Designation: D6703 – 07

StandardTest 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 (**1**,**2**)[2] that estimate the colloidal stability of asphalts and asphalt cross blends (**1**,**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. Referenced Documents

2.1 *ASTM Standards:*[3]

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* (**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 petroleum.

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

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.

3.1.8 *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).

3.1.9 *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).

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

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

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

3.1.14 *Heithaus compatibility parameters, n*—three parameters: asphaltene peptizability (p_a), maltene peptizing power

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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.

Current edition approved Dec. 1, 2007. Published January 2008. Originally approved in 2001. Last previous edition approved in 2001 as D6703 – 01. DOI: 10.1520/D6703-07.

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

[3] 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.

(p_o), and asphalt state of peptization (P), measured using Heithaus titration methods.

3.1.15 *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 deasphaltened 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 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 (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 titrated with isooctane (2,2,4-trimethyl pentane) or some other titrant that promotes a flocculation of material within 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 Each reaction vial is separately placed into a 250-mL, water-jacketed reaction vessel (Fig. 1). Water-jacketing is required for 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 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 (0.2-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 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 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.

4.3 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.

4.4 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 $(1/\,C_{min} + 1)$.

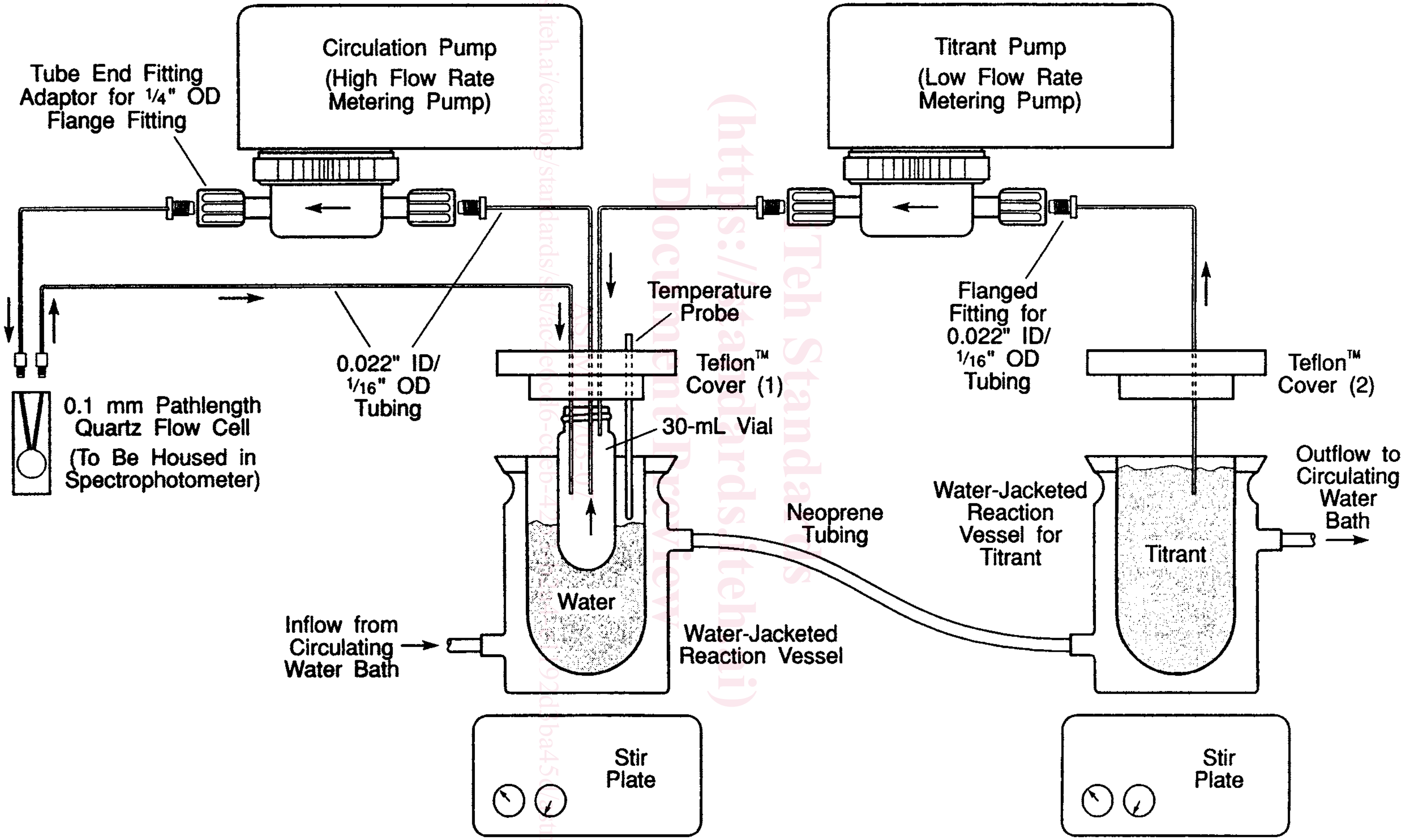

FIG. 1 Automated Titration Apparatus

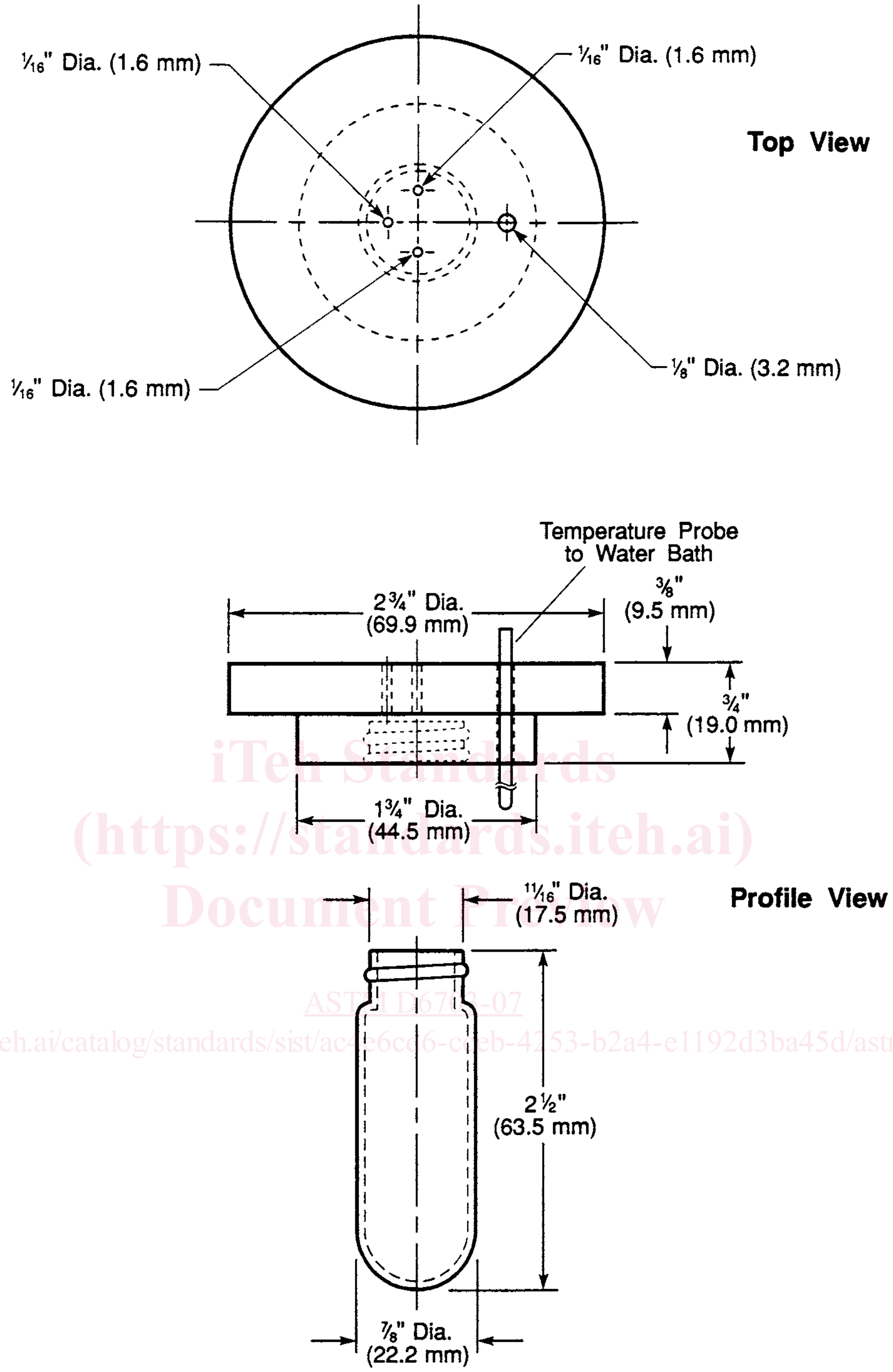

FIG. 2 Reaction Vial (30 mL) with TFE-fluorocarbon Cover and Temperature Probe

5. Significance and Use

5.1 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) (refer to 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 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*

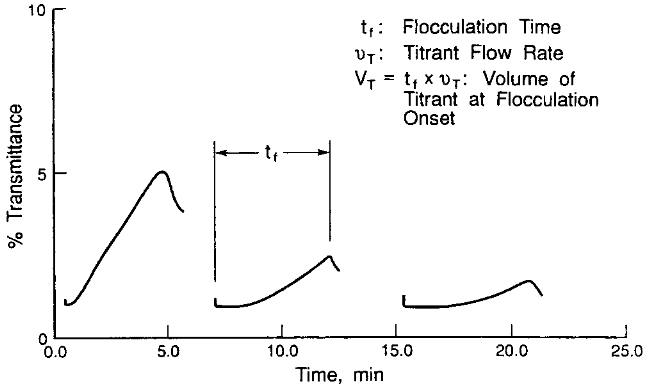

FIG. 3 Onset of Flocculation Peaks Measured at Three Successively Increasing Concentrations (Solvent: Toluene, Titrant: Isooctane)

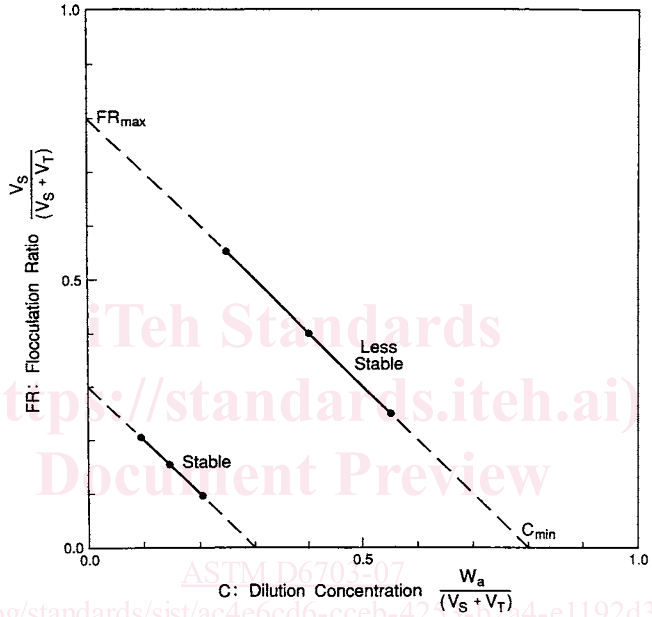

FIG. 4 Flocculation Ratio Versus Dilution Concentration for One Stable Asphalt and One Less Stable Asphalt

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 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).

6. Apparatus

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

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

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

6.4 *TFE-fluorocarbon Covers,* two.

6.4.1 *TFE-fluorocarbon Cover No. 1,* (see Fig. 2), threaded to hold a 30-mL reaction vial. Dimensions: thickness, 2.0 mm (9⁄16 in.); diameter, 70 mm (2¾ 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 (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 (9⁄16 in.); diameter, 70 mm (2¾ in.). One hole 1.5 mm (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 (⅛ 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.

6.6 *Low Flow Rate Metering Pump*—Piston diameter, 3.0 mm (⅛ 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.

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, ±0.1°C (0.2°F); temperature range from 0 to 100°C (32 to 212°F). Coupled to fit neoprene tubing, 13-mm (½-in.) in inside diameter.

6.9 *Quartz Flow Cell,* 0.20-mm path length[4] 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 (1⁄16-in.) outside diameter TFE-fluorocarbon tubing.

6.10 *TFE-fluorocarbon Tubing,* 0.56-mm (0.022-in.) inside diameter/1.59-mm (1⁄16-in.) outside diameter.

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

6.12 *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.

6.13 *Stopwatch.*

6.14 *Syringe,* 2.500 cm^3, glass, gas-sealed, and resistant to solvents that it will be used to sample.

6.15 *TFE-fluorocarbon Tube Fittings.* Including standard 6.2-mm (¼-in.) flange fittings for 0.56-mm (0.022-in.) inside diameter/1.59-mm (1⁄16-in.) outside diameter TFE-fluorocarbon tubing.

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

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

6.18 *Probe Thermometer,* °C (±0.1°C). Probe contact length, >80-mm (>3-in.), probe contact diameter, <3.0–mm (<⅛ –in.).

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

6.20 *Argon Gas Supply.*

6.21 *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.

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

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

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

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.[5] 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, for cleaning.

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). The fume hood should be of sufficient size to accommodate all pieces of the apparatus and supplies used to perform this 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. 1):

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 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 (¼-in.) flange fittings adaptable to 0.56-mm (0.022-in.) inside diameter/1.59-mm (1⁄16-in.) outside diameter tubing.

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 Finally, position the high flow rate metering pump on a laboratory jack next to the stir plate. Attach a standard 6.2-mm (¼-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.

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[4] 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,[1] which you may attend.

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *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.