



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 D 7157; 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 D 396 Grades No. 5L, 5H, and 6, and D 2880 Grades No. 3-GT and 4-GT, and to crude oils, providing these products contain 0.5 mass% or greater concentration of asphaltenes (see Test Method D 6560).

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*₀) and the solvency requirements of the peptized asphaltenes (*S*_a).

1.4 The values stated in SI units are to be regarded as the 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 and health practices and determine the applicability of regulatory limitations prior to use*

2. Referenced Documents

2.1 ASTM Standards:²

D 396 Specification for Fuel Oils

D 2880 Specification for Gas Turbine Fuel Oils

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4175 Terminology Relating to Petroleum, Petroleum Products, and Lubricants

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

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

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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.

D 4870 Test Method for Determination of Total Sediment in Residual Fuels

D 6560 Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products

D 6792 Guide for a Quality System in Petroleum Products and Lubricant Testing Laboratories

3. Terminology

3.1 Definitions:

3.1.1 For definitions of some terms used in this test method, refer to Terminology D 4175.

3.1.2 *asphaltene, n*—in petroleum technology, a molecule of high molecular mass, high carbon/hydrogen ratio, and containing hetero-atoms.

3.1.2.1 *Discussion*—Asphaltenes are found largely in crude oils and in heavy fuel oils containing residual fractions. They are insoluble in alkanes such as *n*-heptane and cetane, but soluble in aromatic solvents such as benzene, toluene, and 1-methylnaphthalene.

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.

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 *Sa, 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*—*Sa* can also be described as one minus the ratio of *So* to *S*. *Sa* is linked to the length and number of aromatic chains within the asphaltenes.

3.2.4 *So, n*—the *S*-value of an oil.

3.2.4.1 *Discussion*—*So* 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:

<i>FR</i>	= flocculation ratio
<i>FR</i> _{max}	= maximum flocculation ratio
<i>S</i>	= the intrinsic stability of an oil
<i>Sa</i>	= the peptizability of an asphaltene
<i>So</i>	= the peptizing power of an oil
<i>X</i> _{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 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 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 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 **D 4870**.

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. Apparatus

7.1 *General*—(See **Fig. 1**) This test method uses an integrated automated analytical measurement system^{3,4} comprised of a PC-based computer and three titration stations.

7.1.1 *Computer*, PC-based computer with associated software, capable of controlling up to three independent titration stations, controlling test sequencing, and acquisition of optical

³ The sole source of supply of the apparatus (Automated Stability Analyser) known to the committee at this time is Rofa France, 6 Rue Raymond Poincare, F-25300, Les Allies, 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.

⁴ The Rofa stability analyzer is covered by a patent; INPI, date 18/05/04, registration number 04.05406. Interested parties are invited to submit information regarding the identification of an alternative(s) to this patented item to the ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

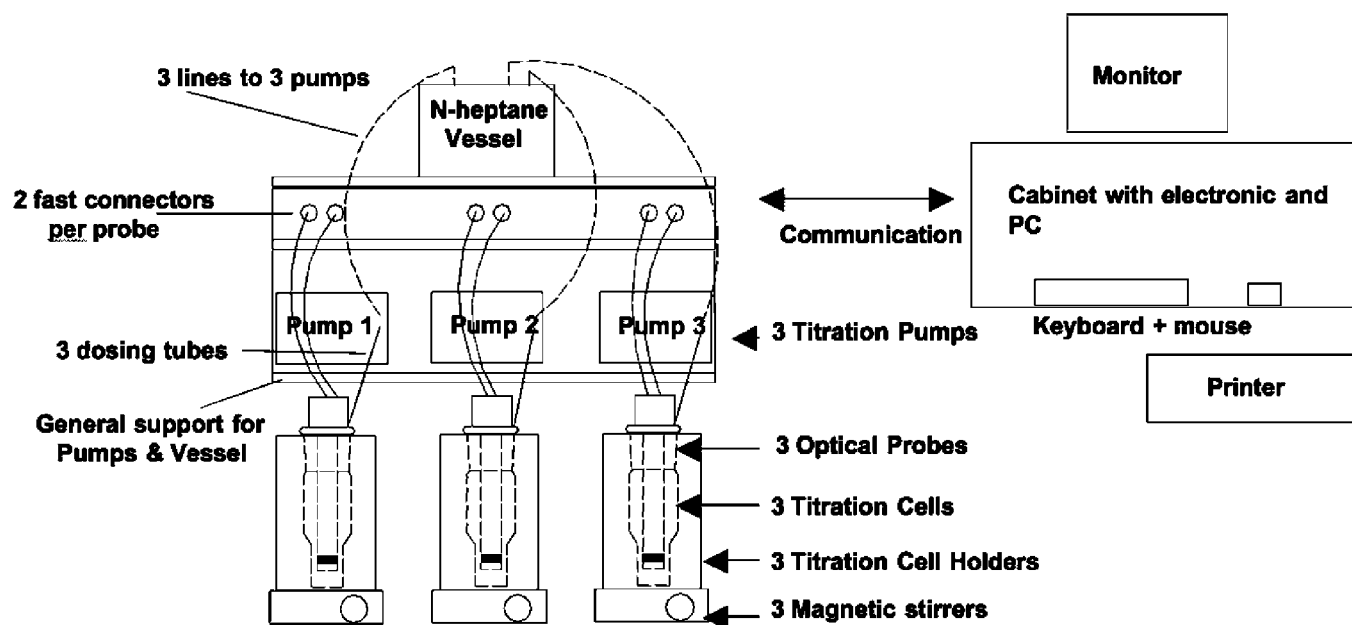


FIG. 1 Schematic Drawing of the Integrated Automated Stability Analyser System

probe signal data. The associated software also provides for processing calculations and automatically produces a report of important test parameters.

7.1.2 Titration Stations:

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

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

7.1.2.3 *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.

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

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

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

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

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

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

8. Reagents and Materials

8.1 *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.⁵ 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.

8.1.1 *Toluene*. (**Warning**—Flammable. Health hazard. Vapor may cause flash fire.) (See Annex A1.)

8.1.2 *n-Heptane*. (**Warning**—Flammable. Vapor harmful. Vapor may cause flash fire.) (See Annex A1.)

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

9. Sampling and Test Specimens

9.1 Sampling:

9.1.1 Obtain representative samples in accordance with recognized sampling procedures such as Practices D 4057 or D 4177.

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

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

9.2 Test Specimen Preparation:

9.2.1 *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.

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

9.2.2 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 **D 4870** filtration apparatus. Specimen should be representative of the whole sample.

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

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

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

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

9.3.4 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 12.

9.3.5 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.

9.3.6 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 12.

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

10. Preparation of Apparatus

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

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

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

10.4 *Cleaning Instructions*—Perform the following cleaning procedure after the test procedure (see **12.1.8**).

10.4.1 Carefully remove the dosing tube and the optical probe from the titration cell. Clean the optical probe with an appropriate solvent (toluene) (see **8.1.1**).

10.4.2 Remove the stirrer bar. Empty the titration cell. Clean the reactor cell and stirrer bar with an appropriate solvent (toluene) (see **8.1.1**).

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 – 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 (see 12.1.7 & 12.1.10)	Mass sample, g	3	2	1
	Volume toluene, mL	1	2	3

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 **D 6792** can be used for guidance.

12. Procedure

12.1 *Test Procedure:*

12.1.1 Place the titration cells containing the specimen solutions (**9.3.4** and **9.3.6**) into their slot positions in the measurement system.

12.1.2 Position the optical probes in the titration cells.

12.1.3 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.

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

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

12.1.6 *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.

12.1.7 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.

12.1.8 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.

12.1.9 Draw a straight line through the three points (see **Fig. 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 **9.3** onwards.

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

12.1.10 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 **9.3** onwards, using fresh dilutions as given in **Table 1** under “Very stable samples.”

13. Calculation of Results

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