



Standard Test Method for Automated Heithaus Titrimetry¹

This standard is issued under the fixed designation D 6703; 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 describes a procedure for quantifying three Heithaus compatibility parameters that estimate the colloidal stability of asphalts and asphalt cross blends (**1,2**)², aged asphalts (**3**), and pyrolyzed heavy oil residua and asphalt (**4**) using automated Heithaus titrimetry as a stability diagnostic tool.

1.2 *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. Terminology

2.1 *Definitions of Terms Specific to This Standard:*

2.1.1 *asphalt* (**5**), *n*—a dark brown to black cementitious material, solid or semisolid in consistency, in which the predominating constituents are bitumens, which occur in nature as such or are obtained as residue by refining petroleum.

2.1.2 *asphalt cross-blend*, *n*—any mixture of two or more asphalts blended together to form a consistent material.

2.1.3 *asphaltene peptizability*, *n*—the tendency of asphaltenes to exist as a stable dispersion in a maltene solvent, measured by the Heithaus parameter p_a .

2.1.4 *asphaltenes*, *n*—the high molecular weight hydrocarbon fraction precipitated from asphalt by a designated paraffinic naphtha solvent at a specified solvent-asphalt ratio.

2.1.4.1 *Discussion*—The asphaltene fraction should be identified by the solvent and solvent-asphalt ratio used.

2.1.5 *asphalt state of peptization*, *n*—a measure of the ability of the combination of a maltene solvent and dispersed asphaltenes to form a stable dispersed system. Equivalent to compatibility of the system.

2.1.6 *bitumen*, *n*—a class of black or dark-colored (solid, semisolid, or viscous) cementitious substances, natural or manufactured, composed principally of high-molecular weight hydrocarbons, of which asphalts, tars, pitches, and asphaltites are typical.

2.1.7 *coke*, *n*—the solid product resulting from the destruc-

tive distillation of coal, petroleum residuum, or bitumen in an oven or closed chamber, or from imperfect combustion of these materials, consisting principally of carbon.

2.1.8 *colloidal suspension*, *n*—an intimate mixture of two substances, one of which, called the dispersed phase (or colloid), is uniformly distributed in a finely divided state through the second substance, called the dispersion medium (or dispersing medium).

2.1.9 *compatibility*, *n*—the state of peptization of an asphalt, which is measured quantitatively by the Heithaus parameter P .

2.1.10 *core asphalts*, *n*—the eight asphalts selected for intensive study in the Strategic Highway Research Program (SHRP).

2.1.11 *dispersed phase*, *n*—one phase of a dispersion consisting of particles or droplets of one substance distributed through a second phase.

2.1.12 *dispersing medium*, *n*—one phase of a dispersion that distributes particles or droplets of another substance, the disperse phase.

2.1.13 *flocculation*, *n*—the process of aggregation and coalescence into a flocculent mass.

2.1.14 *Heithaus compatibility parameters*, *n*—three parameters: asphaltene peptizability (p_a), maltene peptizing power (p_o), and asphalt state of peptization (P), measured using Heithaus titration methods.

2.1.15 *maltene peptizing power*, *n*—the ability of a maltene solvent to disperse asphaltenes, measured by the Heithaus parameter p_o .

2.1.16 *maltenes*, *n*—a red-brown to black heavy oil material derived from asphalt after precipitation with normal or branched alkanes (for example, *n*-pentane, *n*-hexane, *n*-heptane, isooctane, and so forth), filtration of asphaltenes, and distillation of alkane precipitating agent from the filtrate. Equivalent to deasphalted materials. Maltenes are the solvent moiety of an asphalt.

2.1.17 *oxidatively age-hardened asphalt*, *n*—an asphalt that has reacted with oxygen at elevated temperatures in an oven, usually under greater than atmospheric oxygen pressure. The reaction is run for a time sufficient to simulate asphalt aging in pavement.

2.1.18 *pyrolysis*, *n*—the breaking apart of complex molecules into simpler units by the use of heat, as in the pyrolysis of heavy oil to make gasoline.

2.1.19 *residuum*, *n*—a quantity or body of matter remaining

¹ This test method is under the jurisdiction of ASTM Committee D04 on Road and Paving Materials and is the direct responsibility of Subcommittee D04.47 on Miscellaneous Asphalt Tests.

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² The boldface numbers in parentheses refer to the list of references at the end of this standard.

after evaporation, combustion, or distillation.

3. Summary of Test Method

3.1 Three 30-mL reaction vials are tared. Three samples of an asphalt (or a heavy oil residuum), one weighing 0.400 g, a second weighing 0.600 g, and the third weighing 0.800 g, are transferred to the reaction vials, one sample into each vial. Toluene (2.000 mL) is added to each of the reaction vials to dissolve the asphalt (or heavy oil residuum). Thus, each reaction vial contains a solution of different concentration of asphalt (or heavy oil residuum) in toluene. Each of these solutions then is titrated with isooctane (2,2,4-trimethyl pentane) or some other titrant (6) at a constant titrant delivery rate. The titration is performed by installing the reaction vials separately in the apparatus illustrated in Fig. 1. Basically, this apparatus consists of intersecting sample circulation and titration loops.

3.2 Each reaction vial is housed in a 200-mL, water-jacketed reaction vessel (Fig. 1). Water-jacketing is required because careful temperature control of the system is essential. The reaction vessel is filled with enough water such that the reaction vial and temperature probe are immersed. Water flowing through the water jacket maintains the temperature of the water in the reaction vessel, which maintains the temperature of the solution in the reaction vial. The connection with the sample circulation loop is made by covering the reaction vial with a screw top TFE-fluorocarbon cover penetrated by three small bore TFE-fluorocarbon tubes (Fig. 2). A fourth hole in the cover accommodates a temperature probe. One of these tubes (1.6-mm (1/16-in. diameter)) leads to a short path length (0.1-mm) quartz cell housed in a ultraviolet- (UV) visible spectrophotometer. A second tube (1.6-mm diameter) leads to a high flow rate metering pump and then to the quartz cell. This system is the sample circulation loop. The third tube (1.6-mm diameter) connects the reaction vial to the titration loop and leads to a low flow rate metering pump and then to another water-jacketed reaction vessel filled with titrant (usually isooctane). This reaction vessel is covered with another TFE-fluorocarbon cover penetrated by one TFE-fluorocarbon tube. This TFE-fluorocarbon cover has the same dimensions as the one illustrated in Fig. 2, but does not require threading because the cover fits directly over the reaction vessel and no vial is screwed into it. Also it has only one hole. The second reaction vessel is filled with titrant. While the sample solution circulates through the sample circulation loop, the titrant is pumped into the sample reaction vial at a constant rate using the low flow rate metering pump. During this process, the output signal from the spectrophotometer is recorded using an integrator or some other data gathering device. The change in percent transmittance (%*T*) of detected radiation at 740 nm (7) passing through the quartz cell is plotted versus the time, *t*, during which the titrant is added to the sample reaction vial.

3.3 The spectrophotometer output signal detects the onset of turbidity of the sample solution. This is the flocculation onset point, corresponding to the beginning of the precipitation of asphaltenes from the sample solution. Fig. 3 illustrates a typical series of plots of %*T* versus *t* for the three test solutions. Values of %*T* increase with time until maximum values of %*T* are observed, after which values of %*T* decrease. The reason that

the curves in Fig. 3 exhibit maxima is that, at the beginning of each titration, %*T* increases due to dilution with titrant. At the flocculation onset point, the formation of asphaltene particles causes an immediate decrease in %*T* due to light scattering effects. The time required to reach the maximum in %*T* from the onset of titration of a sample is defined as the flocculation time, *t_f*. When the value of *t_f* for each sample is multiplied by the titrant flow rate, the titrant volume, *V_T*, required to cause the onset of flocculation for each sample is obtained.

3.4 The weight of each asphalt (or heavy oil residuum) sample, *W_a*, the volume of toluene used to dissolve each sample, *V_S* (2.00 mL in each case), and the volume of titrant required to cause the onset of flocculation, *V_T* are recorded for each sample solution. Values of these three quantities for each set of three test sample solutions are used to calculate the quantities *C* (referred to as the dilution concentration) and *FR* (referred to as the flocculation ratio). *C* is defined as $W_a/(V_S + V_T)$. *FR* is defined as $V_S/(V_S + V_T)$. Values of *C* are plotted versus *FR* for each of the three recorded sets of values of *W_a*, *V_S*, and *V_T* (Fig. 4). Customarily, the *C* values are along the *x*-axis, and the *FR* values are the *y*-axis. The three data points are connected by a line, and the line is extrapolated to both axes. The point at which the line intercepts the *x*-axis is defined as *C_{min}*. The point at which the line intercepts the *y*-axis is defined as *FR_{max}*. These two values are used to calculate the three Heithaus compatibility parameters, designated *p_a*, *p_o*, and *P*. The parameter *p_a*, the peptizability of asphaltenes, is defined as the quantity $(1 - FR_{max})$. The parameter *p_o*, the peptizing power of maltenes, is defined as the quantity $FR_{max} [(1/C_{min}) + 1]$. The parameter *P*, the overall compatibility of the system, is defined as $[p_o/(1 - p_a)]$, or $(1/C_{min} + 1)$.

4. Significance and Use

4.1 This test method is intended primarily as a laboratory diagnostic tool for estimating the colloidal stability of asphalt, asphalt cross blends, aged asphalt, pyrolyzed asphalt, and heavy oil residuum. Historically, asphalt and heavy oil residua have been modeled as colloidal suspensions (8,9) in which a polar, associated asphaltene moiety (the dispersed phase) is suspended in a maltene solvent moiety (the dispersing medium). The extent to which these two moieties remain in a given state of peptization is a measure of the compatibility of the suspension. Compatibility influences important physical properties of these materials, including rheological properties, for example, phase angle and viscosity (10,11). Compatibility also influences coke formation in refining processes (4). This test method and other similar test methods (7, 12-15), along with the classical Heithaus test (1,2), measures the overall compatibility of a colloidal system by determining a designated parameter referred to as the state of peptization, *P*. The value of *P* commonly varies between 2.5 and 10 for unmodified or neat asphalts. Materials calculated to have low values of *P* are designated as incompatible, where as materials calculated to have high *P* values are designated as compatible. Values of *P* may be calculated as a function of two other designated parameters that relate to the peptizability of the asphaltene moiety (the asphaltene peptizability parameter, *p_a*) and the solvent power of the maltene moiety (the maltene peptizing power parameter, *p_o*). Values of *p_a* and *p_o* are calculated as

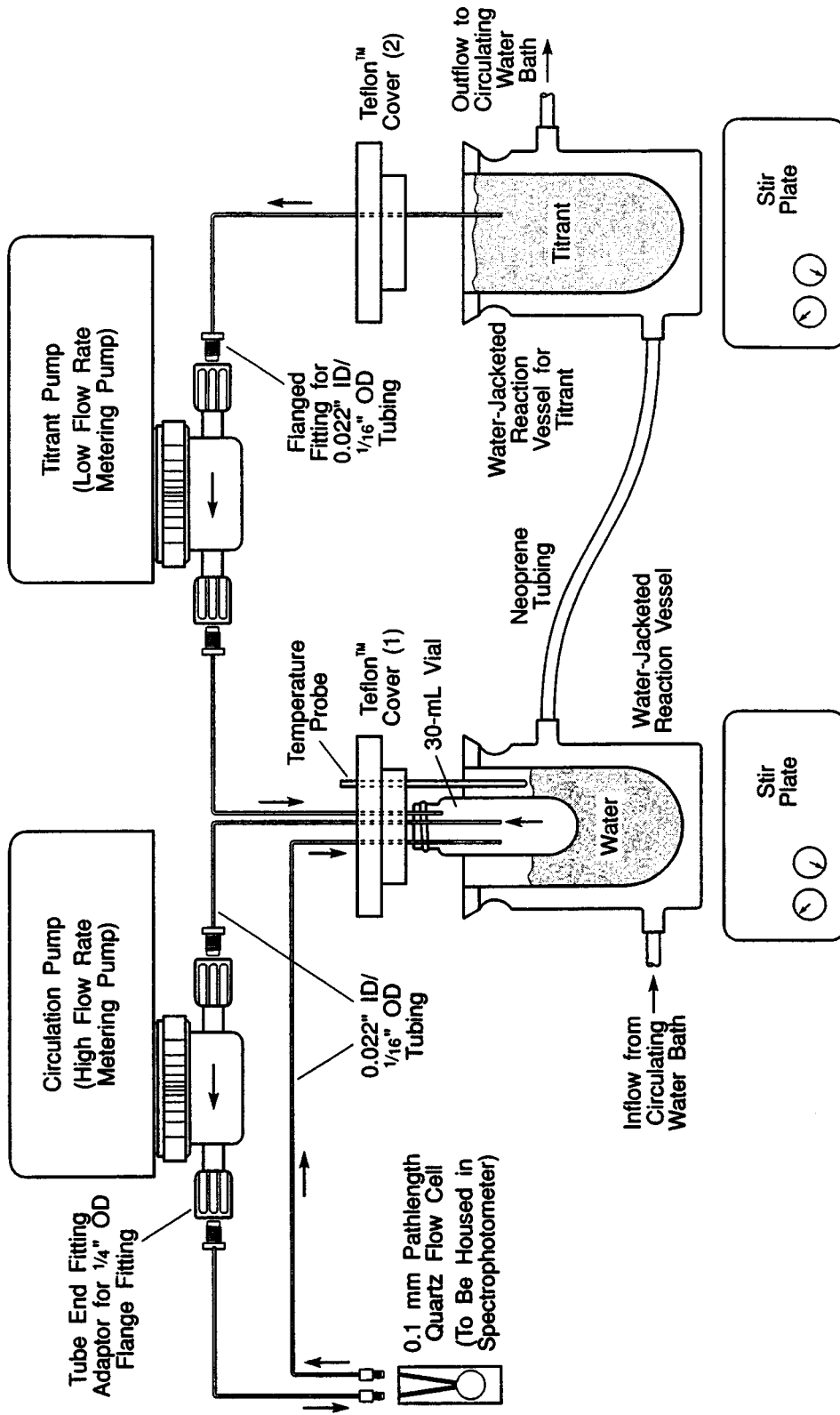


FIG. 1 Automated Titration Apparatus

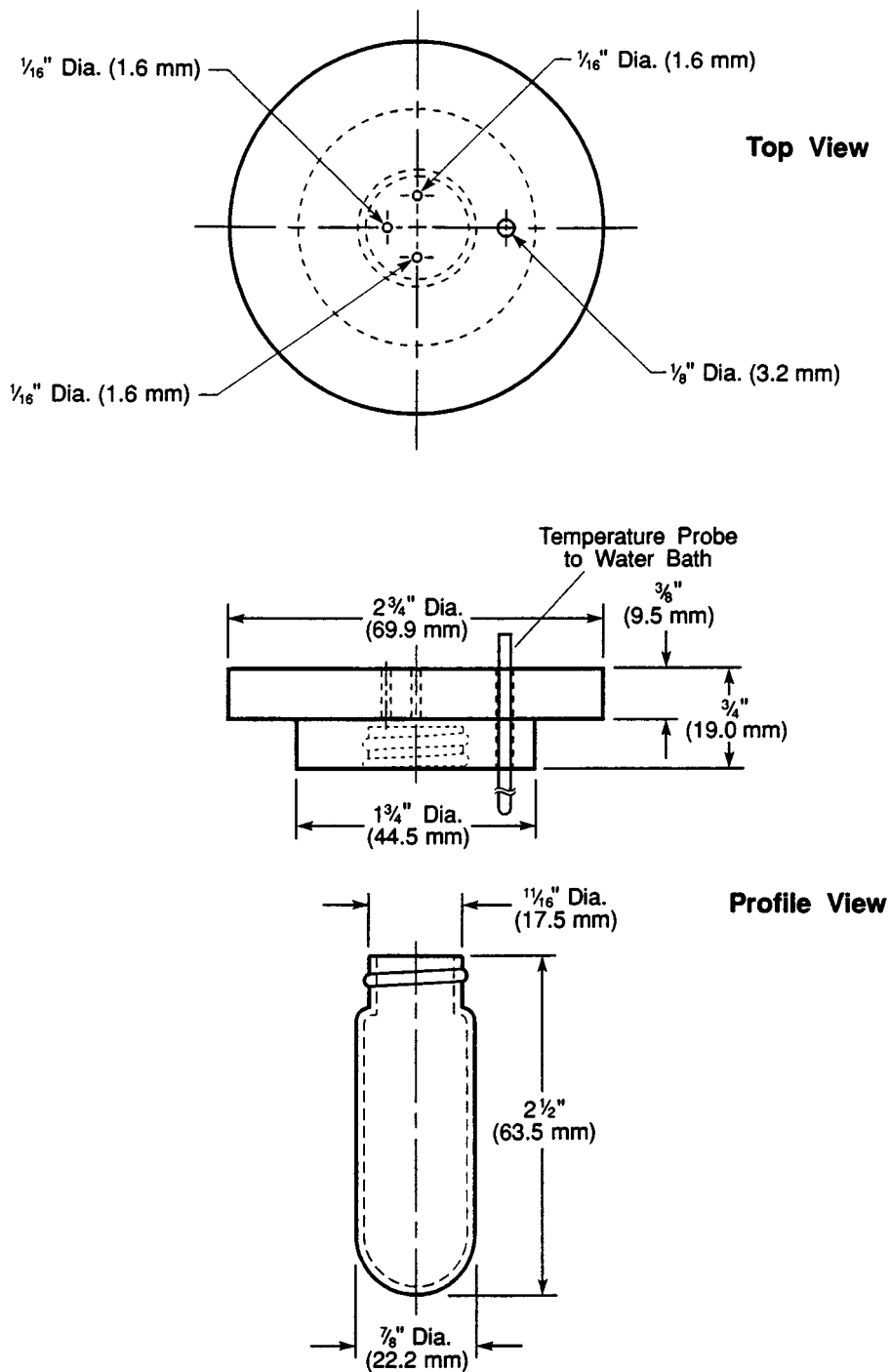


FIG. 2 Reaction Vial (30 mL) with TFE-fluorocarbon Cover and Temperature Probe

functions of the quantities C_{min} and FR_{max} , the values of which are obtained from three experimental variables, the weight of residuum or asphalt (W_a), the volume of solvent (V_S), and the volume of titrant added up to the flocculation point (V_T).

5. Apparatus

5.1 *UV-visible Spectrophotometer*, wavelength scanning range from 200 to 1000 nm, with adjustable aperture or attenuator.

5.2 *Digital Integrator*, or data acquisition system (computer). One-millisecond data sampling rate.

5.3 *Water-Jacketed Reaction Vessel*, 200-mL, two.

5.4 *TFE-fluorocarbon Covers*, two.

5.4.1 *TFE-fluorocarbon Cover No. 1*, (see Fig. 2), threaded to hold a 30-mL reaction vial. Dimensions: thickness, 2.0 mm (3/16 in.); diameter, 70 mm (2 3/4 in.), threaded to 30-mL reaction vial. Three holes, 1.5 mm (1/16 in.) in diameter, concentric to the cover's center, are arranged in a triangle, are tapped to set within the inside diameter of the vial when attached to the TFE-fluorocarbon cover, with a distance between holes roughly equal to 10 mm (3/8 in.). One additional hole, 3.0 mm

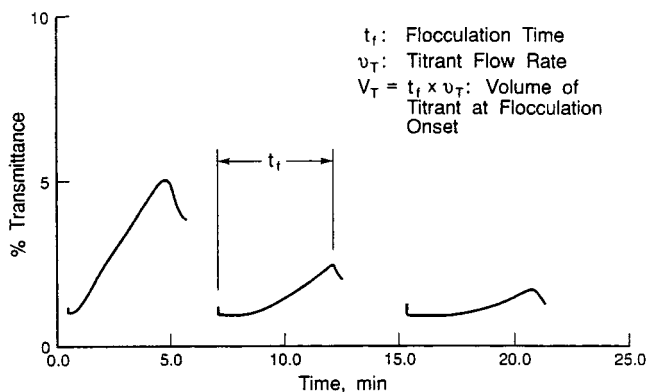


FIG. 3 Onset of Flocculation Peaks Measured at Three Successively Increasing Concentrations (Solvent: Toluene, Titrant: Isooctane)

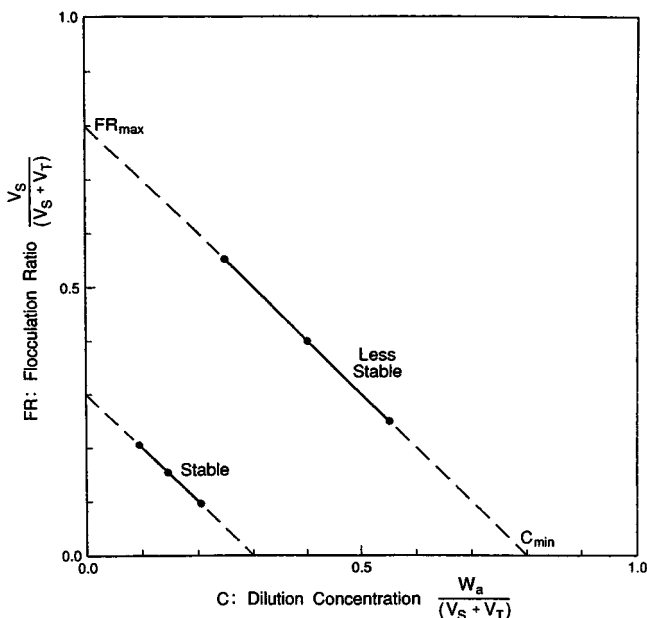


FIG. 4 Flocculation Ratio Versus Dilution Concentration for One Stable Asphalt and One Less Stable Asphalt

($\frac{1}{8}$ in.), is tapped off center, positioned just to the outside of where the reaction vial is positioned in the TFE-fluorocarbon cover. This hole allows the temperature probe to be inserted into the water-filled reaction vessel.

5.4.2 *TFE-fluorocarbon Cover No. 2*, as a lid for the second 200-mL, water-jacketed reaction vessel, containing titrant. Dimensions: thickness, 2.0 mm ($\frac{1}{16}$ in.); diameter, 70 mm ($2\frac{3}{4}$ in.). One hole 1.5 mm ($\frac{1}{16}$ in.) in diameter tapped through the cover's center. This cover is identical to the cover described in 5.4.1 except for the number of holes, and is not threaded.

5.5 *High Flow Rate Metering Pump*—Piston diameter, 3.0 mm ($\frac{1}{8}$ in.); piston displacement < 0.1 mL; flow rate range from 1.0 to 20.0 mL/min; flow rate consistency, ± 0.1 mL/min; and piston chamber resistant to damage from solvent contact.

5.6 *Low Flow Rate Metering Pump*—Piston diameter, 3.0 mm ($\frac{1}{8}$ in.); flow rate range from 0.100 to 1.000 mL/min; flow rate consistency, ± 0.001 mL/min; and piston chamber resistant to damage from solvent contact.

5.7 *Magnetic Stirring Plates*, two.

5.8 *Refrigerated Water Bath Circulator* (for greater temperature control)—Temperature control in this procedure is at

25°C (77°F). Temperature variation, $\pm 0.1^\circ\text{C}$ (0.2°F); temperature range from 0 to 100°C (32 to 212°F). Coupled to fit neoprene tubing, 13-mm ($\frac{1}{2}$ -in.) in inside diameter.

5.9 *Quartz Flow Cell*, 0.1-mm path length³ with tube end fittings. Fit to standard 10- by 10-mm base cuvette cell holder. Tapped to fit 0.56-mm (0.022-in.) inside diameter/1.59-mm ($\frac{1}{16}$ -in.) outside diameter TFE-fluorocarbon tubing.

5.10 *TFE-fluorocarbon Tubing*, 0.56-mm (0.022-in.) inside diameter/1.59-mm ($\frac{1}{16}$ -in.) outside diameter.

5.11 *Reaction Vials*, 30-mL, (3 for each sample) (provisional patent applied for by Western Research Institute).

5.12 *TFE-fluorocarbon-Coated Magnetic Stir Bars*, disk or cylinder-shaped, approximately 10 mm (0.04 in.) in diameter and 8.0 mm (0.03 in.) in height.

5.13 *Stopwatch*.

5.14 *Syringe*, 2.500 cm³, glass, gas-sealed, and resistant to solvents that it will be used to sample.

5.15 *TFE-fluorocarbon Tube Fittings*. Including standard 6.2-mm ($\frac{1}{4}$ -in.) flange fittings for 0.56-mm (0.022-in.) inside

³ Quartz flow cell, 0.10-mm path length, available from Starna Cells, Inc.

diameter/1.59-mm ($1/16$ -in.) outside diameter TFE-fluorocarbon tubing.

5.16 *Neoprene Tubing*, 13-mm ($1/2$ -in.) inside diameter.

5.17 *Tubing Clamps*, sized to fit 13-mm ($1/2$ -in.) inside diameter tubing.

5.18 *Probe Thermometer*, °C ($\pm 0.1^\circ\text{C}$). Probe contact length, >80-mm (>3-in.), probe contact diameter, <3.0-mm (< $1/8$ -in.).

5.19 *Graduated Cylinders*, two. Volumes: 1.000 ± 0.001 mL and 10.0 ± 0.1 mL.

5.20 *Argon Gas Supply*.

5.21 *Laboratory Jacks*—Laboratory jacks are used as stands for the metering pumps previously listed. The size requirements of these laboratory jacks will vary depending on the size to the metering pumps.

5.22 *Beakers*, two. Volume: 500 mL.

5.23 *Polypropylene Squirt Bottles*, two. Volume: 200 mL.

5.24 *TFE-fluorocarbon Lined Caps*, for closing reaction vials and storing solutions.

6. Reagents and Materials

6.1 *Purity of Reagents*—HPLC grade chemicals shall be used in all sample preparations and 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 available⁴. 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.

6.2 *isooctane* (2,2,4-trimethylpentane), HPLC grade.

6.3 *Toluene*, HPLC grade.

6.4 *Toluene*, reagent grade, for cleaning.

7. Assembly

7.1 *Installation Requirements*:

7.1.1 It is recommended that the following assembly be conducted in a fume hood (ventilation of toluene, isooctane or all other solvents required, or combination thereof). The fume hood should be of sufficient size to accommodate all pieces of the apparatus and supplies used to perform this test method.

7.1.2 The fume hood should be equipped with a pump or house vacuum line for the assembly of a vacuum trap, used during the procedural cleanup step (see 9.2.8).

7.2 *Assembly* (Fig. 1):

7.2.1 *Circulation Loop Assembly*—A sample (circulation loop) is assembled using a high flow rate metering pump plumbed between a short path length flow cell and a TFE-fluorocarbon cover (fitted to a 30-mL reaction vial/200-mL water-jacketed reaction vessel assembly) using 0.56-mm (0.022-in.) inside diameter/1.59-mm ($1/16$ -in.) outside diameter TFE-fluorocarbon tubing fitted with standard 6.2-mm ($1/4$ -in.)

flange fittings adaptable to 0.56-mm (0.022-in.) inside diameter/1.59-mm ($1/16$ -in.) outside diameter tubing.

7.2.1.1 Position one of the 200-mL, water-jacketed reaction vessels on one of the stir plates, next to the cuvette cell housing of the UV-visible spectrophotometer.

7.2.1.2 Position a 0.1-mm path length flow cell in the cell housing of the spectrophotometer and secure it into place.

7.2.1.3 Finally, position the high flow rate metering pump on a laboratory jack next to the stir plate. Attach a standard 6.2-mm ($1/4$ -in.) flange tube end fitting to one end of a 100-mm (4-in.) long piece of 0.56-mm (0.022-in.) inside diameter/1.59-mm ($1/16$ -in.) outside diameter TFE-fluorocarbon tubing and attach the flange fitting provided with the flow cell to the opposite end of this piece of tubing. Fasten the tubing between the inflow end of the flow cell and the outflow end of the high flow rate metering pump.

7.2.1.4 Attach the remaining flange tube end fitting (provided with the flow cell) to one end of a second 300-mm (12-in.) long piece of 0.56-mm (0.022-in.) inside diameter/1.59-mm ($1/16$ -in.) outside diameter TFE-fluorocarbon tubing, leaving the other tubing end free. Fasten the flange fitting end of this tubing to the outflow end of the flow cell.

7.2.1.5 Attach one standard 6.2-mm ($1/4$ -in.) flange tube end fitting to a third 200-mm (8-in.) long piece of 0.56-mm (0.022-in.) inside diameter/1.59-mm ($1/16$ -in.) outside diameter TFE-fluorocarbon tubing, leaving the other tubing end free. Fasten this fitting to the inflow end of the high flow rate metering pump. The two free ends of tubing (7.2.1.4 and 7.2.1.5) run to the 30-mL reaction vial, through the holes provided in the top of the TFE-fluorocarbon cover.

7.2.2 *Titration Loop Assembly*—A titrant dispenser (titrant loop) is assembled using a low flow rate metering pump plumbed between a second TFE-fluorocarbon cover/200-mL, water-jacketed reaction vessel assembly, and the first TFE-fluorocarbon cover with 30-mL reaction vial/200-mL, water-jacketed reaction vessel assembly (circulation loop) using 0.56-mm (0.022-in.) inside diameter/1.59-mm ($1/16$ -in.) outside diameter TFE-fluorocarbon tubing fitted with standard 6.2-mm ($1/4$ -in.) flange fittings for 0.56-mm (0.022-in.) inside diameter/1.59-mm ($1/16$ -in.) outside diameter TFE-fluorocarbon tubing.

7.2.2.1 Position the second 200-mL water-jacketed reaction vessel on the remaining stir plate, next to the first high flow rate metering/laboratory jack assembly.

7.2.2.2 Position the low flow rate metering pump on a second laboratory jack and set this assembly next to the second 200-mL water-jacketed reaction vessel/stir plate assembly.

7.2.2.3 Attach a 300-mm (12-in.) long piece of 0.56-mm (0.022-in.) inside diameter/1.59-mm ($1/16$ -in.) outside diameter TFE-fluorocarbon tubing fitted with one standard 6.2-mm ($1/4$ -in.) flange fitting to the inflow end of a low flow rate metering pump.

7.2.2.4 The free end of this tubing is placed through the hole provided in the second TFE-fluorocarbon cover/200-mL, water-jacketed reaction vessel assembly, and extends through the hole in the TFE-fluorocarbon cover to the bottom inside of the second 200-mL water-jacketed reaction vessel.

7.2.2.5 Attach a 200-mm (8-in.) long piece of 0.56-mm (0.022-in.) inside diameter/1.59-mm ($1/16$ -in.) outside diameter

⁴ *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.

TFE-fluorocarbon tubing fitted with a standard 6.2-mm (1/4-in.) flange fitting to the outflow end of the low flow rate metering pump. This free end of tubing runs to the 30-mL reaction vial.

7.2.3 *Refrigerated Water Bath Circulator Assembly* (see Fig. 1):

7.2.3.1 Plumb, using 13-mm (1/2-in.) inside diameter neoprene tubing and tubing clamps, between the water outflow nozzle of the first 200-mL water-jacketed reaction vessel and the inflow nozzle of the second 200-mL water-jacketed reaction vessel.

7.2.3.2 Plumb two additional pieces of 13-mm (1/2-in.) inside diameter per outside diameter neoprene tubing between the inflow and outflow couplers of the refrigerated water bath circulator and the two 200-mL water-jacketed reaction vessel's nozzles.

8. Preparation and Calibration

8.1 *UV-Visible Spectrophotometer:*

8.1.1 For specific operation of the UV-visible spectrophotometer see the manufacturer's instructions and specifications.

8.1.2 Set the UV-visible spectrophotometer to the percent transmittance detection mode.

8.1.3 Set the wavelength of the spectrophotometer to 740 nm.

8.1.4 Calibrate the spectrophotometer in accordance with the manufacturer's instruction and specifications. Calibration is to be performed using toluene as the 100 % transmittance spectral background.

8.2 *Refrigerated Water Bath Circulator and Water-Jacketed Reaction Vessel Assembly:*

8.2.1 Set the refrigerated circulating water bath temperature to $25 \pm 0.1^\circ\text{C}$ ($77 \pm 0.1^\circ\text{F}$), in accordance with the manufacturer's instruction and specifications.

8.2.2 Fill the first 200-mL water-jacketed reaction vessel chamber roughly one-half full with water. Place a small TFE-fluorocarbon stir bar in the bottom of the reaction vessel chamber. Adjust the water level in the chamber to accommodate the 30-mL reaction vial. Proceed to fill the reaction vessel chamber to approximately 13 mm (1/2 in.) from the bottom of the TFE-fluorocarbon cover, with the reaction vial present.

8.2.3 Fill the second 200-mL water-jacketed reaction vessel chamber roughly 90 % full of isooctane (2,2,4-trimethylpentane). Place a small clean stir bar into the reaction vessel chamber.

8.3 *Pumps and Tubing Assemblies:*

8.3.1 Adjust (using a tubing cutter) the lengths of the tubing of the high flow rate metering pump/tubing/flow cell assembly to achieve an approximate minimum total solution-circulation loop assembly volume of less than 0.25 mL.

8.3.2 Calibrate (see the manufacturer's instruction and specifications) the high flow rate metering pump to flow at 10 mL/min. Time the flow rate with a stopwatch and 10.0-mL graduated cylinder. Report the average and standard deviation flow rate values for three measurements.

8.3.3 Calibrate (see the manufacturer's instruction and specifications) the low flow rate metering pump to flow 0.500 mL/min. Time the flow rate with a stopwatch and 1.000-mL graduated cylinder. Report the average and standard deviation flow rate values for three measurements.

8.4 *Integrator/Data Acquisition System*—Specific setup and operation of integrator/data acquisition system should be performed using the manufacturer's instructions and specifications.

9. Procedure

9.1 *Preparation of Samples:*

9.1.1 For a single material analysis, label and tare three 30-mL reaction vials fitted with TFE-fluorocarbon lined caps. Weigh into each of the three vials, 0.400 g, 0.600 g, and 0.800 g, respectively, of asphalt or heavy residua to an accuracy of ± 0.001 g. Record these sample weights.

9.1.2 Flood each sample vial with argon gas. Seal the reaction vials with TFE-fluorocarbon lined caps (Note 1).

NOTE 1—Dry samples in TFE-fluorocarbon lined capped vials sealed under a blanket of argon gas may be stored for several weeks before samples are tested, if stored in a cool dark place.

9.1.3 A minimum of 4 h prior to testing, add 2.000 ± 0.001 cm³ of HPLC-grade toluene to each of three samples in a set using a 2.500-cm³ syringe and allow the samples to dissolve completely (Note 2).

NOTE 2—The four-hour dissolution period is a minimum time requirement for complete dissolution of most concentrated samples, when dissolving at room temperature. Twelve to twenty-four hour periods of dissolution may be recommended for non-time-restricted applications.

9.2 *Sample Analysis:*

9.2.1 Place a small TFE-fluorocarbon coated magnetic stir bar gently into the 30-mL reaction vial containing the sample solution, then screw the 30-mL reaction vial into the "4-hole" TFE-fluorocarbon cover. Place the 30-mL reaction vial with sample/TFE-fluorocarbon cover assembly into the solution circulator's 200-mL water-jacketed reaction vessel, and adjust the stir plate stirring rate. Stir the sample solution at a relatively high stirring rate. Adjust the flow rate to avoid splashing and high vortexing in the solution.

9.2.2 Clear the high flow rate metering pump of solvent that may have remained during calibration or the cleaning step (see 9.2.8). Run the two free ends of the TFE-fluorocarbon tubing (extending from the high flow metering pump and flow cell), through the first and second tapped holes in the TFE-fluorocarbon cover, down toward the bottom of the 30-mL reaction vial into the solution. Engage the high flow rate metering pump to begin circulating the sample. Adjust the two tube end heights in the solution to eliminate air bubbles in the tubing line and pump. As the sample solution begins to circulate through the flow cell, the percent transmittance (%T) reading of the spectrophotometer decreases and eventually stabilizes. The stabilized %T reading of the spectrophotometer corresponds to the percent of light transmitted through the sample solution prior to titrant added.

9.2.3 Place the free end of the TFE-fluorocarbon tubing (extending from the low flow rate metering pump), through the third hole in the TFE-fluorocarbon cover, down into the 30-mL reaction vial. The tubing should be positioned only 12 mm (1/2 in.) below the neck of the 30-mL reaction vial, well above the surface of the solution.

9.2.4 Place a temperature probe thermometer through the remaining fourth larger hole in the TFE-fluorocarbon cover.

The probe is used to monitor the temperature of the water bath so that it is regulated to be maintained at $25 \pm 0.1^\circ\text{C}$ ($77 \pm 0.1^\circ\text{F}$).

9.2.5 Engage the low flow rate metering pump and the integrator/data acquisition system simultaneously to start the analysis.

9.2.6 Allow the titration to proceed until the maximum inflection point in %T is observed. If an integrator is used to plot the spectrophotometer output signal, a retention time value is printed out above the plotted peak by the integrator. The retention time printout also signifies the onset of flocculation.

9.2.7 Record the temperature of the solution and the flocculation time (t_f) at the flocculation onset.

9.2.8 At the completion of a test, disengage the pump and withdraw the two ends of tubing from the solution. Reengage the pump and flush the remaining solution into a large solvent waste beaker. Use the squirt bottle, filled with toluene, to rinse the ends of the tubing. Flush the pump/tubing/flow cell assembly with several millilitres of fresh toluene by placing the drawing tubing end into a container of toluene and the solvent exiting tubing end into a 50-mL waste beaker. When the assembly is flushed and the solvent is clear, remove the one end of the tubing from the toluene and pump the remaining solvent out of the line. Use the vacuum to draw any remaining solvent from the pump/tubing/flow cell assembly.

9.2.9 Repeat the steps given in 9.2 for the remaining solutions.

10. Calculation

10.1 Measured Variables:

10.1.1 Sample weight, W_a (g).

10.1.2 Volume of solvent (toluene), V_S (mL).

10.1.3 Detection wavelength, λ_D (nm).

10.1.4 Titrant flow rate, v_T (mL/min).

10.1.5 Flocculation time at peak apex (flocculation onset), t_f (min).

10.1.6 Solution temperature at flocculation onset, T_{sln} ($^\circ\text{C}$).

10.2 Calculate the volume of titrant (V_T (mL)) required to initiate flocculation by multiplying the time required to deliver titrant (reported as the peak flocculation time t_f , (min) and the titrant flow rate, v_T (mL/min) as shown in Eq 1.

$$V_T = t_f v_T \quad (1)$$

10.3 Calculate the flocculation ratio (FR) and the dilution ratio concentration (C) for each of the three samples using the values of V_T , V_S , and W_a and Eq 2 and 3.

$$FR = \frac{V_S}{V_S + V_T} \quad (2)$$

$$C = \frac{W_a}{V_S + V_T} \quad (3)$$

10.4 Plot the values of FR versus values of C for each of the three samples (Fig. 4). Draw a line through the three points. Extrapolate the line to the x - and y -axes to determine the dilution ratio concentration minimum (C_{min}) and the flocculation ratio maximum (FR_{max}). The value of C_{min} is the point at which the line intercepts the x -axis. The y intercept is FR_{max} .

10.5 Using values of FR_{max} and C_{min} , calculate Heithaus parameters p_a , the peptizability of asphaltenes, p_o , solvent power of maltenes, and P , state of peptization for the sample set using Eq 4-6 respectively.

$$p_a = 1 - FR_{max} \quad (4)$$

$$p_o = FR_{max} \left[\left(\frac{1}{C_{min}} \right) + 1 \right] \quad (5)$$

$$P = \frac{p_o}{1 - p_a} \quad (6)$$

11. Report

11.1 Report the calculated values of p_a , p_o , and P for each material tested. For duplicate samples tested, report the average values of p_a , p_o , and P .

11.2 Report the average temperature of the solution of flocculation onset calculated from temperatures measured for all titrations in a set vessel to calculate Heithaus parameters.

12. Precision and Bias

12.1 *Precision*⁵—The standard deviation range for this test method has been determined using automated Heithaus Titrimetry, as a diagnostic tool, to estimate the colloidal stability of asphalts. The eight SHRP core asphalts were evaluated, where the repeatability standard deviation ranges from 0.002 to 0.866, depending upon the core asphalt being evaluated (16). The reproducibility of this test method is being determined and will be available on or before June 2006.

12.2 *Bias*—Since there is no accepted reference material suitable for determining the bias of the procedure in this test method, no statement on bias is being made⁶.

13. Keywords

13.1 asphalt; bitumen; coke; colloidal stability; compatibility; heavy oil residua

⁵ A copy of the research report used to develop the precision statement is available from ASTM Headquarters. Request RR: D04-1019.

⁶ The development of an automated Heithaus procedure was undertaken by the Western Research Institute, under FHWA contract, to bring precision to an acceptable level.

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