



Designation: **D6703 – 07 D6703 – 13**

## 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 (1,2) that estimate quantify the colloidal stability of asphalts and asphalt cross blends (1,2), aged asphalts (3), and pyrolyzed heavy oil residua and asphalt aged asphalts (4) using automated Heithaus titrimetry as a stability diagnostic tool.

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>

D3279 Test Method for 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, 5), n*—a dark brown to black cementitious material, solid or semisolid in consistency, in which the predominating constituents are bitumen, which occur in nature as such or are obtained as residue by the refining of asphalt which may or may not contain an asphalt modifier (see *of petroleum 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.

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

3.1.4 *asphaltenes, asphaltene, n*—the high molecular weight hydrocarbon fraction precipitated from asphalt by a designated paraffinic naphtha solvent at a specified solvent-asphalt ratio; insoluble fractions of asphalt that are precipitated by use of selected solvents, such as n-heptane.

#### 3.1.4.1 *Discussion*—

The asphaltene fraction should be identified by the solvent and solvent-asphalt ratio used.

3.1.5 *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.

3.1.6 *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.

3.1.7 *coke, n*—the solid product resulting from the destructive distillation of coal, petroleum residuum, or bitumen in an oven or closed chamber, or from imperfect combustion of these materials, consisting principally of carbon.

3.1.6 *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).

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

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

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

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

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

3.1.11 *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.

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

3.1.16 *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.

3.1.17 *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.

3.1.18 *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.

3.1.19 *residuum, n*—a quantity or body of matter remaining after evaporation, combustion, or distillation.

#### 4. Summary of Test Method

4.1 Three 30-mL–40 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, asphalt of weights 0.400 g, 0.600 g and 0.800 g are transferred to the reaction vials, one sample into each vial—each of three reaction vials. Toluene (3.000 mL) is added to each of the reaction vials to dissolve the asphalt (or heavy oil residuum). Each reaction vial contains a solution which differs by concentration of asphalt (or heavy oil residuum) prepared in toluene. All solutions that are prepared for a given asphalt material are constituting three solutions which differ by concentration. Each solution is titrated with isooctane (2,2,4-trimethyl pentane) or some other titrant that promotes a flocculation of material within the solution to promote onset of flocculation of the solution. (6) conducted at a constant titrant delivery rate. The titration is performed by placing the reaction vials separately in the apparatus illustrated in Fig. 1. The apparatus depicted in Fig. 1 consists of intersecting sample circulation and titration loops.

4.2 Titrations are performed by placing reaction vials separately in the apparatus illustrated in Fig. 1. Each reaction vial is separately placed into a 250-mL, 250 mL water-jacketed reaction vessel (Fig. 1). Water-jacketing is required for—) to provide temperature control of the system. Furthermore, the water-jacketed reaction vessel is filled with enough water such that the reaction vial and temperature probe are 75 % immersed. Water flowing through the water jacket maintains the temperature of the water in the reaction vessel, which further maintains the temperature of the solution in the reaction vial. The connection with the—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 (pumping the solution through a 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 (0.2-mm) quartz flow cell housed in an 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 ultraviolet-visible spectrophotometer then back to the reaction vial with high flow rate metering pump and then to another water-jacketed reaction vessel filled with titrant (usually iso-octane). 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 pump. A Fig. 2, but does not require threading because the cover fits directly over the reaction vessel and no vial

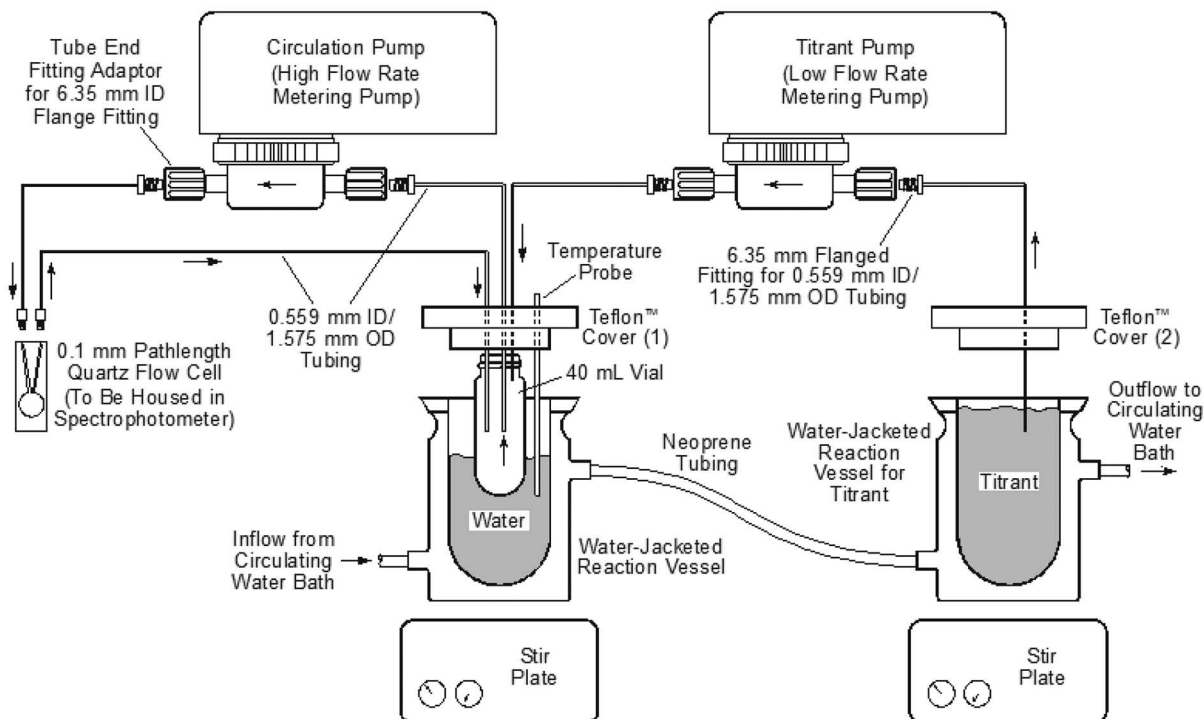


FIG. 1 Automated Titration Apparatus

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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 flow rate using the low flow rate metering pump. During this process, a titration loop is made by pumping titrant into the sample reaction vial at a constant flow rate using the low flow rate metering pump. During this process, a titration the output signal from the spectrophotometer is recorded using an integrator or some other data gathering device. The a Data acquisition system (computer) to record 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. titrant.

4.3 The spectrophotometer output signal detects the onset of measures turbidity of the sample solution. This is the solution as a titration experiment proceeds to a flocculation onset point, corresponding to the beginning of the precipitation of asphaltene onset of flocculating asphaltene phase separating from the sample solution. Fig. 32 illustrates a typical series of plots of plot of %T versus  $t$  for the three test solutions. Values of %T are observed to increase with time until maximum values of %T to the flocculation onset point, after which values of %T decrease. The reason that the curves in are observed to decrease. The 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, flocculation onset  $t_f$ . When the value of  $t_f$  for each sample is multiplied by the titrant flow rate, rate gives the titrant volume, flocculation volume  $V_{f_2}$ , required to cause the onset of flocculation for each sample is obtained.

4.4 The weight Given the weights of each asphalt (or heavy oil residuum) sample,  $W_a$ , the volume of toluene initially used to dissolve each sample, sample  $V_S$  (2.00 mL in each case), and the volume of titrant required to cause the at onset of flocculation, 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 values of  $C$  (referred referred to as the dilution concentration) concentration and  $FR$  (referred referred to as the flocculation ratio): ratio are calculated as  $C$  is defined as  $\equiv W_a / (V_S + V_T)$  and  $FR$  is defined as  $\equiv V_S / (V_S + V_T)$ . Values of  $C$  are plotted along an  $x$ -axis versus  $FR$  for each of the three recorded sets of values of plotted  $W_a$ ,  $V_S$ , 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  $-axis$  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 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  $(1/C_{min} + 1)$ .

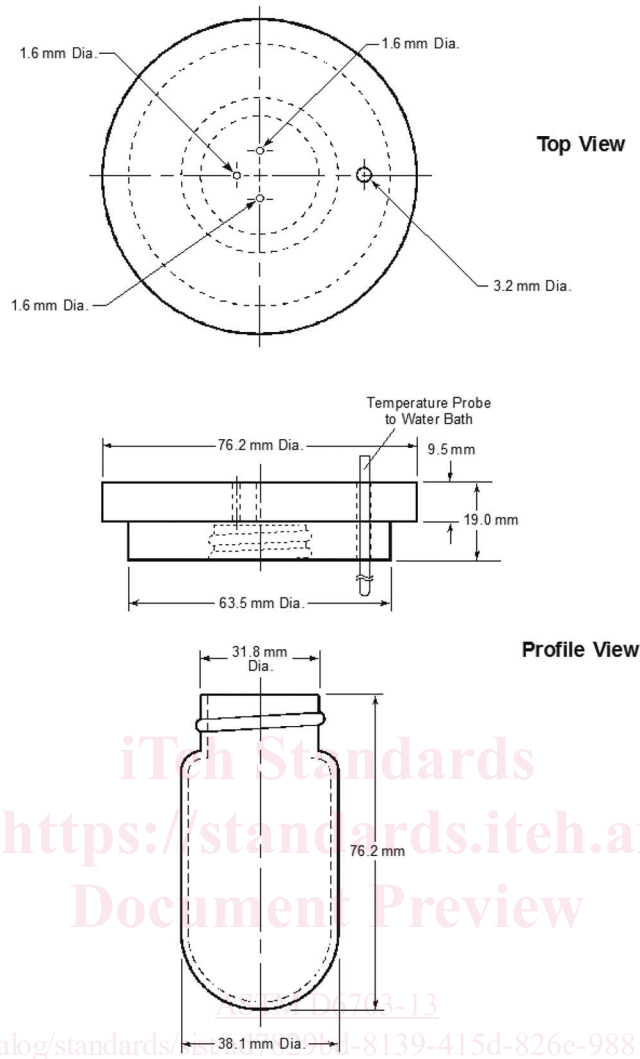


FIG. 24 Reaction Vial (30 mL) with TFE-fluorocarbon Cover and Temperature Probe

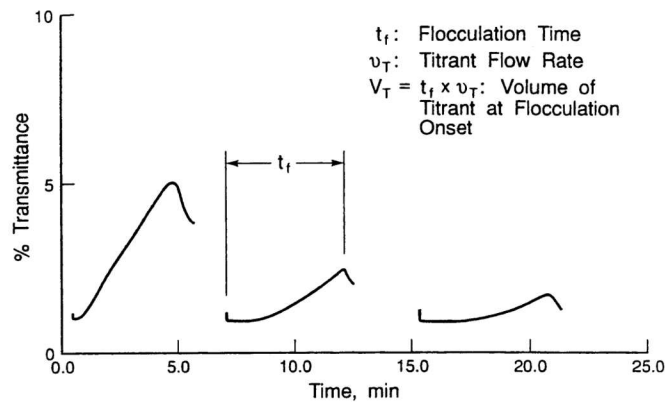


FIG. 32 Onset of Flocculation Peaks Measured at Three Successively Increasing Concentrations (Solvent: Toluene, Titrant: Isooctane)

## 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, pyrolyzed asphalt, and heavy oil residuum. Historically, bituminous asphalt and heavy oil residua have been modeled as colloidal suspensions (8,9) in which a polar, polar associated asphaltene moiety (the dispersed phase)

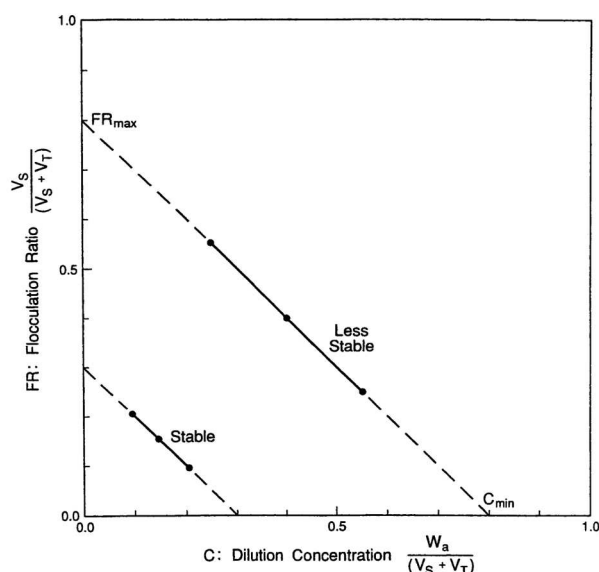


FIG. 43 Flocculation Ratio Versus Dilution Concentration for One Stable Asphalt and One Less Stable Asphalt

is suspended in a maltene solvent moiety (the dispersing medium) (refer to test methods Test Methods D3279, D4124, and D5546 for further definition of asphalt fraction materials). The extent to which these two moieties remain in a given state of peptization is a measure of the compatibility (colloidal stability) of the suspension. Compatibility influences important the physical properties of these materials, including rheological properties, for example, phase angle and viscosity. 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, whereas materials incompatible. 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 functions of the quantities  $C_{min}$  and  $FR_{max}$ . the values of which  $C_{min}$  and  $FR_{max}$  are obtained determined from three experimental variables, the weight of residuum or asphalt ( $W_a$ ), the volume of solvent ( $V_s$ ) to dissolve the weight of asphalt, and the volume of titrant added up to the flocculation point ( $V_t$ ) 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 Integrator, Acquisition System (computer)*, or data acquisition system (computer). One-millisecond data sampling rate.

6.3 *Water-Jacketed Reaction Vessel*, 200-mL, 250-mL, two.

6.4 *TFE-fluorocarbon Covers*, two.

6.4.1 *TFE-fluorocarbon Cover No. 1*, (see Fig. 24), threaded to hold a 30-mL-40 mL reaction vial. Dimensions: thickness, 2.0 mm ( $\frac{9}{64}$  in.); diameter, 70 mm ( $2\frac{3}{4}$  in.), threaded to 30-mL reaction vial. Three holes, 1.5 mm ( $\frac{1}{16}$  in.) in diameter, concentric to the cover's center, are arranged in a triangle, are center 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 (cover,  $\frac{3}{8}$  in.). One additional hole, 3.0 mm (mm,  $\frac{1}{8}$  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.

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 (mm;  $\frac{9}{64}$  in.); diameter, 70 mm (2mm.  $\frac{3}{4}$  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 6.4.1 except for the number of holes, and is not threaded.

6.5 *High Flow Rate Metering Pump*—Piston diameter, 3.0 mm (Flow  $\frac{1}{8}$  in.); piston displacement  $< 0.1$  mL; flow-rate range from 1.00.5 to 20.010.0 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*—Piston diameter, 3.0 mm (Flow  $\frac{1}{8}$  in.); flow-rate range from 0.100 to 1.000 mL/min; flow rate consistency,  $\pm 0.001 \pm 0.002$  mL/min; and piston chamber resistant to damage from solvent contact.



6.7 *Magnetic Stirring Plates*, two.

6.8 *Refrigerated Water Bath Circulator—(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); variation,  $\pm 0.1^\circ\text{C}$ ; temperature range from 0 to 100°C (32 to 212°F). Coupled to fit neoprene tubing, 13-mm (100°C, ½-in.) in inside diameter.

6.9 *Quartz Flow Cell*, 0.20-mm 0.20 mm path length<sup>3</sup> 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 (6.35 mm flanged fittings, ¼-in.) outside diameter TFE-fluorocarbon tubing.

6.10 *TFE-fluorocarbon Tubing*, 0.56-mm (0.022-in.) inside diameter/1.59-mm (0.559 mm inside diameter/1.575 mm ¼-in.) outside diameter.

6.11 *Reaction Vials*, 30-mL, (3 for each sample) (provisional patent applied for by Western Research Institute); 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, Bars.* disk or cylinder-shaped, approximately 10 mm (0.04 in.) in diameter and 8.0 mm (0.03 in.) in height.

6.14 *Stopwatch.*

6.15 *Syringe*, 2.500-cc 5.000 cc,<sup>3</sup> glass, gas-sealed, and resistant to solvents that it will be used to sample.

6.16 *TFE-fluorocarbon Tube Fittings—Fittings (4)*, including including standard 6.2-mm (6.35 mm ¼-in.) flange flanged fittings for 0.56-mm (0.022-in.) inside diameter/1.59-mm (0.559 mm inside diameter/1.575 mm ¼-in.) outside diameter TFE-fluorocarbon tubing.

6.17 *Neoprene Tubing*, 13-mm (13 mm ½-in.) inside diameter.

6.18 *Tubing Clamps*, sized to fit 13-mm (13 mm ½-in.) inside diameter tubing.

6.19 *Digital Probe Thermometer*, °C ( $\pm 0.1^\circ\text{C}$ ). Probe contact length, >80 mm (>3-in.), probe contact diameter, <3.0 mm (<(calibrated to  $\pm 0.2^\circ\text{C}$ )). Probe length, >80-mm, probe diameter, 3.0 mm. ¼-in.)

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 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.

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

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

6.25 *TFE-fluorocarbon Lined Caps*, for closing reaction vials and storing solutions; 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 Isooctane* (2,2,4-trimethylpentane), HPLC grade.

7.3 *Toluene*, HPLC grade.

7.4 *Toluene*, reagent grade, for cleaning grade.

## 8. Assembly

8.1 *Installation Requirements:*

8.1.1 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). hood. The fume hood should be of sufficient size to accommodate all pieces of the apparatus and supplies used needed to perform this the test method.

<sup>3</sup> The sole source of supply of the apparatus known to the committee at this time is Quartz flow cell, 0.20-mm path length, available from 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.