure B:

14.2.1 Repeatability—The difference between successive results obtained by the same operator with the same apparatus, under constant operating conditions, on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 3 only in one case in twenty.

14.2.1.1 Repeatability was measured on four samples with 11 tests per sample.

14.2.1.2 All the tests were carried out on the same device and in the same lab.⁸

⁸ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-2034. Contact ASTM Customer Service at service@astm.org.

TABLE 3 Repeatability (r) for S, Sa, and So

	S	Sa	So
Repeatability (r)	0.06 * X ^A	0.02	0.10 * X ^A

^A X is the average of two results.

14.2.2 Reproducibility—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of this test method, is not yet defined.

14.2.2.1 The reproducibility precision of Procedure B has not yet been established with an interlaboratory study.

14.2.2.2 A full ILS will be completed within five years after approval of Procedure B.

14.2.3 Bias—This test method has no bias because the results of the test are defined only in terms of this test method.

NOTE 11—A comparison study⁸ of the results between the Procedure A device and the Procedure B device was performed on single site with 13 different samples covering all 4 product types (4 sample of type 1; 4 samples of type 2; 2 samples of type 3 and 3 samples of super stable products). This comparison study covered the S value range from 1.31 to 7.90, the Sa range from 0.14 to 0.86, and the So range from 0.51 to 1.25. Results obtained by the Procedure B did not show any significant bias .

15. Keywords

15.1 asphaltenes; compatibility; crude oil; heavy fuels oils; intrinsic stability; S-value; phase separation; residual oil

ANNEX

(Mandatory Information)

A1. HAZARDS INFORMATION

A1.1 Introduction

A1.1.1 In the performance of this test method, there are hazards to personnel. These are indicated in the text. For more detailed information regarding the hazards, refer to the appropriate

Material Safety Data Sheet (MSDS) for each of the applicable substances to establish risks, proper handling, and safety precautions.

APPENDIXES

(Nonmandatory Information)

X1. DETAILED AUTOMATIC TEST PROGRAM PROCEDURE A (MANUAL DILUTION)

X1.2 The automated test procedure is started when the blend is homogeneous and reaches ambient temperature (9.4.5). The test is initiated by clicking the START button.

X1.3 The user is requested to enter the relevant dilution parameters, M_{oil} (9.2.3.2) and M₁ (9.2.3.4).

X1.4 After pressing the icon START, the stepwise titration with n-heptane is automatically initiated and the optical probes' signals are continuously monitored until the formation of flocculated asphaltenes is detected.

NOTE X1.1—As the start of flocculation is interpreted, the point where the light intensity as detected by the probe inverts from an increase to a decrease, indicating that asphaltene flocculation is in progress. The received light is electronically transformed into a voltage signal.

X1.5 The test is finished when the optical probe detects flocculation of asphaltenes or when the total amount of liquids in the titration cell reaches 50 mL and a report is printed (9.4.8). If R-squared (12.2) <0.98, an error message is displayed.

X1.6 Fig. X1.2 shows the optical sensor signals during the flocculation determination of the three blends for a Type 1 sample. The inversion point indicates the point where the increase of light intensity through dilution by n-heptane is inverted to a decrease in light intensity resulting from the flocculation of asphaltenes. The volume of added n-heptane at the inversion point (V_{para}) is used as input for the calculation of the stability parameters S, Sa, and So (Section 12). An example of the final regression report is shown in Fig. X1.3.