Designation: ~~D6703 – 14~~ D6703 – 19

Standard Test Method for Automated Heithaus Titrimetry[1]

This standard is issued under the fixed designation D6703; 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 quantify the colloidal stability of asphalts and asphalt cross blends and aged asphalts.

1.2 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 The text of this standard references notes and footnotes which provide explanatory material. These notes and footnotes (excluding those in tables and figures) shall not be considered as requirements of the standard.

1.4 *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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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]

D8 Terminology Relating to Materials for Roads and Pavements

D3279 Test Method for *n*-Heptane Insolubles

D3666 Specification for Minimum Requirements for Agencies Testing and Inspecting Road and Paving Materials

D4124 Test Method for Separation of Asphalt into Four Fractions

~~D5546~~D8055 ~~Test Method for Solubility of Asphalt Binders in Toluene by Centrifuge~~Guide for Selecting an Appropriate Electronic Thermometer for Replacing Mercury Thermometers in D04 Road and Paving Standards ~~(Withdrawn 2017)~~

E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis

E563 Practice for Preparation and Use of an Ice-Point Bath as a Reference Temperature

E644 Test Methods for Testing Industrial Resistance Thermometers

3. Terminology

3.1 Refer to Terminology D8 for definitions of terms relating to materials for roads and pavements.

3.2 *Definitions of Terms Specific to This Standard:*

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

3.2.2 *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.

3.2.3 *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).

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

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[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] 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.

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

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

3.2.7 *flocculation, n*—the process of aggregation and coalescence into a flocculent mass. See Test Method D3279.

3.2.8 *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.

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

4. Summary of Test Method

4.1 Three ~~40 mL~~ 40-mL reaction vials ~~are~~ shall be tared (Fig. 1). Three samples of asphalt of weights 0.400 g, 0.600 g, and 0.800 g ~~are~~ shall be transferred to each of three reaction vials. Toluene (3.000 mL) ~~is~~ shall be added to each reaction vial to dissolve the asphalt constituting three solutions which differ by concentration. Each solution is titrated with isooctane (2,2,4-trimethyl pentane) to promote onset of flocculation of the solution.

4.2 Titrations are performed by placing reaction vials separately in the apparatus illustrated in Fig. 2. Each reaction vial is separately placed into a ~~250 mL~~ 250-mL water-jacketed reaction vessel. A sample circulation loop is made by pumping the solution through a short path length quartz flow cell housed in an ultraviolet-visible spectrophotometer then back to the reaction vial with high flow rate metering pump. A titration loop is made by pumping titrant into the sample reaction vial at a constant flow rate using a low flow rate metering pump, thus a second reaction vessel containing titrant is placed into a second ~~250 mL~~ 250-mL

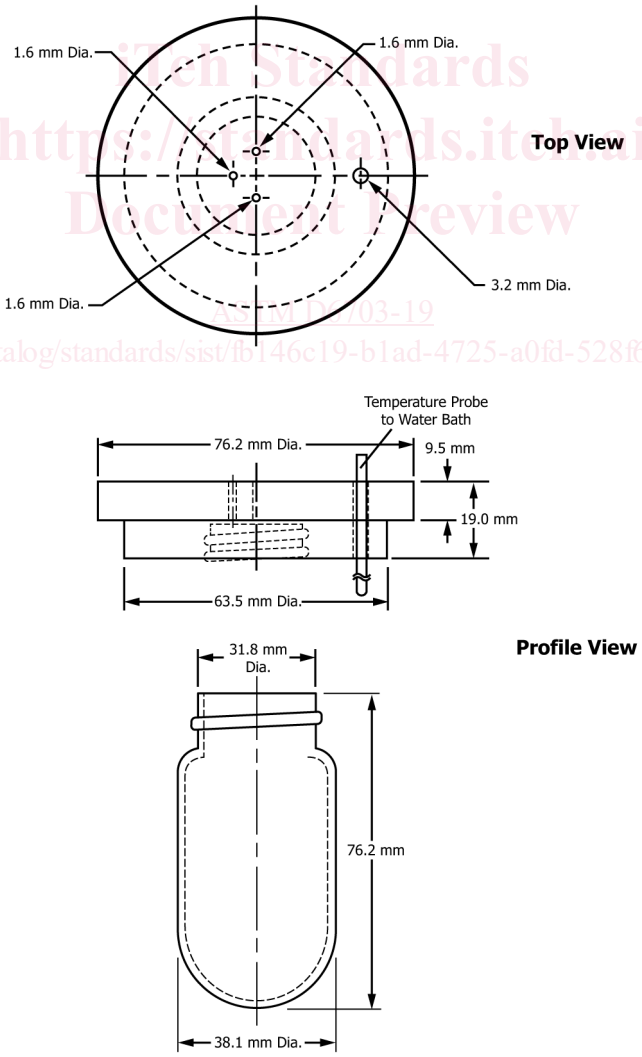

FIG. 1 Reaction Vial (40 mL) with TFE-fluorocarbon Cover and Temperature Probe

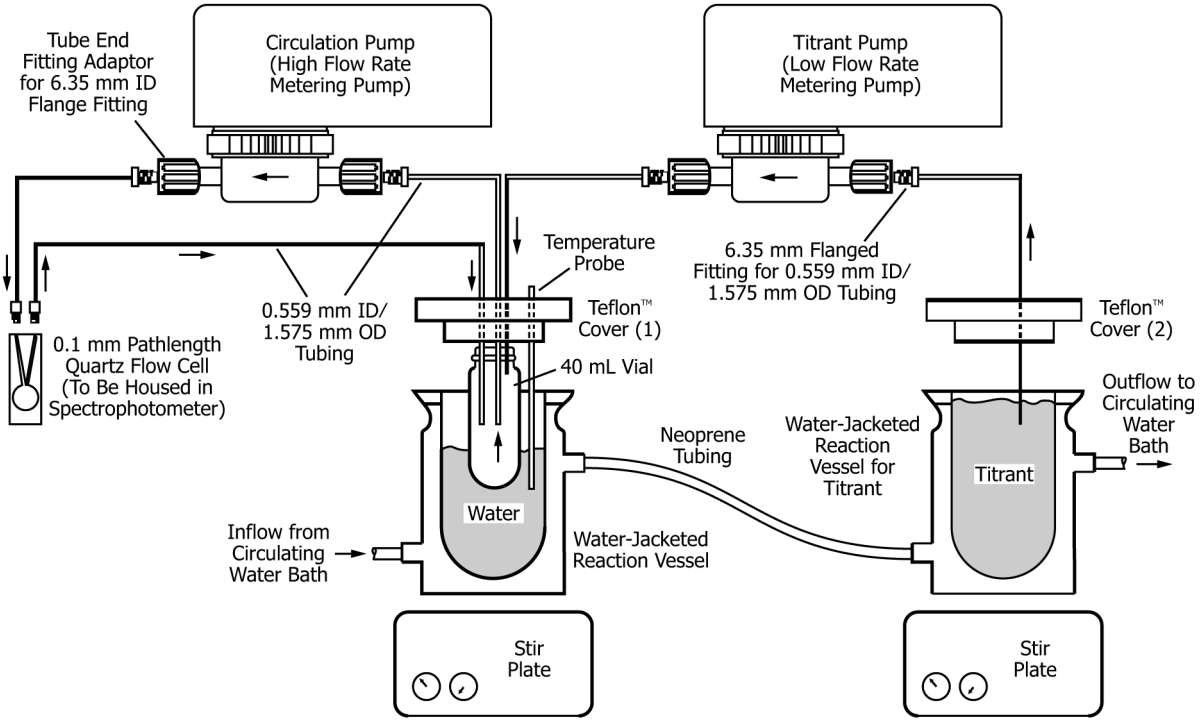

FIG. 2 Automated Titration Apparatus

water-jacketed reaction vessel. During a titration the output signal from a spectrophotometer is recorded using a data acquisition system (computer) to record the change in percent transmittance *%T* of detected radiation at 740 nm plotted as a function of time *t* (Fig. 3), as the titrated solution passes through a quartz flow cell.

4.3 The spectrophotometer output signal measures turbidity of the sample solution as a titration experiment proceeds to a flocculation onset point, corresponding to the onset of flocculating asphaltene phase separating from the solution. Fig. 3 illustrates a plot of *%T* versus *t* for three test solutions. Values of *%T* ~~are observed to~~ increase with time up to the flocculation onset point, after which values of *%T* ~~are observed to~~ decrease with time. The time required to reach flocculation onset t_f multiplied by the titrant flow rate gives the titrant flocculation volume V_T.

4.4 The measured weight of each asphalt sample, W_a, the volume of toluene initially used to dissolve each sample, V_S, and the volume of titrant at onset of flocculation, V_T, ~~represent~~ shall be used as the input data required to calculate compatibility parameters.

5. Significance and Use

5.1 This test method is intended ~~primarily~~ as a laboratory diagnostic tool for estimating the colloidal stability of bitumen asphalt, asphalt cross blends, aged asphalt, and heavy oil residuum. Historically, bituminous asphalt and heavy oil residua have been modeled as colloidal suspensions in which a polar associated asphaltene moiety (the dispersed phase) is suspended in a maltene

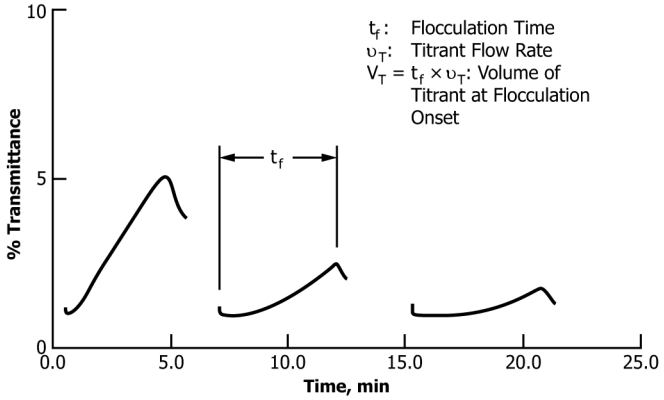

FIG. 3 Onset of Flocculation Peaks Measured at Three Successively Increasing Concentrations (Solvent: Toluene, Titrant: Isooctane)

solvent moiety (the dispersing medium) (refer to Test Methods D3279~~,~~ ~~D4124, and~~and D4124 ~~D5546~~for further definition of asphalt fraction materials). The extent to which these two moieties remain in state of peptization is a measure of the compatibility (colloidal stability) of the suspension. Compatibility ~~influences~~ may influence the physical properties of these materials, including rheological properties, for example, phase angle and viscosity. This test method and other similar test methods, along with the classical Heithaus test, ~~measures~~ may be recommended as a measure of the overall compatibility of a colloidal system by determining a parameter referred to as the state of peptization, *P*. The value of *P* commonly varies between 2.5 to 10 for unmodified or neat asphalts. Materials calculated to have low values of *P* are designated incompatible. Materials calculated to have high *P* values are designated compatible. Values in *P* are calculated as a function of two 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 functions of the quantities C_{min} and FR_{max}. Values of C_{min} and FR_{max} are determined from experimental variables, the weight of asphalt (W_a), the volume of solvent (V_S) to dissolve the weight of asphalt, and the volume of titrant (V_T) added to initiate flocculation.

6. Apparatus

6.1 ~~*UV-visible*~~*UV-Visible Spectrophotometer,* shall have a wavelength scanning range from 200 to 1000 nm, with adjustable aperture or attenuator.

6.2 *Digital Acquisition System (computer).*

6.3 *Water-Jacketed Reaction Vessel,* ~~250-mL,~~ shall be of volume: 250 mL, two.

6.4 ~~*TFE-fluorocarbon*~~*TFE-Fluorocarbon Covers,* two.

6.4.1 ~~*TFE-fluorocarbon*~~*TFE-Fluorocarbon Cover No. 1,* (see Fig. 1), shall be threaded to hold a ~~40 mL~~ 40-mL reaction vial. Three holes, ~~1.5 mm~~ 1.5-mm diameter, concentric to the cover's center ~~are~~ shall be tapped to set within the inside diameter of the vial when attached to the TFE-fluorocarbon cover. One additional hole, 3.0 mm, ~~is~~ shall be tapped off center, positioned just to the outside of where the reaction vial is positioned in the TFE-fluorocarbon cover. This hole ~~allows the~~ shall allow for a temperature probe (refer to Guide D8055, Practice E563, and Test Methods E644) to be inserted into the water-filled reaction vessel.

6.4.2 ~~*TFE-fluorocarbon*~~*TFE-Fluorocarbon Cover No. 2,* may be used as a lid for the second ~~200-mL,~~200-mL water-jacketed reaction vessel, containing titrant. Dimensions: thickness, 2.0 mm; diameter, 70 mm. One hole 1.5 mm in diameter tapped through the cover's center. This cover ~~is~~ shall be identical to the cover described in 6.4.1 except for the number of holes, and ~~is not threaded.~~should be threaded to hold a second 40-mL reaction vial as a titration reservoir.

6.5 *High Flow Rate Metering* ~~*Pump—*~~*Pump,* ~~Flow~~ shall have a flow rate range from 0.5 to 10.0 mL/min; flow rate consistency, ~~± 0.1~~ ±0.1 mL/min; and piston chamber resistant to damage from solvent contact.

6.6 *Low Flow Rate Metering* ~~*Pump—*~~*Pump,* ~~Flow~~ shall have a flow rate range from 0.100 to 1.000 mL/min; flow rate consistency, ±0.002 mL/min; and piston chamber resistant to damage from solvent contact.

6.7 *Magnetic Stirring Plates,* two.

6.8 *Refrigerated Water Bath* ~~*Circulator—*~~*Circulator,* ~~Temperature variation, ±0.1°C; temperature range from 0 to 100°C.~~shall have a temperature variation of ±0.1 °C and temperature range from 0 °C to 100 °C.

6.9 *Quartz Flow Cell,* ~~0.20 mm~~ shall have a 0.20-mm path length[3] with ~~6.35 mm~~ 6.35-mm flanged fittings.

6.10 ~~*TFE-fluorocarbon*~~*TFE-Fluorocarbon Tubing,* ~~0.559 mm inside diameter/1.575 mm~~ shall have a 0.559-mm inside diameter/1.575-mm outside diameter.

6.11 *Reaction Vials,* ~~40 mL~~ shall be of a 40-mL volume capacity.

6.12 *"4-hole"* ~~*TFE-fluorocarbon cover*~~*TFE-Fluorocarbon Cover and "1-hole"* ~~*TFE-fluorocarbon cover.*~~*TFE-Fluorocarbon Cover.*

6.13 *TFE-fluorocarbon-Coated Magnetic Stir Bars.*

6.14 *Stopwatch.*

6.15 *Syringe,* shall be 5.000 ~~cc,~~mL, glass, gas-sealed, and resistant to solvents ~~that it will be used to sample.~~ toluene and n-heptane.

6.16 ~~*TFE-fluorocarbon*~~*TFE-Fluorocarbon Tube Fittings (4),* ~~including standard 6.35 mm~~ which shall include standard 6.35-mm flanged fittings for ~~0.559 mm inside diameter/1.575 mm~~ 0.559-mm inside diameter/1.575-mm outside diameter TFE-fluorocarbon tubing.

~~[3] The last approved version of this historical standard is referenced on www.astm.org.~~

[3] The sole source of supply of the apparatus known to the committee at this time is Starna Cells, Inc. 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.

6.17 *Neoprene Tubing,* shall be 13 mm inside diameter.

6.18 *Tubing Clamps,* shall be sized to fit ~~13 mm~~ 13-mm inside diameter tubing.

6.19 ~~*Digital Probe*~~ *Thermometer,* ~~°C (calibrated to ±0.2°C). Probe length, >80-mm, probe diameter, 3.0 mm.~~shall be a platinum resistance thermometer (PRT) readable to the nearest 0.1 °C, with a Pt 100 Class AA tolerance rating with probe length >80 mm, and probe diameter 3.0 mm. Standardize the PRT system (probe and readout device) in accordance with Test Methods E644. Corrections shall be applied to ensure accurate measurements within 0.1 °C (shall be calibrated to ±0.1 °C, and shall conform to Guide D8055, Practice E563, and Test Methods E644).

6.20 *Graduated Cylinders,* two. ~~Volumes:~~ Shall be of volumes: 1.000 ± 0.001 mL and 10.0 ± 0.1 mL.

6.21 *Argon Gas Supply.*

6.22 *Laboratory Jacks*—Laboratory jacks may be used as stands for metering pumps.

6.23 *Beakers,* two. ~~Volume:~~ Shall be of volume: 500 mL.

6.24 *Polypropylene Rinse Bottles,* two. ~~Volume:~~ Shall be of volume: 200 mL.

6.25 ~~*TFE-fluorocarbon*~~*TFE-Fluorocarbon Lined Caps,* ~~for 40 mL~~shall be 40-mL reaction vials.

7. Reagents

7.1 *Purity of Reagents*—~~HPLC grade~~ HPLC-grade chemicals ~~shall~~should 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 available.[4] 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.

7.2 *Isooctane* (2,2,4-trimethylpentane), HPLC grade.

7.3 *Toluene,* HPLC grade.

7.4 *Toluene,* reagent grade.

8. Assembly

8.1 *Installation Requirements:*

8.1.1 ~~It is recommended that the~~ The following assembly should be conducted in a fume hood. The fume hood should be of sufficient size to accommodate all pieces of the apparatus and supplies needed to perform the test method.

8.1.2 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 10.2.8).

8.2 *Assembly* (Fig. 2):

8.2.1 *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 ~~40 mL reaction vial/200 mL~~ 40-mL reaction vial/200-mL water-jacketed reaction vessel assembly) using ~~0.559 mm~~ 0.559-mm inside diameter/1.575-mm outside diameter TFE-fluorocarbon tubing fitted with standard ~~6.2 mm~~ 6.35-mm flange fittings adaptable to ~~0.559 mm inside diameter/1.575 mm~~ 0.559-mm inside diameter/1.575-mm outside diameter tubing.

8.2.1.1 ~~Position one~~ One of the ~~200-mL,~~200-mL water-jacketed reaction vessels should be positioned on one of the stir plates, next to the cuvette cell housing of the UV-visible spectrophotometer.

8.2.1.2 ~~Position a~~ A 0.1-mm path length flow cell should be positioned in the cell housing of the spectrophotometer and ~~secure it~~ secured into place.

8.2.1.3 ~~Position the~~ The high flow rate metering pump should be positioned on a laboratory jack next to the stir plate. Attach a ~~6.35 mm~~ 6.35-mm flanged fitting to one end of a ~~100 mm~~ 100-mm long piece of ~~0.559 mm inside diameter/1.575 mm~~ 0.559-mm inside diameter/1.575-mm outside diameter TFE-fluorocarbon tubing and attach the flanged 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.

8.2.1.4 ~~Attach a~~ A second flanged fitting provided with the flow cell is attached to one end of a second ~~300 mm~~ 300-mm long piece of ~~0.559 mm inside diameter/1.575 mm~~ 0.559-mm inside diameter/1.575-mm outside diameter TFE-fluorocarbon tubing, leaving the other tubing end free. ~~Fasten the~~ The flanged fitting end of this tubing is fastened to the outflow end of the flow cell.

8.2.1.5 ~~Attach a 6.35 mm~~ A 6.35-mm flanged fitting is attached to a third ~~200 mm~~ 200-mm long piece of ~~0.559 mm inside diameter/1.575 mm~~ 0.559-mm inside diameter/1.575-mm outside diameter TFE-fluorocarbon tubing, leaving the other tubing end

[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 ~~*Annual*~~*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.

free. Fasten this fitting to the inflow end of the high flow rate metering pump. The two free ends of tubing (8.2.1.4 and 8.2.1.5) ~~will~~ lead to the ~~40 mL~~ 40-mL reaction vial, positioned through the holes provided in the top of the "4-hole" TFE-fluorocarbon cover.

8.2.2 *Titrant Loop Assembly*—A titrant dispenser (titrant loop) is assembled using a low flow rate metering pump plumbed between the reaction vial and titrant vial using ~~0.559 mm inside diameter/1.575 mm~~ 0.559-mm inside diameter/1.575-mm outside diameter flanged fitting.

8.2.2.1 ~~Position a 200 mL~~ A 200-mL water-jacketed reaction vessel should be positioned on a second stir plate, next to the high flow rate metering pump/laboratory jack assembly.

8.2.2.2 ~~Position the~~ The low flow rate metering pump should be positioned on a second laboratory jack next to the ~~200 mL~~ 200-mL water-jacketed reaction vessel/stir plate assembly.

8.2.2.3 ~~Attach a 300 mm~~ A 300-mm piece of ~~0.559 mm inside diameter/1.575 mm~~ 0.559-mm inside diameter/1.575-mm outside diameter TFE-fluorocarbon tubing fitted with one ~~6.35 mm~~ 6.35-mm flanged fitting is attached to the inflow end of a low flow rate metering pump.

8.2.2.4 The free end of the tubing is placed through the hole provided in the second TFE-fluorocarbon cover into the ~~200 mL~~ 200-mL water-jacketed reaction vessel.

8.2.2.5 ~~Attach a 200 mm~~ A 200-mm piece of ~~0.559 mm inside diameter/1.575 mm~~ 0.559-mm inside diameter/1.575-mm outside diameter TFE-fluorocarbon tubing fitted with a standard ~~6.35 mm flange fitting~~ 6.35-mm flanged fitting is attached to the outflow end of the low flow rate metering pump. The free end of tubing runs to the ~~30 mL~~ 30-mL reaction vial.

8.2.3 *Refrigerated Water Bath Circulator Assembly:*

8.2.3.1 ~~Using 13 mm~~ A 13-mm inside diameter neoprene tubing and tubing ~~clamps, plumb~~ clamps is plumbed between the water outflow nozzle of the first ~~200 mL~~ 200-mL water-jacketed reaction vessel and the inflow nozzle of the second ~~200 mL~~ 200-mL water-jacketed reaction vessel.

8.2.3.2 ~~Plumb two~~ Two additional pieces of ~~13 mm~~ 13-mm inside diameter neoprene tubing are plumbed between the inflow and outflow couplers of the refrigerated water bath circulator and the two ~~200 mL~~ 200-mL water-jacketed reaction vessel's nozzles.

9. Preparation and Calibration

9.1 *UV-Visible Spectrophotometer:*

9.1.1 ~~See the~~ The manufacturer's instructions and specifications should be consulted for operation of the UV-visible spectrophotometer.

9.1.2 ~~Set the~~ The UV-visible spectrophotometer ~~to~~ shall be operated in the percent transmittance detection mode.

9.1.3 ~~Set the wavelength of the spectrophotometer to 740 nm~~ The spectrophotometer wavelength shall be set to 740 nm (see Note 1).

NOTE 1—A wavelength of 740 nm has been selected as the detection wavelength for the present test method. At this wavelength the light source scatters light when transmitted through a turbid solution of flocculating particles, but will otherwise not promote absorption of light by molecular species (asphaltenes) present in a test sample.

9.1.4 ~~Calibrate the spectrophotometer~~ The spectrophotometer should be calibrated in accordance with the manufacturer's instruction and specifications. Calibration ~~is to~~ shall be performed using toluene as the 100 % transmittance spectral background.

9.1.4.1 Guidelines for properly obtaining a reference background spectrum for a reference solvent are referenced in Practices E169.

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

9.2.1 ~~Set the~~ The refrigerated circulating water bath ~~temperature to 25.0 ± 0.1°C~~shall be set to a temperature of 25.0 ± 0.1 °C in accordance with the manufacturer's instruction and specifications.

9.2.2 ~~Fill both 200 mL~~ Both 200-mL water-jacketed reaction vessel chambers are filled one-half full with water. ~~Place a~~ A small TFE-fluorocarbon stir bar should be placed in the bottom of each reaction vessel chamber.

9.2.3 ~~Fill a 40 mL~~ A 40-mL reaction vial is filled with isooctane (2,2,4-trimethylpentane). ~~Place a small~~ A small, clean stir bar is placed into the reaction vial chamber.

9.3 *Pumps and Tubing Assemblies:*

9.3.1 ~~Cut the lengths of the tubing~~Tubing should be cut and attached from the high flow rate metering pump ~~and~~ to the low cell assembly to achieve a minimum total solution-circulation loop assembly volume, ~~< 0.25~~ <0.25 mL.

9.3.2 ~~Adjust the~~ The high flow rate metering pump is attached to flow at 10 mL/min. ~~Time the~~ The flow rate ~~with a stopwatch and 10.0 mL graduated cylinder. Report the~~ may be measured with a stopwatch, timing the flow of solvent into a 10.0-mL graduated cylinder. The average and standard deviation of the flow rate shall be reported for three measurements.

9.3.3 ~~Adjust the~~ The low flow rate metering pump ~~to flow at 0.350 mL/min. Time the flow rate~~ is attached and adjusted to a flow rate of 0.350 mL/min. The flow rate is adjusted by timing the flow of solvent with a stopwatch ~~and 1.000 mL~~into a 1.000-mL graduated cylinder. ~~Report the~~ The average and standard deviation of the flow rate shall be reported for three measurements.

9.4 *Data Acquisition System*—~~Setup and operation of~~ The data acquisition system ~~is performed based on~~ should be set up and operated in accordance with the manufacturer's instructions and specifications.