Designation: D7157 – 12

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 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 (*So*) and the solvency requirements of the peptized asphaltenes (*Sa*).

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 and health practices and determine the applicability of regulatory limitations prior to use*

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, Petroleum Products, 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 System in Petroleum Products 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.

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 colloidally 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.

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[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 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.

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

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:*

FR	=	flocculation ratio
FR_{max}	=	maximum flocculation ratio
S	=	the intrinsic stability of an oil
Sa	=	the peptizability of an asphaltene
So	=	the peptizing power of an oil
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 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 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. 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

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[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; Rofa France, 6 Rue Raymond Poincare, F-25300, Les Allies, France.

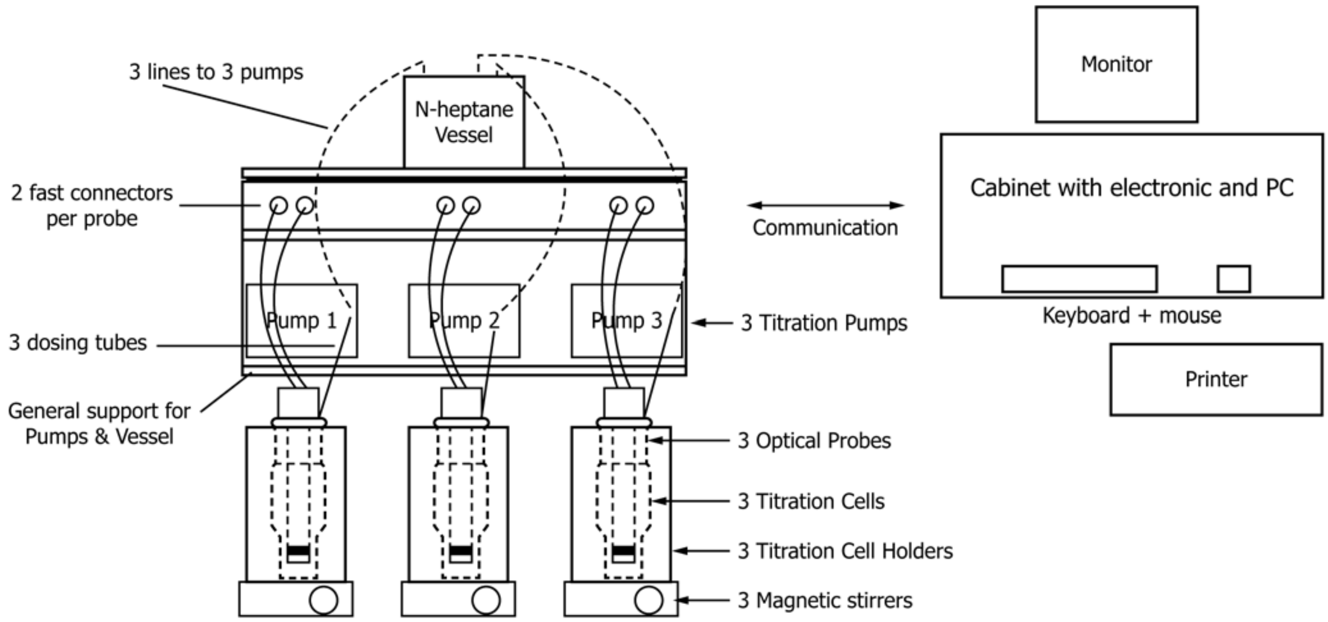

FIG. 1 Schematic Drawing of the Integrated Automated Stability Analyser System

optical 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, PFTE-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 D4057 or D4177.

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.