



Designation: ~~D6703~~—~~13~~ D6703 – 14

## Standard Test Method for Automated Heithaus Titrimetry<sup>1</sup>

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 ( $\epsilon$ ) 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 *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*:<sup>2</sup>

[D8 Terminology Relating to Materials for Roads and Pavements](#)

[D3279 Test Method for n-Heptane Insolubles](#)

[D4124 Test Method for Separation of Asphalt into Four Fractions](#)

[D5546 Test Method for Solubility of Asphalt Binders in Toluene by Centrifuge](#)

[E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis](#)

### 3. Terminology

3.1 *Definitions of Terms Specific to This Standard*:

3.1.1 *asphalt binder, n*—asphalt which may or may not contain an asphalt modifier (see **asphalt modifier**).

<sup>1</sup> 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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<sup>2</sup> 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.

~~3.1.1.1 Discussion—~~

~~This term is often used in the Performance Graded Binder system.~~

~~3.1.2 asphalt cross-blend, n—any mixture of two or more asphalts blended together to form a consistent material.~~

~~3.1.1 asphaltene peptizability, n—the tendency of asphaltenes to exist as a stable dispersion in a maltene solvent, measured by the Heithaus parameter  $p_a$ .~~

~~3.1.4 asphaltene, n—insoluble fractions of asphalt that are precipitated by use of selected solvents, such as n-heptane.~~

~~3.1.2 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.~~

~~3.1.3 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).~~

~~3.1.4 compatibility, n—the state of peptization of an asphalt, which is measured quantitatively by the Heithaus parameter  $P$ .~~

~~3.1.5 dispersed phase, n—one phase of a dispersion consisting of particles or droplets of one substance distributed through a second phase.~~

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

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

3.1.8 *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.

3.1.12 *maltene, n*—soluble fractions of asphalt that are recovered from an eluate by use of selected solvents, such as n-heptane.

3.1.9 *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 reaction vials are ~~tared.~~ tared (Fig. 1). Three samples of asphalt of weights 0.400 g, 0.600 g and 0.800 g are transferred to each of three reaction vials. Toluene (3.000 mL) is 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. 12. Each reaction vial is separately placed into a 250 mL water-jacketed reaction vessel (vessel A Fig. 1) to provide temperature control of the system. The 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 second reaction vessel is filled with titrant is placed into a second 250 mL water-jacketed reaction vessel. A titration loop is made by pumping titrant into

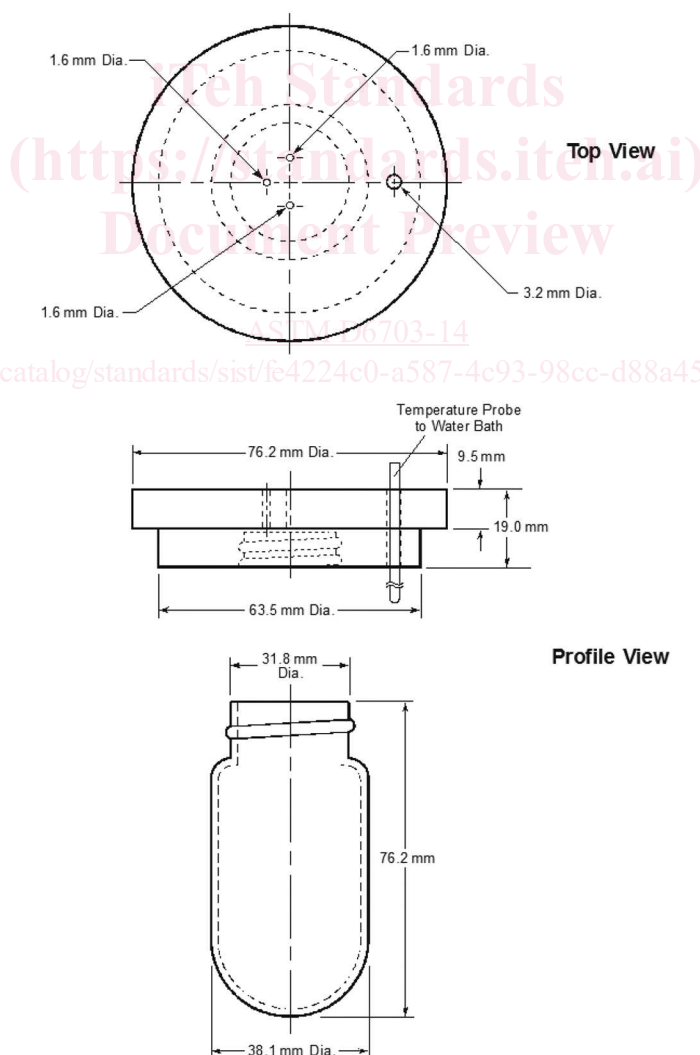


FIG. 41 Reaction Vial (30(40 mL) with TFE-fluorocarbon Cover and Temperature Probe

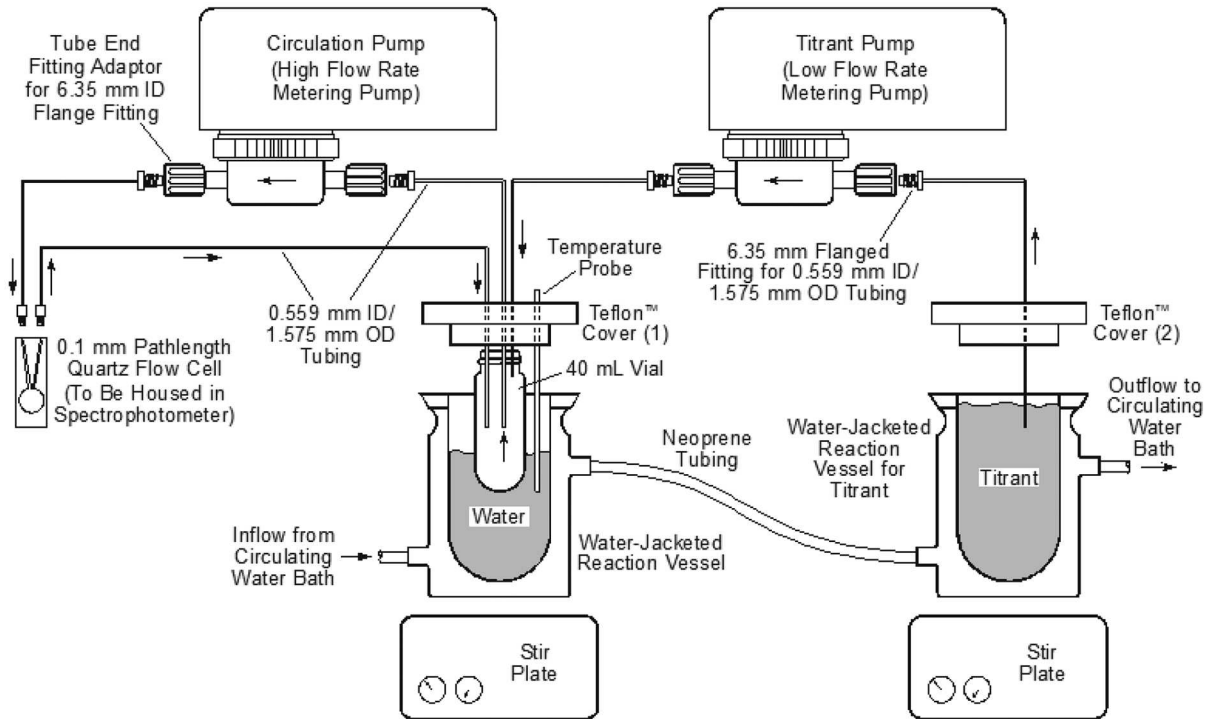


FIG. 42 Automated Titration Apparatus

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 water-jacketed reaction vessel. During a titration the output signal from the spectrophotometer is recorded using a data acquisition system (computer) to record the change in percent transmittance (%T) of detected radiation at 740 nm passing through the quartz cell plotted versus time, plotted as a function of time  $t$ , during (Fig. 3 which the titrant.), 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. 23 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. The time required to reach flocculation onset  $t_f$  multiplied by the titrant flow rate gives the titrant flocculation volume  $V_f$ .

4.4 Given the weights The measured weight of each asphalt sample,  $W_a$ , the volume of toluene initially used to dissolve each sample  $V_{S_0}$  and the volume of titrant at onset of flocculation  $V_f$ , values of  $C$  referred to as the dilution concentration and the input data required FR referred to as the flocculation ratio are calculated as to  $C = W_a / (V_S + V_T)$  and  $FR = V_S / (V_S + V_T)$ . Values of  $C$  plotted along an x-axis versus FR plotted along a y-axis result in a linear regression line (Fig. 3). This 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

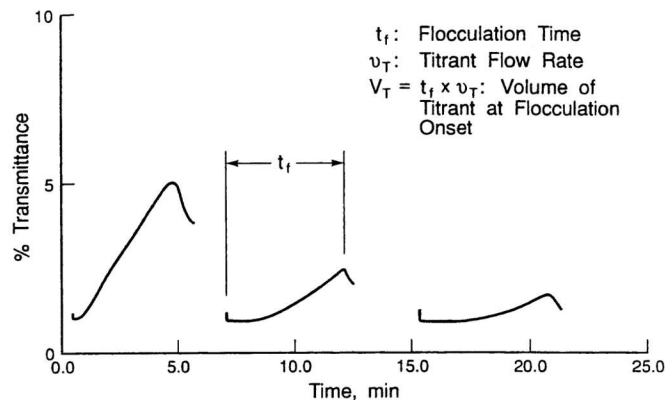


FIG. 23 Onset of Flocculation Peaks Measured at Three Successively Increasing Concentrations (Solvent: Toluene, Titrant: Isooctane)

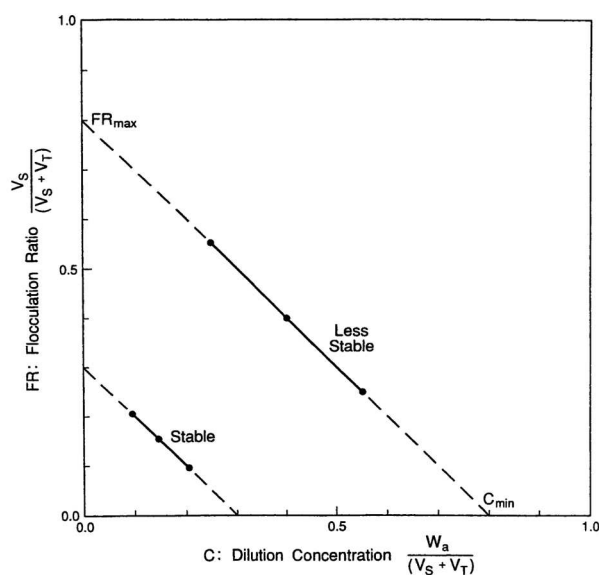


FIG. 34 Flocculation Ratio Versus Dilution Concentration for One Stable Asphalt and One Less Stable Asphalt

the y-axis is defined as  $FR_{max}$ . These two values are used to calculate the three Heithaus compatibility parameters, designated calculate compatibility parameters  $p_a$ ,  $p_o$ , 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  $(1/C_{min} + 1)$ .

## 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 solvent moiety (the dispersing medium) (refer to Test Methods D3279, D4124, and 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 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 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 Spectrophotometer*, 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, two.

6.4 *TFE-fluorocarbon Covers*, two.

6.4.1 *TFE-fluorocarbon Cover No. 1*, (see Fig. 41), threaded to hold a 40 mL reaction vial. Three holes, 1.5 mm diameter, concentric to the cover's center are tapped to set within the inside diameter of the vial when attached to the TFE-fluorocarbon cover, cover. One additional hole, 3.0 mm, 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.

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

6.5 *High Flow Rate Metering Pump*—Flow rate range from 0.5 to 10.0 mL/min; flow rate consistency,  $\pm 0.1$  mL/min; and piston chamber resistant to damage from solvent contact.

6.6 *Low Flow Rate Metering Pump*—Flow rate range from 0.100 to 1.000 mL/min; flow rate consistency,  $\pm 0.002$  mL/min; and piston chamber resistant to damage from solvent contact.

6.7 *Magnetic Stirring Plates*, two.

6.8 *Refrigerated Water Bath Circulator*—Temperature variation,  $\pm 0.1^\circ\text{C}$ ; temperature range from 0 to  $100^\circ\text{C}$ .

6.9 *Quartz Flow Cell*, 0.20 mm path length<sup>3</sup> with 6.35 mm flanged fittings.

6.10 *TFE-fluorocarbon Tubing*, 0.559 mm inside diameter/1.575 mm outside diameter.

6.11 *Reaction Vials*, 40 mL volume capacity.

6.12 “4-hole” *TFE-fluorocarbon cover* and “1-hole” *TFE-fluorocarbon cover*.

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

6.14 *Stopwatch*.

6.15 *Syringe*, 5.000 cc, glass, gas-sealed, and resistant to solvents that it will be used to sample.

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

6.17 *Neoprene Tubing*, 13 mm inside diameter.

6.18 *Tubing Clamps*, sized to fit 13 mm inside diameter tubing.

6.19 *Digital Probe Thermometer*,  $^\circ\text{C}$  (calibrated to  $\pm 0.2^\circ\text{C}$ ). Probe length, >80-mm, probe diameter, 3.0 mm.

6.20 *Graduated Cylinders*, two. Volumes:  $1.000 \pm 0.001$  mL and  $10.0 \pm 0.1$  mL.

6.21 *Argon Gas Supply*.

6.22 *Laboratory Jacks*—Laboratory jacks are may be 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~~ metering pumps.

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

6.24 *Polypropylene Rinse Bottles*, two. Volume: 200 mL.

6.25 *TFE-fluorocarbon Lined Caps*, for 40 mL reaction vials.

## 7. Reagents

7.1 *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 available.<sup>4</sup> 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 following assembly 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. 12):*

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 water-jacketed reaction vessel assembly) using 0.559 mm inside diameter/1.575-mm outside diameter TFE-fluorocarbon tubing fitted with standard 6.2 mm flange fittings adaptable to 0.559 mm inside diameter/1.575 mm outside diameter tubing.

<sup>3</sup> 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,<sup>1</sup> which you may attend.

<sup>4</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.2.1.1 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.

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

8.2.1.3 Position the high flow rate metering pump on a laboratory jack next to the stir plate. Attach a 6.35 mm flanged fitting to one end of a 100 mm long piece of 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 second flanged fitting provided with the flow cell to one end of a second 300 mm long piece of 0.559 mm inside diameter/1.575 mm outside diameter TFE-fluorocarbon tubing, leaving the other tubing end free. Fasten the flanged fitting end of this tubing to the outflow end of the flow cell.

8.2.1.5 Attach a 6.35 mm flanged fitting to a third 200 mm long piece of 0.559 mm inside diameter/1.575 mm 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 (8.2.1.4 and 8.2.1.5) will lead to the 40 mL reaction vial, positioned through the holes provided in the top of the “4-hole” TFE-fluorocarbon cover.

8.2.2 *Titration Loop Assembly*—A titrant dispenser (titration 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 outside diameter flanged fitting.

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

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

8.2.2.3 Attach a 300 mm piece of 0.559 mm inside diameter/1.575 mm outside diameter TFE-fluorocarbon tubing fitted with one 6.35 mm flanged fitting 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 water-jacketed reaction vessel.

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

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

8.2.3.1 Using 13 mm inside diameter neoprene tubing and tubing clamps, plumb 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.

8.2.3.2 Plumb two additional pieces of 13 mm inside 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.

## 9. Preparation and Calibration

9.1 *UV-Visible Spectrophotometer*:

9.1.1 See the manufacturer’s instructions and specifications for operation of the UV-visible spectrophotometer.

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

9.1.3 Set the wavelength of the spectrophotometer 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 in accordance with the manufacturer’s instruction and specifications. Calibration is to 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 refrigerated circulating water bath temperature to  $25.0 \pm 0.1^\circ\text{C}$  in accordance with the manufacturer’s instruction and specifications.

9.2.2 Fill both 200 mL water-jacketed reaction vessel chambers one-half full with water. Place a small TFE-fluorocarbon stir bar in the bottom of each reaction vessel chamber.

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

9.3 *Pumps and Tubing Assemblies*:

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

9.3.2 Adjust 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 for three measurements.