Designation: ~~D7112 – 12 (Reapproved 2017)~~ D7112 – 18

Standard Test Method for Determining Stability and Compatibility of Heavy Fuel Oils and Crude Oils by Heavy Fuel Oil Stability Analyzer (Optical Detection)[1]

This standard is issued under the fixed designation D7112; 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~~ Scope*

1.1 This test method covers an automated procedure involving titration and optical detection of precipitated asphaltenes for determining the stability and compatibility parameters of refinery residual streams, residual fuel oils, and crude oils. Stability in this context is the ability to maintain asphaltenes in a peptized or dissolved state and not undergo flocculation or precipitation. Similarly, compatibility relates to the property of mixing two or more oils without precipitation or flocculation of asphaltenes.

1.2 This test method is applicable to residual products from atmospheric and vacuum distillation, from thermal, catalytic, 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 0.05 mass % or greater concentration of asphaltenes.

1.3 This test method is not relevant to oils that contain less than 0.05 % asphaltenes, and would be pointless to apply to unstable oils that already contain flocculated asphaltenes.

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.*

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
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6560 Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of some terms used in this test method, such as crude oil, repeatability, reproducibility, and residual fuel oil, refer to Terminology D4175.

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[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 D02.14 on ~~on~~ Stability, Cleanliness and Compatibility 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**

3.1.2 *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 xylene and the paraffinic solvent is n-heptane.

3.1.3 *compatibility, n—of crude oils ~~and~~or of heavy fuel oils*, the ability of two or more crude oils or fuel oils to ~~be blended~~ blend together within ~~specified ratios~~ certain concentration ranges without evidence of separation, such as ~~flocculation or separation of asphaltenes.~~ 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 ~~in~~from crude oils or heavy fuel oils*, the aggregation of colloidally dispersed asphaltenes into ~~larger, visible~~visibly larger masses ~~that~~which may or may not settle.

3.1.5 *stability reserve, n—of crude oils, heavy fuel oils, and residual streams containing asphaltenes*, the property of an oil to maintain asphaltenes in a peptized (colloidally dispersed) state and prevent their flocculation when stored or when blended with other oils.

3.1.5.1 *Discussion*—

An oil with a high stability reserve can be stored for a long period of time or blended with a range of other oils without flocculation of asphaltenes.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *aromatic solvent equivalent (xylene equivalent), SE, n*—the lowest aromatic solvent (xylene) content, expressed as a volume %, in a mixture containing aromatic and paraffinic solvents (xylene and *n*-heptane) which, when mixed with oil, will not result in flocculation of asphaltenes. See *flocculation ratio*.

3.2.1.1 *Discussion*—

SE is defined as $FR_{5/1}$ multiplied by 100 %, as shown in Eq 2.

3.2.2 *evaporation correction coefficient, n*—the rate of evaporation of aromatic solvent (xylene) from the sample cup, measured in grams per hour.

3.2.3 *flocculation ratio (FR), n*—the lowest aromatic solvent (xylene) concentration, expressed as a proportion of xylene to xylene plus *n*-heptane which, when mixed with an oil, will not result in flocculation of asphaltenes. See 15.1, Eq 1.

3.2.4 $FR_{5/1}$, *n*—the flocculation ratio at a dilution of 5 mL of xylene and *n*-heptane solvent mixture to 1 g of oil.

3.2.4.1 *Discussion*—

The ratio 5 to 1 is used internally by a number of oil companies involved with the stability and compatibility of heavy fuel oils and crude oils. This ratio is chosen so that a *P*-value of six represents an $FR_{5/1}$ of zero.

3.2.5 *insolubility number, I_N, n*—a crude oil blending model parameter which can be used to determine if blends of oils are compatible or incompatible. See *solubility blending number*.

3.2.5.1 *Discussion*—

Insolubility numbers for individual oils are determined and calculated from the density of the oil, aromatic solvent equivalent value and volume of paraffinic solvent (*n*-heptane) that can be added to 5 mL of oil without asphaltene precipitation. The equations are given under Calculation of Results (see 15.2).

3.2.6 *maximum flocculation ratio, FR_{max}, n—of asphaltenes in residual fuel oils and crude oils*, the minimum required solvency power of a solvent mixture, expressed as a ratio by volume of aromatic solvent (xylene) to aromatic solvent plus paraffinic solvent (*n*-heptane) to keep the asphaltenes in an oil colloidally dispersed.

3.2.6.1 *Discussion—*

FR_{max} is determined from a plot of flocculation ratios versus the oil concentration in solvent, extrapolated to infinite dilution of the sample at the *y*-axis (where $(1/X) = 0$. See Eq 3).

3.2.7 *oil matrix, n*—that portion of a sample of heavy fuel oil or crude oil that surrounds and colloidally disperses the asphaltenes.

3.2.7.1 *Discussion—*

For purposes of this test method, an oil sample is considered to be composed of an oil matrix (sometimes called an oil medium) and asphaltenes.

3.2.8 *P-value, n—of refinery residual steams*, residual fuel oils and crude oils, an indication of the stability or available solvency power of an oil with respect to precipitation of asphaltenes.

3.2.8.1 *Discussion—*

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

3.2.9 P_a, *n*—the *P*-value of an asphaltene, which is the peptizability or ability of an asphaltene to remain colloidally dispersed.

3.2.10 P_o, *n*—the *P*-value of an oil matrix. See *oil matrix*.

3.2.11 *peptize, v—of an oil or cutter stock*, to dissolve an asphaltene or to maintain an asphaltene in colloidal dispersion.

3.2.12 *solubility blending number, S_{BN}, n*—a crude oil blending model parameter which can be used to determine if blends of oils are incompatible or compatible. See *insolubility number*.

3.2.12.1 *Discussion—*

Solubility blending numbers for individual oils are determined and calculated from the density of the oil, aromatic solvent equivalent value, and volume of paraffinic solvent that can be added to 5 mL of oil without asphaltene precipitation. The equations are given under Calculation of Results (see 15.2).

3.2.13 *step size, n*—the volume in mL of each portion of *n*-heptane added to the stock solution in the course of the test procedure.

3.2.14 *stock solution, n*—a solution of a sample dissolved in a specific amount of xylene.

3.3 *Symbols:*

FR = flocculation ratio
$FR_{5/1}$ = flocculation ratio at a dilution of 5 mL solution (xylene plus *n*-heptane) to 1 g of oil
FR_{max} = maximum flocculation ratio
I_N = insolubility number
P = the *P*-value of an oil
P_a = the *P*-value of an asphaltene
P_o = the *P*-value or peptizing power of an oil matrix
S_{BN} = solubility blending number
SE = xylene equivalent, volume %
X_{min} = *n*-heptane consumption of undiluted oil, in mL/g of oil

4. Summary of Test Method

4.1 Stability and compatibility parameters are determined by titration and optical detection of precipitated asphaltenes. A stock solution is prepared and three different mixtures of the sample oil plus xylene are titrated with *n*-heptane to cause precipitation of asphaltenes. The titrated mixture is continuously circulated through an optical detector which detects precipitated asphaltenes by back-scattering of visible light. The amounts of oil, xylene, and *n*-heptane are used to calculate stability parameters: solvent equivalent, P-value, and $FR_{5/1}$. If the density of a crude oil sample is known, then the compatibility parameters (S_{BN} and I_N) of the crude oil may also be calculated.

5. Significance and Use

5.1 Automatic determination of stability parameters using a light back-scattering technique improves accuracy and removes human errors. In manual testing, operators have to visually compare oil stains on pieces of filter paper to determine if asphaltenes have been precipitated.

5.2 Refinery thermal and hydrocracking processes can be run closer to their severity limits if stability parameters can be calculated more accurately. This gives increased yield and profitability.

5.3 Results from the test method could be used to set a standard specification for stability parameters for fuel oils.

5.4 The compatibility parameters of crude oils can be used in crude oil blending in refineries to determine, in advance, which crude oil blends will be compatible and thus can be used to minimize plugging problems, unit shut downs, and maintenance costs. Determination of crude oil compatibility parameters also enables refineries to select crude oil mixtures more economically.

5.5 This test method can measure stability and compatibility parameters, and determine stability reserve on different blends for particular applications to optimize the blending, storage, and use of heavy fuel oils

NOTE 1—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 heavily 'use dependent,' and is beyond the scope of this test method.

6. Interferences

6.1 Free water present in the oil can cause difficulties with the optical detector and should be removed by centrifuging prior to testing.

6.2 Solid particles, such as coke or wax particles, mud, sand, or catalyst fines, in the oil will not affect the optical detector or interfere with the results.

7. Apparatus

7.1 *PORLA Heavy and Crude Oil Stability and Compatibility Analyzer*[3,4]—See Figs. 1 and 2.

7.1.1 A portion of the apparatus is shown diagrammatically in Fig. 2 and is comprised of the following parts:

7.1.1.1 *Sample Cup,* light weight, inert cups designed to fit the sample carousel, with a smooth, flat bottom, volume approximately 100 mL. Typically, aluminum cups have been used.

7.1.1.2 *Sample Carousel,* typically a four-position sample cup holder delivering the sample cups sequentially to the measurement position.

7.1.1.3 *Mixer Lift System,* vertically moving lift system, forming a seal with the sample cup in the measurement position and incorporating a mechanical stirrer which starts to rotate when the seal is made. It also incorporates delivery lines for *n*-heptane and xylene addition, the circulation line for passing the sample through the detector and the exhaust line, which empties the sample cup after analysis.

7.1.1.4 *Aromatic Solvent Pump,* accurate and adjustable ceramic piston pump, capable of delivering xylene at a rate of 0.01 mL⁄s to 0.5 mL/s.

7.1.1.5 *Paraffinic Solvent Pump,* accurate and adjustable ceramic piston pump, capable of delivering *n*-heptane at a rate of 0.01 mL⁄s to 0.5 mL/s.

7.1.1.6 *Circulation Pump,* accurate and adjustable ceramic piston pump used to circulate the sample under test through the detector system.

7.1.1.7 *Exhaust Pump,* accurate and adjustable ceramic piston pump used to empty the sample cup at the end of the measurement.

7.1.1.8 *Detector System,* (see Fig. 3) optical detector through which the sample solution is continuously circulated. The detector is composed of a visible light source and a photodiode for recording the light reflecting from asphaltene particles in the test sample.

7.1.1.9 *Hot Plate,* a temperature controlled heating system may be located below the sample cups, which will warm up the sample so that the titration may be performed at an elevated temperature. The temperature of the hot plate should be adjustable between 20 °C and 100 °C.

7.1.2 *Computer,* controls the measurement and calibration programs and is an interface between the operator and the analyzer.

7.1.3 *PORLA Step Measurement Screen,* computer display, allowing data about the sample and operator to be input as well as showing the results of each titration (see Fig. 4).

[3] The PORLA Heavy and Crude Oil Stability and Compatibility Analyzer is covered by Euro patent EP 0737309 and U.S. patent US5715046. 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.

[4] The sole source of supply of the PORLA Heavy and Crude Oil Stability and Compatibility Analyzer known to the committee at this time is Finnish Measurement Systems Limited, Koskikuja 5, FIN-71570 Syvanniemi, Finland,
www.finnmeassys.com. 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.

FIG. 1 PORLA Heavy and Crude Oil Stability and Compatibility Analyzer

7.1.4 *Parameter Screen,* computer display, allows all of the measurement cycle parameters to be adjusted from the default values and also allows the pump calibration procedure to be run (see Fig. 5).

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall 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 determined that the reagents are of sufficiently high purity to permit their use without lessening the accuracy of the determination.

8.2 *Xylene (C_8H_{10})*—The xylene used is generally a mixture of ortho, meta, and para isomers and may contain some ethyl benzene. (**Warning—**Flammable, health hazard.)

8.3 *n*-heptane (C_7H_{16})—(**Warning—**Flammable, health hazard.)

9. Hazards

9.1 Place the analyzer in a fume hood or similar well ventilated area to minimize exposure of operators to harmful vapors.

[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 *Analar 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.

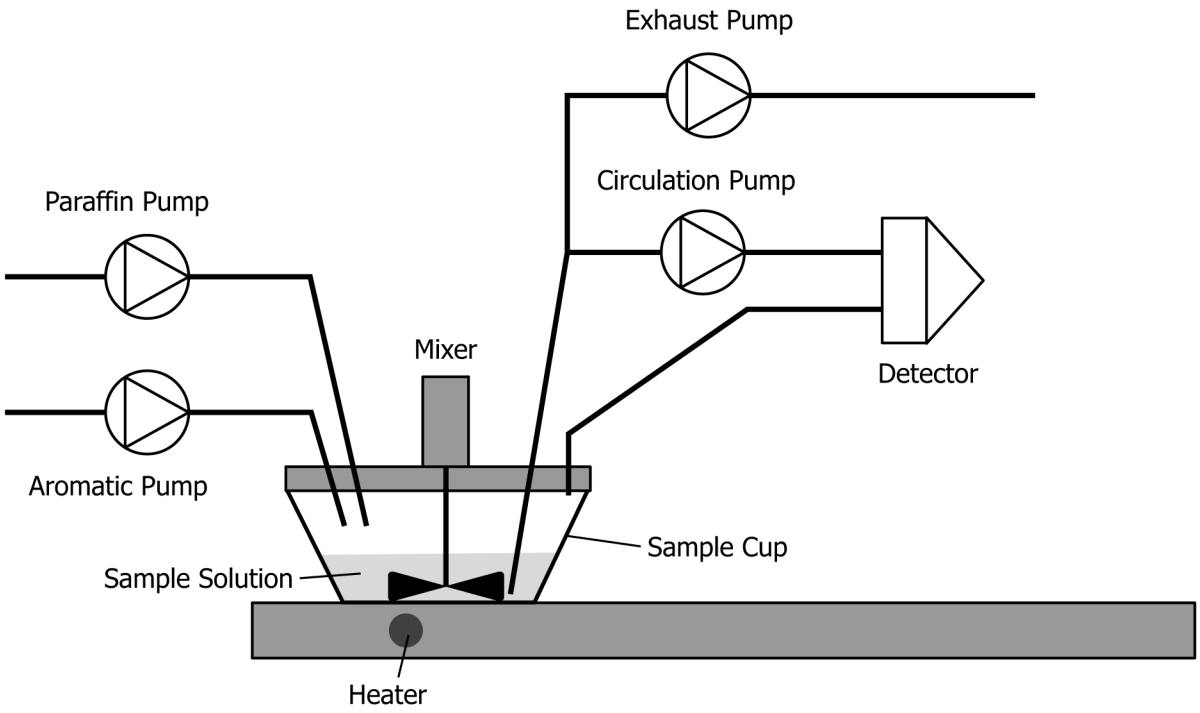

FIG. 2 Schematic Diagram of PORLA Heavy and Crude Oil Stability and Compatibility Analyzer

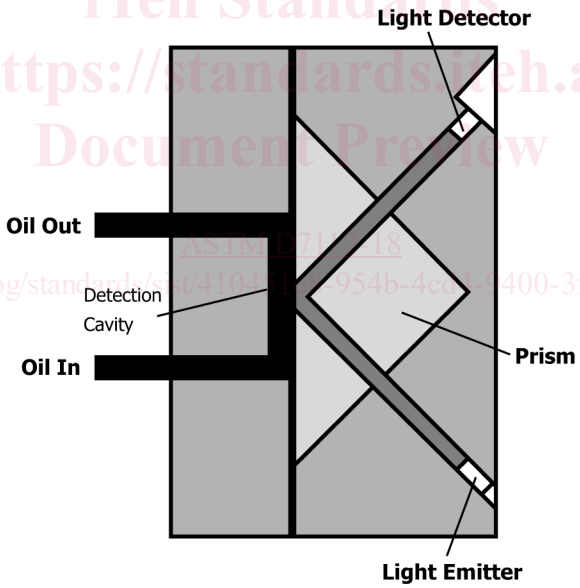

FIG. 3 Schematic Diagram of PORLA Heavy and Crude Oil Stability and Compatibility Analyzer Detector

9.2 Operators should use proper protective laboratory clothing and gloves to avoid skin exposure to oil samples and solvents. In addition, operators should be careful when handling hot oil containers when preparing the stock solutions from very viscous oils as oil spills on exposed skin will cause burns.

10. Sampling and Test Specimens

10.1 Obtain samples in accordance with procedures described in Practices D4057 or D4177. Ensure that samples are representative of the whole batch of oil.

10.2 A minimum sample size of 40 g is required for a single test. It is preferable to collect a larger sample such as 200 g to 500 g to allow for multiple testing, if necessary.

10.3 Ensure that the sample is homogeneous before withdrawing an aliquot or test specimen for testing.