Designation: D7112 – 05a

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*

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 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

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.

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

3.1.2.1 *Discussion*—Asphaltenes are generally found in crude oils and in heavy fuel oils containing residual fractions. Their presence is determined by their insolubility in alkanes such as *n*-heptane and solubility in aromatics such as xylene.

3.1.3 *compatibility*, *n—of crude oils and of heavy fuel oils*, the ability of two or more crude oils or fuel oils to be blended together within specified ratios without evidence of separation, such as flocculation or separation of asphaltenes.

3.1.4 *flocculation*, *n—of asphaltenes in crude oils or heavy fuel oils*, the aggregation of colloidally dispersed asphaltenes into larger, visible masses that 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.

[1] This test method is under the jurisdiction of ASTM 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.

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

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 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 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 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).

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.)

[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, Outilantie 3, Fin-83750 Sotkuma, Finland. 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.

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

9. Hazards

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

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 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.

10.4 To avoid changes or degradation of oil samples, minimize exposure to air, temperatures above 25°C, and light. Store samples in sealed, opaque containers such as metal cans or dark glass bottles.

11. Preparation of Apparatus

11.1 Review the operations manual for the apparatus,[6] and follow all recommended steps. The following actions summarize the preparation of the apparatus:

11.1.1 Place the apparatus on a level surface, in a well-ventilated area such as a fume hood.

11.1.2 Connect the analyzer and the computer to a suitable ac power source, and connect the analyzer, keyboard, monitor, and mouse to the computer with the cables supplied.

[6] Obtain the operator's manual from the supplier of the apparatus.

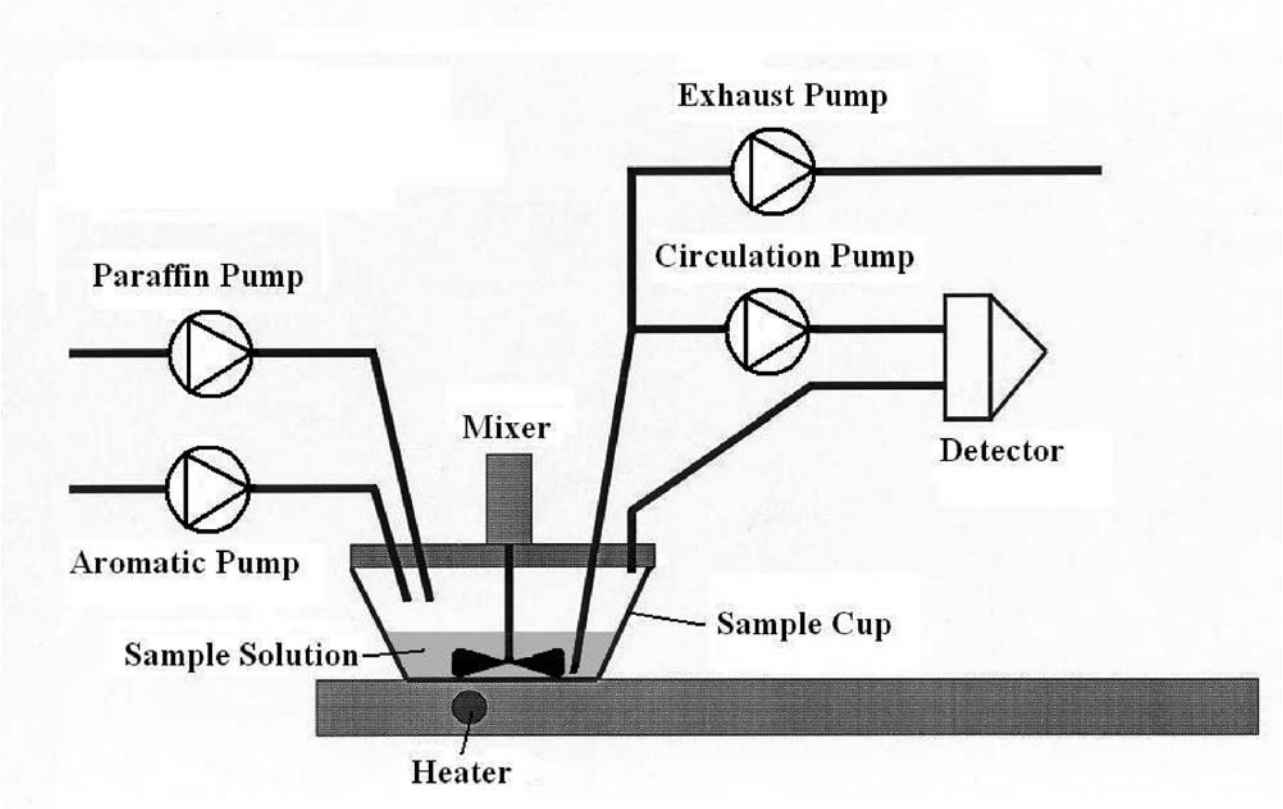


FIG. 2 Schematic Diagram of PORLA Heavy and Crude Oil Stability and Compatibility Analyzer

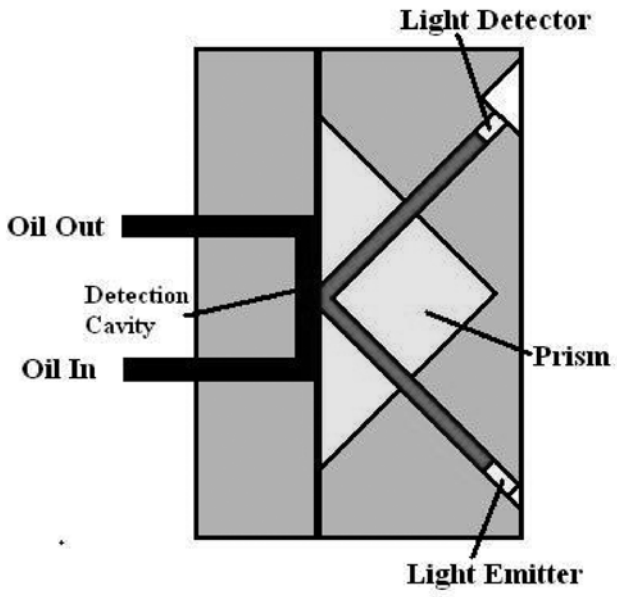


FIG. 3 Schematic Diagram of PORLA Heavy and Crude Oil Stability and Compatibility Analyzer Detector

NOTE 2—All of the controls for the instrument except for the main power switch are accessed by means of the keyboard and mouse of the computer.

11.1.3 Fill the aromatic and paraffinic solvent bottles with xylene and *n*-heptane, respectively, and ensure the waste bottle is empty. Connect the three plastic bottles, labeled aromatic solvent, paraffinic solvent and waste, to the appropriate lines from the analyzer.

11.1.4 Switch the analyzer on using the rocker switch on the back panel. A green lamp will illuminate on the upper right of the front panel.

11.1.5 Switch on the computer and allow it to boot up.

11.1.6 Select either PORLA Step or PORLA Test by double clicking the mouse on the appropriate icon to bring up the PORLA Step measurement screen (see Fig. 4) or the system test screen.

12. Calibration and Standardization

12.1 *Pump Calibration*—Perform the pump calibration at the initial set-up and whenever the instrument has been serviced. When in continuous service, perform pump calibrations monthly to verify the pumping rates.

12.1.1 On the PORLA Step measurement screen (Fig. 4) select the Parameter screen (see Fig. 5). Calibrate the xylene and *n*-heptane pumps by starting the automatic procedure under Pump Calibration.

12.1.2 Identify two clean sample cups as 'xylene' and '*n*-heptane,' and accurately weigh to two decimal places. These are the tare weights of the cups.

12.1.3 The instrument automatically pumps solvent over a constant period of time (60 s) into a tared sample cup.

12.1.4 Weigh the collected solvent and sample cup and subtract the tare weight of the sample cup to give the weight of solvent pumped in the set time period (60 s).

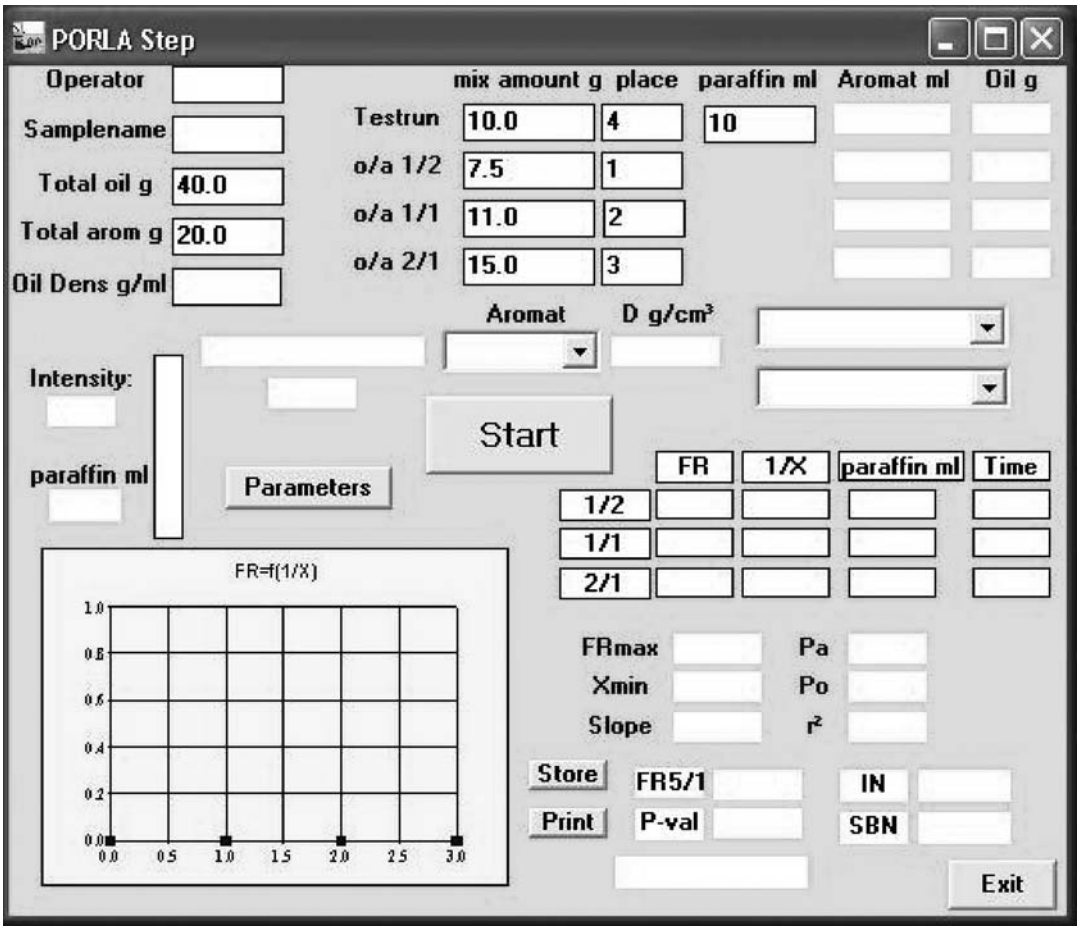


FIG. 4 PORLA Step Measurement Screen

12.1.5 Enter the weight of solvent collected in the appropriate screen.

12.1.5.1 For the xylene pump rate, the instrument calculates the updated pump rate in g/s and displays it in the appropriate field in the parameter screen.

12.1.5.2 For the *n*-heptane pump rate, the instrument calculates the updated pump rate and displays it in mL/s in the appropriate field in the parameter screen.

12.2 *Evaporation Correction Coefficient*—Determine the evaporation correction coefficient for the xylene by weighing (accurate to two decimal places) a sample cup containing a stock solution after 0.5, 1.0, and 1.5 h of standing in the sample carousel and calculate the average solvent loss by evaporation in g/h. Input this information into the PORLA parameter screen, which is accessed by means of the Parameter button in the PORLA Step measurement screen.

12.2.1 Verify the evaporation correction coefficient quarterly when the instrument is in continuous service.

12.2.2 If a specific sample contains volatile components, such as a whole crude oil, use the semi-automatic *Light Ends* mode of operation. In this mode of operation, evaporation is minimized by loading the stock solution cups one at a time into the carousel. See 14.9.

NOTE 3—No significant evaporation of solvent or sample occurs during the titration procedure because the sample cup is sealed in the test position in the instrument. However, evaporation of xylene does occur when several sample cups sit in the sample carousel during the fully automatic mode of operation.

13. Quality Control Monitoring

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

13.1.1 The QC sample(s) should be a stable and homogeneous residual fuel oil or crude oil similar in composition and viscosity to the type of samples routinely tested, and containing from 1 to 10 mass % asphaltene. Asphaltene content may be measured by Test Method D6560.

13.2 Prior to monitoring the measurement process, determine the average value and control limits for the QC sample (see Practice D6299 and Section 3 of Manual 7[7]).

13.3 Record QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total test process.[7,8] Investigate any

[7] ASTM MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th edition, Section 3: Control Chart for Individuals. Available from ASTM International Headquarters.

[8] In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.

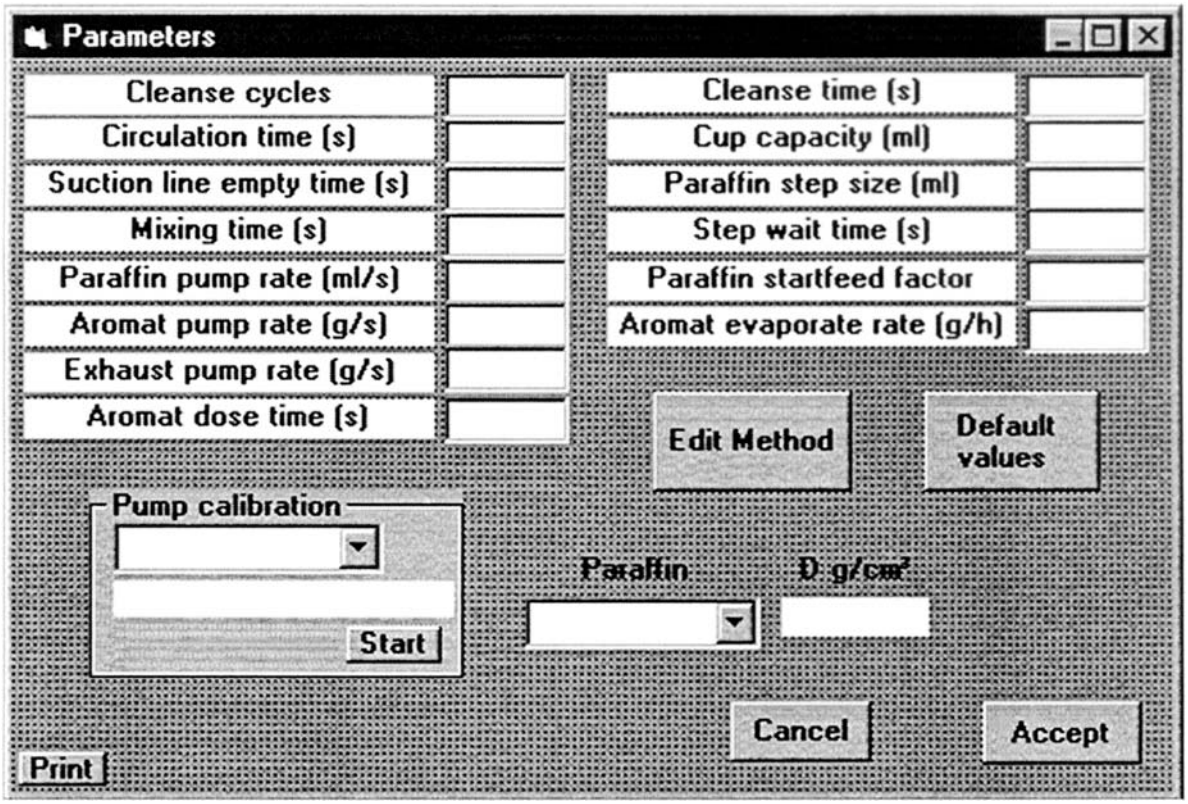


FIG. 5 PORLA Parameter Screen

out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

13.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process and customer requirements.[8] Generally, a QC sample should be analyzed each testing day for routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM method precision to ensure data quality.[7]

13.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and shall be homogeneous and stable under the anticipated storage conditions.

13.6 See Practice D6299 and Manual 7[7] for further guidance on test method QC and control charting techniques.

14. Procedure

14.1 *Sample Preparation*:

14.1.1 *Stock Solution*—Prepare a stock solution in a sealable container such as a screw cap glass bottle (volume about 100 mL) from 40 g of the oil under test and 20 g of xylene, as described below.

14.1.2 Thoroughly mix the oil by vigorously shaking the sample container for at least 2 min. If the viscosity of the oil is high, warm up the oil in an oven before shaking. A temperature of 80°C is normally sufficient.

14.1.3 Weigh out 20 g of the xylene into the sealable container (bottle), accurate to two decimal places, and then add 40 g of the oil, also weighed to two decimal places.

14.1.4 Shake the stock solution container until the oil has dissolved in the xylene. Ensure that the oil has completely dissolved before proceeding. A visually homogeneous stock solution mixture usually indicates complete dissolution of oil in the xylene.

14.1.5 In the case of oil samples that are very difficult to dissolve, use a refluxing device instead of shaking the bottle. When using the refluxing device, let the stock solution cool down before pouring it into the sealable container.

14.2 *Test Information and Instrument Settings*:

14.2.1 Open the PORLA Step measurement screen and type in the operator's name and sample name in the appropriate fields.

14.2.2 Type in the oil and xylene weights, accurate to two decimal places, used in the preparation of the stock solution, in the appropriate fields.

14.2.3 Type in the density of a crude oil sample, in g/mL at 15°C, in the appropriate field, if compatibility parameters are desired. Determine density by a method appropriate to the sample type, if required.

14.2.4 Select *xylene* from the drop down list of aromatic solvents displayed under Aromatic.

14.2.5 Before each test, ensure that there is an adequate volume of solvent in the aromatic (xylene) and paraffinic

(*n*-heptane) solvent bottles, and the waste bottle has capacity to accept the volume of waste from the test.

NOTE 4—If the *n*-heptane bottle is empty, or runs empty during a test, the instrument will continue pumping air until the total pumped volume equals the volume set for the cup (typically set at 55 mL), at which point the instrument will shut down and display the message *Sample cup full*.

14.3 The test method is normally performed at laboratory ambient temperature. If particular properties of a sample, such as high viscosity, require testing at an elevated temperature, set a suitable temperature using the hot plate control and record the temperature of the test with the results.

NOTE 5—The temperature of the test is normally slightly above ambient due to heat generated in the apparatus. Testing and results during development of the test method have not indicated any affect of such slight temperature variations.

14.4 If the sample is totally unknown, determine the order of magnitude of the *n*-heptane consumption using the following fast screening procedure.

14.4.1 Weigh out about 15 g of stock solution, accurate to two decimal places, into a sample cup and place the cup in position No. 1 in the sample carousel.

14.4.2 Enter the sample weight, accurate to two decimal places, into the Test Run field and enter 0 in the adjacent Paraffin mL field.

14.4.3 Start the measurement with the Start button. The analyzer will continuously add paraffinic solvent until the asphaltenes precipitate as indicated by the Intensity bar and Intensity screen, which will read full scale and 10.00 respectively.

14.4.4 Read the amount of *n*-heptane consumed from the Paraffin mL field directly below the Intensity field.

14.5 After performing the fast screening procedure, or from previous testing, divide the total *n*-heptane consumption by 20 to obtain the approximate correct step size for the main measurement. Type this calculated step size into the appropriate field in the parameter screen.

14.6 Enter the total expected *n*-heptane consumption for the test sample, determined in 14.4.4 or known from prior experience, into the Paraffin mL field to the right of the Test Run field.

14.7 Select the titration method to be used from a drop down list to the right of the Start button (Fig. 4).

14.7.1 Select *Low Floc. Rate*, which is the normal operation, for high stability products such as crude oils, straight run residues, and residues from visbreaking and lower severity hydrocracking processes.

14.7.2 Select *High Floc. Rate* for low stability oils such as residual products from very severe cracking processes. Low stability oils typically have an $FR_{5/1}$ above 0.7.

NOTE 6—For *Low Floc. Rate* the PORLA instrument selects dilution ratios of xylene to oil of 1 : 2, 1 : 1, and 2 : 1. For *High Floc. Rate* the PORLA instrument selects dilution ratios of xylene to oil of 2 : 1, 3 : 1, and 4 : 1.

NOTE 7—A third mode allows the operator to edit the method and select custom dilution rates. Use of this mode may be useful for research purposes but would be a deviation from the standard method.

14.8 Select the specific titration method to determine the xylene dilution rates applied by the analyzer and the amount of stock solution to be placed in each sample cup.

14.9 The analyzer can be run in fully automatic mode or semi-automatic mode. Select the mode from a drop down list directly above the method list (see Fig. 4). *Normal Operation* is the fully automatic mode and *Light Ends* is the semi-automatic mode.

14.9.1 Use the Light Ends mode only when the oil contains a significant amount of volatile components which could be lost by evaporation if several sample cups were stored in the carousel for an extended period of time (see 12.2). In the Light Ends (semi-automatic) mode, place one sample cup in the carousel at a time. When the analyzer stops after each titration, place the next sample cup in the carousel.

14.10 Fill three sample cups with the amounts of stock solution indicated in the three fields directly below the Test Run field, weighed to an accuracy of two decimal places, and place the sample cups in the sample carousel. Modify the weights in these fields to reflect the actual weights of the stock solution used and type in the carousel positions in the fields directly to the right of these weights.

14.11 Set the measurement parameters that are displayed in the Parameter screen to the expected optimal values for each type of sample.

14.11.1 *Cleanse Cycles*—Determines the number of washing cycles (using xylene) the program performs after the complete analytical procedure. Use a minimum of two washing cycles, but three cycles is recommended. The analyzer performs one washing cycle after the analysis of each sample.

14.11.2 *Circulation Time*—Determines how long the sample is circulated through the detector after the mixing period, followed by the xylene addition before the intensity measurements are started. Set 60 to 70 s, which is normally sufficient circulation time to give a consistent result.

14.11.3 *Suction Line Empty Time*—Determines how long the circulation pump operates to empty the detector after each measurement. Set 30 s, which is normally sufficient.

14.11.4 *Mixing Time*—Determines how long the sample is mixed after the aromatic solvent addition, before starting the circulation of the sample solution to the detector. 60 s is usually sufficient.

14.11.5 *Paraffin Pump Rate*—Determines the pumping rate of the *n*-heptane pump. The pumping rate is adjustable. Set the pumping rate at 0.05 mL/s.

14.11.6 *Aromatic Pump Rate*—Determines the pumping rate of the xylene pump. Set the pumping rate at 0.07 g/s.

14.11.7 *Exhaust Pump Rate*—Determines the pumping rate of the exhaust pump, which will empty the sample cups after the analyses and washing cycle. Set the rate at 0.4 g/s.

14.11.8 *Aromatic Dose Time*—Determines how long the xylene is pumped for each washing cycle. Set the dose time at 45 s.

14.11.9 *Cleanse Time(s)*—Determines the length of the washing time of the detector. Set the washing time at 60 s.

14.11.10 *Cup Capacity*—Determines how much solution is allowed to be pumped into a sample cup before the measurement program will be interrupted with *Sample cup full* message. Spillage of solution from the cups onto the analyzer due to overflow is prevented by the cup capacity limit. While the cup has a nominal capacity of 100 mL, the highest cup capacity value recommended is 55 mL.

NOTE 8—Samples containing less than 0.05 % asphaltenes will reach the sample cup full point, and the titration will be terminated automatically.

14.11.11 *Paraffinic Step Size*—Determines the size (volume) of *n*-heptane addition in each step. When analyzing samples with low stability, use a small step size of 0.3 to 0.5 mL. Use a larger step size of 0.5 to 1 mL for normal visbreaker products and, for high stability products such as crude oil residues from atmospheric or vacuum distillation units, use 1 to 3 mL.

14.11.12 *Step Wait Time*—Determines the waiting time between *n*-heptane addition steps. Use 60 to 120 s.

14.11.13 *Paraffinic Start Feed Factor*—Determines the percentage, shown as a decimal figure (0.4 means 40 %, for example) of the expected total *n*-heptane consumption that will be added as a first portion to the sample cup. This allows the total measurement time to be decreased. If the operator wants to carry out all of the paraffinic solvent addition in small steps without the initial larger portion, enter 0 into the Paraffin start feed factor field. An initial portion larger than 0.4 can be used for research purposes but shall not be used for this standard procedure.

14.11.14 *Aromatic Evaporation Rate (g/h)*—Determines the rate at which the aromatic solvent is evaporating from open sample cups while they are standing on the warm plate of the sample carousel prior to the analyses. The method for calculating this is described under 12.2.

14.12 Press the start button to start the analysis.

14.13 As soon as the analysis has started, an interrupt button will appear to the right of the start button. This allows the analysis to be interrupted immediately, should it be necessary.

14.14 The analyzer will complete the three titrations that make up the analysis and report the results in numerical and graphical form in the bottom half of the measurement screen. See Fig. 4 and Fig. 6.

14.14.1 The computer program plots the flocculation ratio against the ratio of the oil sample to solvent volume. This concentration ratio is used because it gives a straight line relationship.

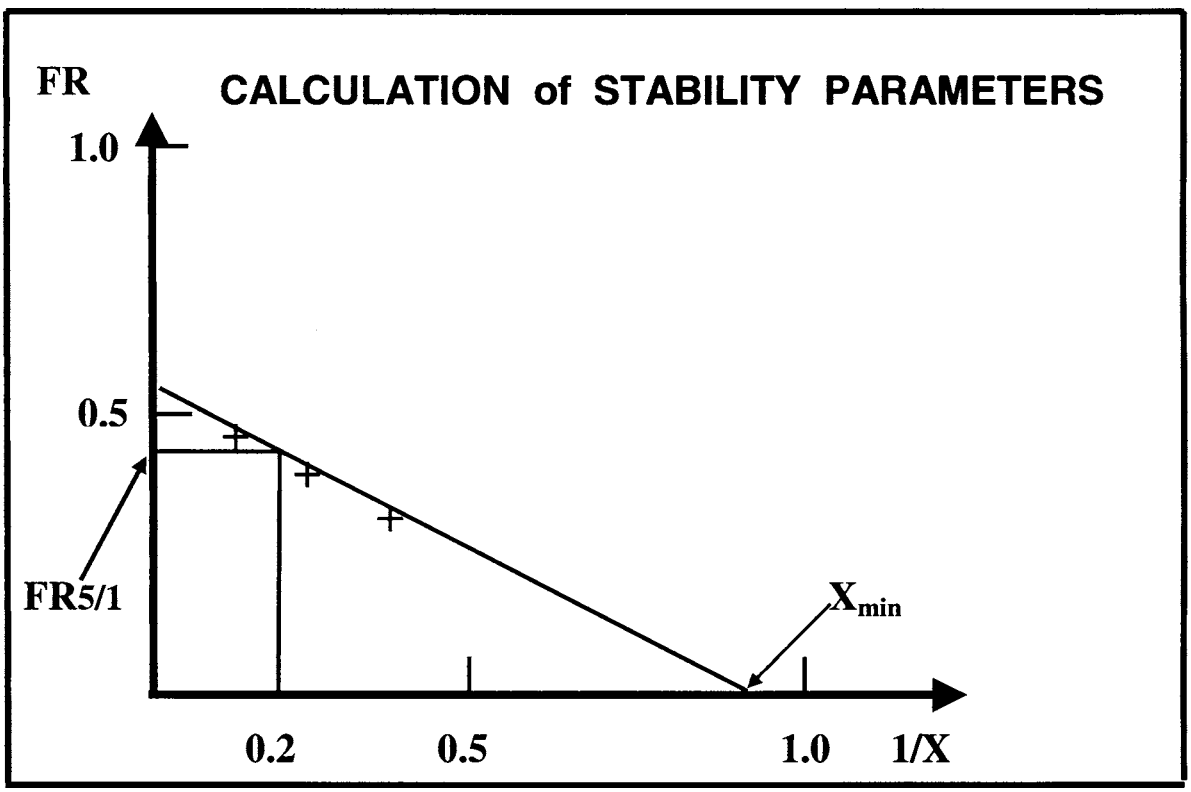
14.15 Values for the solvent ratio and oil-to-solvent ratio for each titration are given in the *FR* field and 1/*X* field respectively.

14.15.1 A straight-line graph is shown using a least squares sum procedure where the intercept on the *y*-axis is given in the FR_{max} field.

14.15.2 The extrapolated *n*-heptane consumption, of the undiluted oil, is given in the X_{min} field.

14.15.3 The slope of the graph is given in the slope field.

14.15.4 The peptizability or *P*-value of the asphaltene is given in the P_a field.



NOTE—1/*X* is the oil to solution ratio, where the solution is the sum of the volumes of the aromatic and paraffinic solvents (xylene and *n*-heptane).

FIG. 6 Typical Analyzer Plot of Stability Results

14.15.5 The peptizing power of the oil matrix is given in the P_o field.

14.15.6 The correlation factor indicating the significance level of the fitting of the straight line is given in the r^2 field.

14.16 The stability parameters, *P*-value and flocculation ratio at a dilution of 5 mL solution to 1 g of oil, are given under the *P*-value and $FR_{5/1}$ fields, respectively.

14.17 If the crude oil compatibility option software is installed and the density of the oil under test has been entered into the *D* (g/mL) field at the start of the measurement, the crude oil blending model parameters of insolubility number (I_N) and solubility blending number (S_{BN}) will be displayed in the I_N and S_{BN} fields, respectively.

15. Calculation of Results

15.1 The instrument automatically calculates the stability parameters by linear regression and by extrapolation (see Fig. 4), using the following equations:

$$FR = \frac{V_{arom}}{(V_{arom} + V_{para})} \quad (1)$$

$$SE = (FR_{5/1})(100\ \%) \quad (2)$$

$$\frac{1}{X} = \frac{M_{oil}}{(V_{arom} + V_{para})} \quad (3)$$

$$P = 1 + X_{min} \quad (4)$$

$$P_a = 1 - FR_{max} \quad (5)$$

$$P_o = (FR_{max})P \quad \text{or} \quad P_o = (FR_{max})(1 + X_{min}) \quad (6)$$

where:

FR = flocculation ratio,
$FR_{1/5}$ = flocculation ratio at a dilution of 5 mL solution to 1 g of oil,
FR_{max} = maximum flocculation ratio (at $1/X = 0$),
SE = aromatic solvent equivalent, expressed as a percent value,
$1/X$ = oil to solution ratio, g/mL,
X_{min} = paraffinic solvent consumption of undiluted oil, mL/g of oil (at $FR = 0$),
M_{oil} = mass of oil, g,
V_{arom} = volume of aromatic solvent in the mixture, mL,
V_{para} = volume of paraffinic solvent in the mixture, mL,
P = *P*-value of an oil,
P_a = peptizability of an asphaltene, and
P_o = peptizing power of the oil matrix.

15.2 The instrument uses the following equations to determine compatibility parameters of crude oil samples, if required:

$$I_N = \frac{SE}{(1 - V_H/25D)} \quad (7)$$

$$S_{BN} = I_N(1 + V_H/5) \quad (8)$$

where:

I_N = insolubility number,
S_{BN} = solubility blending number,
D = density of oil, g/mL,
SE = aromatic solvent equivalent, volume %, and
V_H = volume of paraffinic solvent that can be added to 5 mL of oil without asphaltene precipitation.

16. Report

16.1 Report the following information:

16.1.1 The identity of the sample,

16.1.2 The stability parameters: *SE*, *P*-value, and $FR_{5/1}$,

16.1.3 The compatibility parameters: I_N and S_{BN}, if determined,

16.1.4 Reference to this test method, and

16.1.5 If an elevated temperature above ambient room temperature was used, report the temperature of the test.

17. Precision and Bias

17.1 Precision of this test method, repeatability and reproducibility, will be determined by a proper interlaboratory study within five years of publication of this test method.

17.1.1 Three sets of in-house data are given in Tables X1.1-X1.3 in the Appendix for information. Based on this limited data and other work done by laboratories with the PORLA instrument, preliminary estimates of precision indicate that this test method is significantly better than that of proprietary manual methods (which rely on operators being able to evaluate two different spots on filter paper, the darker of which shows asphaltene precipitation).

NOTE 9—No published precision data on the proprietary manual spot tests has been found.

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

18. Keywords

18.1 asphaltene precipitation; asphaltenes; compatibility; crude oil; heavy fuel oil; insolubility number;*P*-value; residual oil; solubility blending number; solvent equivalent; stability; stability reserve

APPENDIX

(Nonmandatory Information)

X1. INITIAL PRECISION DATA

X1.1 Table X1.1 shows a repeatability study of stability analysis of hydrocracking (H-oil) process samples carried out by the Institut Francais Du Petrole (IFP). The samples were a feed stock (Atmospheric Distillation Residue (A.R.) of Arabic light crude oil), and a residual product (an atmospheric residue after processing in an H-oil process unit (IFP's hydrocracking process)). Twenty repetitive analyses were carried out during a two-week period.

X1.2 Table X1.2 shows the results of tests carried out at Fortum Oil and Gas Ltd, Finland, to satisfy the requirements for a Russian GOST standard. Six repetitive analyses were carried out on four samples. One sample was a feed stock and the other three were residues from a visbreaking process run at different temperatures (severity levels).

X1.3 Table X1.3 shows a stability and compatibility analysis of Athabasca bitumen, carried out by the National Center for Upgrading Technology (NCUT), Canada. Ten repetitive analyses were carried out on the sample.

TABLE X1.1 IFP Data

Run Number	Atmospheric Residue of Arab Light Crude Oil		Atmospheric Residue of H-Oil Process	
	$FR_{5/1}$	*P*-Value	$FR_{5/1}$	*P*-Value
1	0.17	3.25	0.48	1.51
2	0.17	3.22	0.48	1.52
3	0.17	3.15	0.48	1.50
4	0.17	3.30	0.49	1.51
5	0.17	3.09	0.48	1.54
6	0.17	3.29	0.49	1.53
7	0.17	3.15	0.47	1.51
8	0.17	3.21	0.49	1.55
9	0.16	3.32	0.47	1.53
10	0.17	3.35	0.46	1.53
11	0.17	3.20	0.48	1.54
12	0.17	3.28	0.48	1.49
13	0.16	3.46	0.47	1.52
14	0.17	3.20	0.48	1.59
15	0.16	3.37	0.48	1.53
16	0.16	3.37	0.47	1.60
17	0.16	3.45	0.47	1.56
18	0.17	3.36	0.47	1.55
19	0.16	2.98	0.48	1.53
20	0.18	3.02	0.49	1.56
Average	0.17	3.25	0.48	1.53
Standard Deviation, s	0.006	0.13	0.008	0.028

TABLE X1.2 Fortum Oil and Gas Data Three Visbreaking Residues and One Straight Run Feedstock

Run	Residue (450°C)		Residue (435°C)		Residue (420°C)		Feed Stock	
	$FR_{5/1}$	*P*-Value	$FR_{5/1}$	*P*-Value	$FR_{5/1}$	*P*-Value	$FR_{5/1}$	*P*-Value
1	0.56	1.24	0.39	1.92	0.29	2.48	0.05	5.50
2	0.57	1.32	0.39	1.98	0.30	2.45	0.07	5.14
3	0.58	1.27	0.38	1.98	0.28	2.40	0.08	4.92
4	0.58	1.29	0.38	1.98	0.28	2.49	0.08	5.02
5	0.58	1.22	0.38	1.98	0.28	2.52	0.08	4.92
6	0.60	1.27	0.38	1.98	0.29	2.47	0.08	4.92
Average	0.578	1.268	0.383	1.97	0.287	2.468	0.073	5.07
Standard Deviation, s	0.013	0.035	0.005	0.024	0.008	0.041	0.012	0.228

TABLE X1.3 NCUT Data on Athabasca Bitumen

Run	*P*-Value	I_N	S_{BN}
1	3.66	28.1	102.1
2	3.61	26.9	96.4
3	3.80	26.3	99.3
4	3.79	26.1	98.2
5	3.89	26.9	103.6
6	3.67	25.2	91.8
7	3.85	25.3	96.7
8	3.86	24.7	94.7
9	3.64	25.9	93.5
10	3.81	25.3	95.6
Average	3.76	26.1	97.2
Standard Deviation, s	0.10	1.02	3.70

SUMMARY OF CHANGES

Subcommittee D02.14 has identified the location of selected changes to this standard since the last issue (D7112–05) that may impact the use of this standard.

(*1*) Added new Fig. 1, and renumbered the subsequent figures.