Designation: D4124 – 09

Standard Test Method for Separation of Asphalt into Four Fractions[1]

This standard is issued under the fixed designation D4124; 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 covers the separation of four defined fractions from petroleum asphalts. The four fractions are defined as saturates, naphthene aromatics, polar aromatics, and iso-octane insoluble asphaltenes. This method can also be used to isolate saturates, naphthene aromatics, and polar aromatics from distillate products such as vacuum gas oils, lubricating oils, and cycle stocks. These distillate products usually do not contain asphaltenes.

1.2 The values stated in SI units are to be regarded as 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.* Specific precautionary statements are given in Section 8.

1.4 Since a precision estimate for this standard has not been developed, this test method is to be used for research or informational purposes only. Therefore, this standard should not be used for acceptance or rejection of a material for purchasing purposes.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D140 Practice for Sampling Bituminous Materials

2.2 *Other Documents:*

Manual on Hydrocarbon Analysis[3]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *asphaltenes* or *alkane insolubles*—insoluble matter that can be separated from asphalt following digestion of the asphalt in n-alkane (and in some cases, branched alkanes) under the specified conditions in this test method.

3.1.2 *naphthene*—any of a group of hydrocarbon ring compounds of the general formula, C_nH_{2n}, derivatives of cyclopentane and cyclohexane, found in certain petroleum stocks.

3.1.3 *naphthene aromatics*—material that is adsorbed on calcined CG-20 alumina in the presence of *n*-heptane, and desorbed by toluene, after removal of saturates under the conditions specified.

3.1.4 *petrolenes (*also referred to as *maltenes) —(1)* any of the constituents of a bitumen, as asphalt, that are soluble in *n*-alkanes (and in some cases, branched alkanes), which generally range in carbon number between *n*-C_5 to *n*-C_{10} alkanes, *n*-heptane being the most common solvent used; *(2)* the low molecular weight alkane-soluble matter recovered following separation of asphaltenes from the digested mixture under the specified conditions described in this and similar test methods.

3.1.5 *polar aromatics (resins)*—material desorbed from calcined CG-20 alumina absorbent, after the saturates fraction and naphthenic aromatics fraction have been removed, using toluene:methanol (50:50, vol:vol) and trichloroethylene eluate under the conditions specified.

3.1.6 *saturates*—material that, on percolation in an alkane eluate, is not absorbed on calcined CG-20 alumina absorbent under the conditions specified.

4. Summary of Test Method

4.1 The sample containing the four defined fractions is first separated into alkane-insoluble asphaltenes and alkane-soluble petrolenes. Petrolenes are then adsorbed onto calcined CG-20 alumina and further fractionated into saturate, naphthene aromatic, and polar aromatic fractions by pumping an eluotropic series of elution solvents upwards through a glass chromatographic column packed with calcined alumina. Eluted fractions are recovered by solvent removal prior to final weighing. The three eluted fractions plus the alkane-precipitated asphaltenes comprise the four fractions as defined in Section 3.

5. Significance and Use

5.1 This test method separates asphalts into four well-defined fractions. Analysis of these fractions can be used to

[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 in 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] Available from ASTM as PCN 03-332030-12.

evaluate asphalt composition (1, 2). For example, one can compare the ratios of the fractions with other asphalt systems to evaluate processing and aging parameters that relate to performance properties of the asphalt.

6. Apparatus and Materials

6.1 *Reflux Apparatus for Asphaltene/Maltene Separation,* with features as specified in Fig. 1. (see 6.1.1).

6.1.1 *Apparatus (Fig. 1)—(a)* ring stand with clamp; *(b)* heater-stirring plate; *(c)* 500-mL Erlenmeyer flask with 29/42 sintered glass neck; *(d)* reducer, 29/42-to-24/40 sintered glass necks; *(e)* Allihn-type reflux condenser with 24/40 sintered glass neck.

6.2 *Chromatographic Column Apparatus,* with features as specified in Fig. 2, (see 6.2.1 – 6.2.5).

6.2.1 *LC-Apparatus (Fig. 2)—(a)* ring stand w/clamp, flask (25-mL round-bottom or Erlenmeyer flask); *(b)* metering pump; *(c)* sealed glass LC-column; *(d)* UV Detector w/ Data Acquisition System (wavelength range 200-500 nm @ 0.1-nm); *(e)* graduated cylinder (Fig. 2).

6.2.2 *UV Detector with Data Acquisition System (Fig. 2)*—A UV Detector with Data Acquisition System suitable for use with liquid chromatography or HPLC used to detect the occurrence of material fractions (peak response) as they are eluted from the column.

6.2.3 *Metering Pump (Fig. 2)*—Piston and piston chamber will be constructed of materials resistant to deterioration by solvents that will be used to perform the method. Flow rate range of the pump will be 0.1 to 5.0-mL/min ± 0.1-mL/min flow rate stability.

6.2.4 *LC-Column with Water-jacket*—Closed glass liquid chromatography column, 70 cm long and 1.5 cm inside diameter (volume, 124-cc). The LC-column will be a closed column with endplates containing solvent permeable diaphragms and fitting ports for 6.35-mm (¼-in.) tubing fittings.

6.2.5 *Refrigerated/Heating Circulator*—a refrigerated/heating circulator, temperature range between 0°C and 100°C ± 0.1°C stability, with water circulation through the LC-column water jacket via high pressure hose 15.9-mm (⅝ in. ID).

6.3 *Materials:*

6.3.1 *Utilities*—Fume hood, vacuum source, nitrogen gas source, cold water source, nitrogen gas-purged vacuum drying oven, rotary solvent evaporator (water-bath and oil-bath type), nitrogen gas stream evaporator with heater water bath.

6.3.2 *Erlenmeyer Flasks,* 25-mL with Glass Stopper (1), 500-mL with Glass Stoppers (5).

6.3.3 *Pear-shaped Flask,*

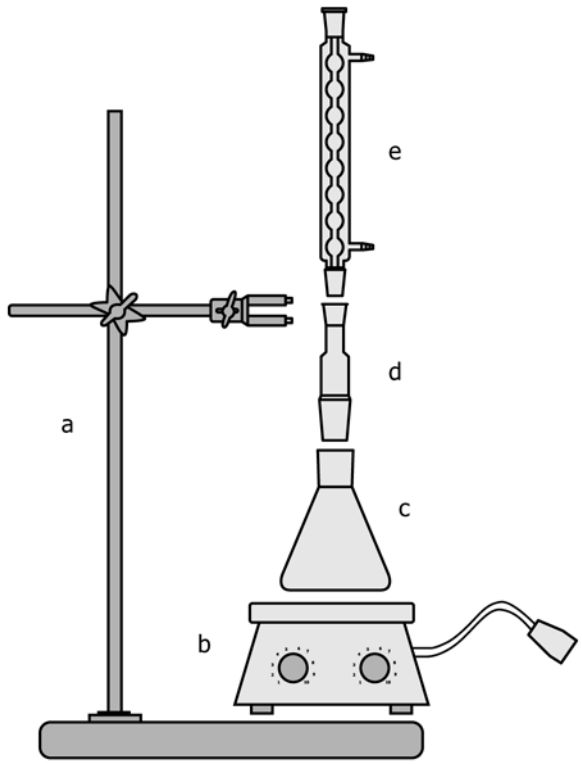
6.3.4 *Graduated Cylinder,*

6.3.5 *Büchner-style Funnel, Fritted-glass,* 60 to 100-mL, ASTM 10-15 µL medium porosity.

6.3.6 *Flask, Suction,* 1 L to 2 L.

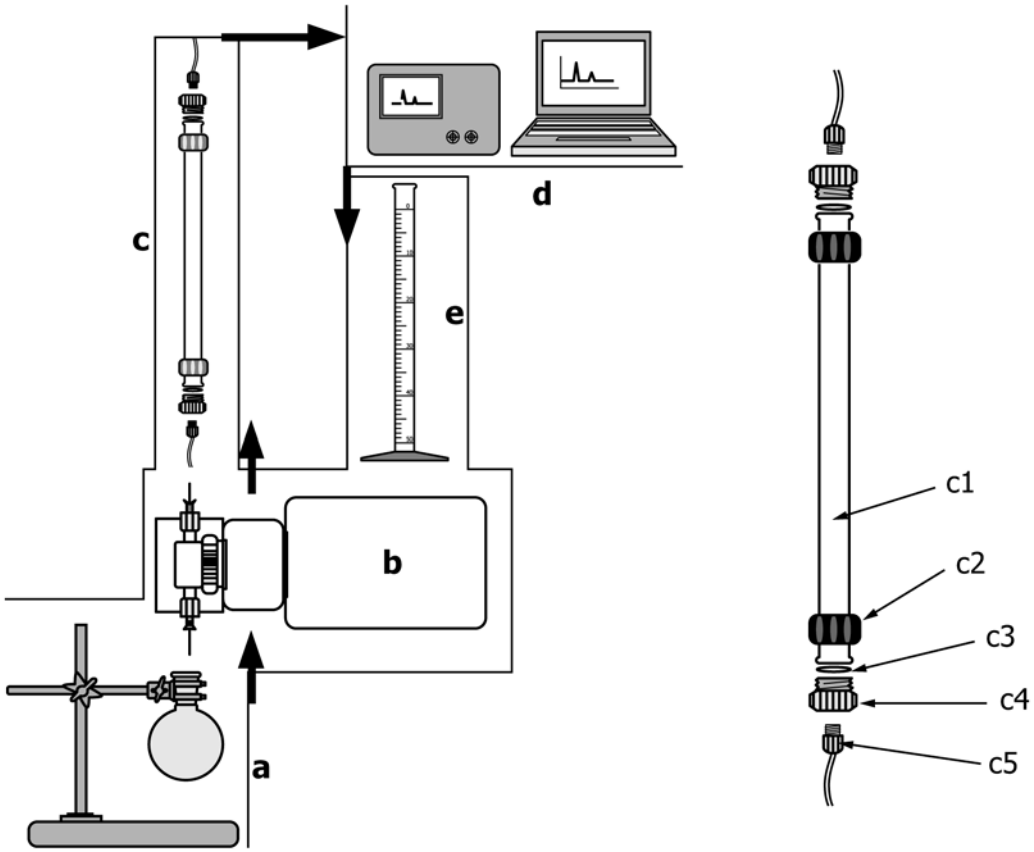
6.3.7 *Rinse Squeeze Bottle,* 0.5-L size, TFE-fluorocarbon.

6.3.8 *Analytical Balance,* 0.0001 g to 250 g ± 0.0001 g.



NOTE 1—Key: a. ring stand w/large test-tube clamp; b. heater/stirring plate; c. 500-mL Erlenmeyer flask with 29/42 sintered glass neck; d. reducer 29/42-to-24/40 sintered glass spout-to-neck; e. Allihn-type reflux condenser with 24/40 sintered glass spout.

FIG. 1 Asphaltene/Maltene Separation Apparatus



NOTE 1—Key: LC-Apparatus: a. clamp stand w/sample or solvent flask (round-bottom or Erlenmeyer type); b. metering pump; c. sealed glass LC column packed with alumina; c1. glass column; c2. collar; c3. diaphragm; c4. endplate; c5. tubing nut/ferrule and tubing; d. UV-VIS spectrophotometric detector (200-500 nm @ 0.1-nm); e. graduated cylinders of various sizes for fraction collection.

FIG. 2 Chromatographic Column for Separation of Asphalt by Elution-Adsorption

6.3.9 *Stirrer/heater Plate,* electric.

6.3.10 *Sample Vials,* Borosilicate, 25-mL (6) and 50-mL (2), clear, with Teflon-lined cap.

6.3.11 *Glass Funnels,* (2), small.

6.3.12 *Teflon or Solvent-resistant Funnels,* (1), small.

6.3.13 *Teflon Flask-neck Sleeves,* (3) 24/40-size, (1) 29/42-size.

6.3.14 *Hose,* reinforced, high pressure, 1.59-mm ID (⅝ in. ID).

6.3.15 *Tubing,* clear, resistant to organic solvents, 1.59-mm ID/3.17-mm OD (1⁄16 in. ID/⅛ in. OD).

6.3.16 *Tubing Fittings,* standard 6.35-mm (¼ in.) nut with 3.17-mm OD (⅛ in. ID)-hole and 3.17-mm (⅛ in.) ferrule.

7. Absorbent and Reagents

7.1 *Alumina,*[4] CG-20 chromatographic grade, calcined at 425°C for 16 h and stored in an evacuated desiccator in airtight bottles for 3 to 5 h.

7.2 *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.

7.3 *Reagents*

7.3.1 *iso-Octane (2,2,4–trimethyl pentane),* HPLC Grade, 0.01 % water.

7.3.2 *n-Heptane,* HPLC Grade, 0.01 % water.

7.3.3 *Methanol,* anhydrous, HPLC Grade, 0.01 % water.

7.3.4 *Toluene,* HPLC Grade, 0.001 % water.

7.3.5 *Trichloroethylene,* ACS Grade, 0.02 % water, boiling point 86.5 to 87.5°C.

[4] Aluminum Oxide available from EMD Chemicals, Inc., P.O. Box 70, 480 Democrat Road, Gibbstown, NJ 08027 (Product Code AX0612), CAS Number:1344-28-1, 2.5 kg Chromatographic Grade Alumina (Al_2O_3) 80-200 mesh CAS 1344-28-1, Cat # EM-AXO612-3.

[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.

8. Safety Precautions

8.1 Most organic solvents used in these methods are flammable and to some degree toxic. Reference should be made to Material Safety Data Sheets available from the supplier. These solvents should be handled with care and only in well-ventilated areas such as a fume hood. All working areas should be kept free of sparks, flames, or other sources of high temperature.

9. Separation of Asphalt into Asphaltenes and Petrolenes (Maltenes)

9.1 Representative asphalt samples free of foreign substances will be collected in accordance with Practice D140. Samples for testing can be transferred by chilling to facilitate fracturing the sample or by heating the sample until it becomes sufficiently fluid to pour. **Warning:** In no case shall the samples be heated more than 50°C above the expected softening point of the material, which is approximately 100°C.

9.2 Transfer to the nearest 0.001 g, 2.000 g of the asphalt into a tared 500-mL Erlenmeyer flask and record the mass of the asphalt, $M_{asphalt}$. Allow the sample to cool if transferred by heating and pouring prior to adding the iso-octane in the ratio of 100 mL of solvent per 1 g of sample. Add 200 mL ± 0.1 mL of HPLC grade iso-octane to the sample asphalt in the 500 mL Erlenmeyer flask.

9.3 In a fume hood of sufficient size to accommodate all required components of the apparatus and supplies used to perform this procedure, assemble a reflux apparatus in accordance with the setup shown in Fig. 1. Place a stir bar into the 500-mL Erlenmeyer flask containing the sample solution. Place the 500-mL Erlenmeyer flask on a stirrer/heater plate. Place an Allihn-type reflux condenser into the neck of 500-mL Erlenmeyer flask (Note 1). Ensure that the reflux apparatus is secured with lab clamps to a heavy ring stand or a laboratory mounting assembly housed in the fume hood by clamping both the neck of the 500-mL Erlenmeyer flask and the Allihn-type reflux condenser. Connect the Allihn-type reflux condenser to a cold water source using high pressure hose 15.9 mm (⅝ in. ID) and secure with hose clamps at all connections.

NOTE 1—Place Teflon flask-neck sleeves between sintered glass fittings to ensure easy disassembly of the reflux apparatus.

9.4 Slowly heat the sample solution on a stirrer/heater plate until the solution is observed to begin to reflux. Maintain the solution temperature near the boiling point of iso-octane (99°C). Begin to stir the contents of the flask at a moderate rate once the solution begins to reflux. Stir the contents of the 500-mL Erlenmeyer flask for 1 to 2 h or until no visual evidence of un-dissolved (un-digested) asphalt adheres to the sides of the flask. Once the sample has been observed to go into solution, stir the solution with refluxing for an additional 1 h (Note 2).

NOTE 2—Normally two hours is a sufficient amount of time to dissolve (digest) straight reduced asphalts, but for air blown or chemically modified asphalts, the dissolution time may need to be extended to three hours.

9.5 After the 2 to 3-h period of time required for refluxing with stirring, turn off the heater element of the stirrer/heater plate and allow the sample solution to cool with stirring. Continue to stir the cooled sample solution for an additional 2 h after cooling, at which time discontinue stirring, remove the Allihn-type reflux condenser, stopper the flask, and allow the sample solution to settle for 2 h prior to filtering (Note 3).

NOTE 3—At some time during the stirring process, after heating has been discontinued, rinse down the reflux assembly with 10 to 20 mL of iso-octane by dispensing solvent from the top of the Allihn-type reflux condenser into the flask using a squeeze bottle.

9.6 Set up a Büchner-style fritted-glass funnel (60-mL, ASTM 10–15-μL medium porosity) by placing the funnel on a 1-L suction flask with a filter ring. Attach the suction flask to a cold-trapped vacuum source with high pressure hose and hose clamps and secure the suction flask to a ring stand or mount rack with a clamp. Prior to filtration, tare the Büchner-style fritted-glass funnel.

9.7 Filter the sample solution prepared in 9.2 – 9.5, by quantitatively decanting the liquid contents of the sample solution from the 500-mL Erlenmeyer flask directly into the Büchner-style fritted-glass funnel while applying suction to the 1-L suction flask.

9.8 Quantitatively transfer the filtered decant, using a glass funnel, to a 1-L pear-shaped flask clamped to a ring stand, (this decant represents the first portion of petrolenes dissolved in iso-octane). Transfer the 1-L pear-shaped flask to a rotary evaporator and distill the iso-octane off of the petrolene fraction. Return the Büchner-style fritted-glass funnel to the suction flask.

9.9 Wash the asphaltenes which remain in the 500-mL Erlenmeyer flask with 100 mL of iso-octane. Place the 500-mL Erlenmeyer flask back onto the heater/stirrer plate and gently heat the contents of the Erlenmeyer flask for approximately 30 min with stirring to remove the remaining soluble materials potentially entrained in the asphaltene phase. Allow the solution to cool and settle (1 to 2 h). Quantitatively transfer all of the remaining contents of the 500-mL Erlenmeyer flask into the Büchner-style fritted-glass funnel while applying suction to the 1-L suction flask in order to filter off the asphaltenes. Toward the end of this transfer step, use a squirt bottle containing iso-octane to rinse the final remaining loose material from the 500-mL Erlenmeyer flask into the Büchner-style fritted-glass funnel. Set the empty 500-mL Erlenmeyer flask aside until 9.15.

9.10 Continue washing the asphaltene filter cake with additional iso-octane dispensed from a squeeze bottle until the eluate draining from the filter cake is observed to become colorless (Note 4).

NOTE 4—Do not allow the filter cake to dry and crack during this step. The filter cake should remain wet with iso-octane during this step to ensure a tight seal between the filter cake and the funnel surface.

9.11 When the eluate draining from the filter cake becomes colorless, discontinue washing and allow the remaining elution solvent to drain off of the filter so that the filter cake dries and cracks, then discontinue the vacuum.

9.12 Quantitatively transfer the eluate collected in the 1-L suction flask to the 1-L pear-shaped flask containing the

petrolenes previously recovered from the filtration of the decant (see 9.7 and 9.8). Attach the 1-L pear-shaped flask to a rotary evaporator and distill off all but 10 to 15 mL of the iso-octane solvent to retain a liquid concentrate. Quantitatively transfer the concentrate to a tared 50-mL Borosilicate screw-cap vial. Remove the remaining iso-octane solvent present in the petrolene concentrate by placing the vial on a 35°C heated nitrogen gas-stream evaporator for 24 to 48 h.

9.13 After solvent removal via the nitrogen gas-stream evaporator, remove the petrolene sample from the nitrogen gas-stream evaporator and further dry the sample to a constant mass on an oil-bath rotary evaporator (22-mm Hg vacuum, 120°C, 30 min to 1 h). Record the mass of recovered pertolenes, $M_{petrolenes}$. Purge the vial with nitrogen or argon gas and store away from light for long-term storage.

9.14 Place the Büchner-style fritted-glass funnel containing the asphalt filter cake prepared in 9.9 – 9.11 onto a 1-L Erlenmeyer flask to hold the funnel upright. Place the Erlenmeyer flask with the Büchner-style fritted-glass funnel into a pre-heated 80°C nitrogen gas-purging vacuum oven. Purge the oven of air with nitrogen gas, then apply full vacuum to the oven. Dry the asphaltene filter cake for 2 to 3 h, or until a constant mass is achieved for the Büchner-style fritted-glass funnel plus asphaltene filter cake. Record the net mass of recovered asphaltenes, $M_{asphaltenes}$ by subtracting the tare weight of the Büchner-style fritted-glass funnel. Quantitatively transfer the dry contents (asphaltenes) from the Büchner-style fritted-glass funnel to a tared 25-mL Borosilicate screw-cap vial. Weigh the vial plus contents, subtract the vial tare, and record the mass of dry asphaltenes, $M_{asphaltenes}$ (dry). Purge the vial with nitrogen or argon gas and store away from light for long-term storage.

9.15 Tare a second 50-mL Borosilicate screw-cap vial. Use a squirt bottle containing toluene to rinse the walls and glass frit of the 500-mL Erlenmeyer flask, which was set aside in 9.9, with 10 to 20 mL of toluene to dissolve any residual materials that may remain on the walls flask. Quantitatively transfer the toluene solution with rinsing to the 50-mL Borosilicate screw-cap vial. Place the vial on a nitrogen gas stream evaporator with heater water bath (35°C), for 24 to 48 h to drive off the solvent toluene. Transfer the vial to an oil bath rotary evaporator (22-mm Hg vacuum, 120°C, 30 min to 1 h) and finish drying the sample to a constant weight. Weigh the vial plus contents, subtract the tare and report the mass of residual asphaltenes, $M_{asphaltenes}$ (residual). Purge vial with nitrogen or argon gas and store away from light for long-term storage.

10. Assembly for Separation of Petrolene (Maltenes) into Three Defined Fractions

10.1 *Assembly of LC-Column Apparatus (Fig. 2)*—The following assembly must be set up in a fume hood. The fume hood should be of sufficient size to accommodate all required components of the apparatus and supplies used to perform this procedure.

10.2 *Pump and Column Assembly (Fig. 2)*—Set up a chromatographic column as shown in Fig. 2. Ensure that the LC-column is secured with lab clamps to a heavy ring stand or a laboratory mounting assembly housed in the fume hood. Assemble a metering pump (flow rate = 0.1 to 10.0 mL/min) by plumbing the metering pump between the sample/solvent flasks that will be used to introduce the solution and eluting solvents into the LC-column and the bottom of the LC-column using two 30.5-cm (12 in.) long pieces of 1.59-mm ID/3.17-mm OD (1⁄16 in. ID/1⁄8 in. OD) TFE-fluorocarbon tubing fitted with standard 6.35-mm (1⁄4 in.) nuts and ferrules. Attach one of the 30.5-cm (12 in.) long pieces of TFE-fluorocarbon tubing with a standard 6.35-mm (1⁄4 in.) nut and ferrule to the in-let side of the pump. Attach the second 30.5-cm (12 in.) piece of TFE-fluorocarbon tubing to both the pump (out-let) and the LC-column in-let with two more standard 6.35-mm (1⁄4 in.) nuts and ferrules.

10.3 *UV Detector w/ Data Acquisition System (Fig. 2)*—Assemble a UV detector by pluming the detector between the out-let port of the LC-column (located at top of column endplate) and the eluate receptacle (graduated cylinders) using additional tubing and tubing fittings adaptable to both the UV detector and the LC-column.

10.4 *Refrigerated Water Bath Circulator Assembly*—Plumb a water bath circulator between the water in-flow nozzle (bottom barbed fitting) of the LC-column water-jacket and the out-flow nozzle of the LC-column water-jacket (top barbed fitting) back to the water bath circulator using 15.9-cm (5⁄8 in.) ID high pressure hose; secure all connection points with hose clamps.

11. Separation of Petrolenes (Maltenes) into Saturates, Naphthene Aromatics and Polar Aromatics Fractions

11.1 Prepare a petrolene (maltene) sample solution by transferring 1.000 ± 0.0001 g of petrolene, prepared in 9 to a tared 25-mL Erlenmeyer flask with stopper (Note 5). Transfer 10.0 ± 0.1-mL of HPLC grade n-heptane to the 25-mL Erlenmeyer flask, stopper the flask and allow the petrolenes to dissolve. Dissolution of the petrolenes will take 3–5 h at ambient temperature (25°C). Dissolution of the petrolene sample may be accelerated by gently agitating (swilling) the sample in a 40–50°C water bath for 30–40 min.

NOTE 5—Petrolenes (maltenes) are generally a much softer material than the asphalt from which they were derived, and thus, may be transferred between flask and vial using a spatula.

11.2 Pack a 70-cm long, 1.5-cm diameter column with calcined alumina (see 7.1) by first removing the top endplate of the column, then slowly pouring alumina into the top of the column with the aid of a small Teflon funnel. Periodically tap on the side of the column with a cork ring while adding the alumna to settle and pack the alumna. The column, which has an open volume of 124-cc should hold 110-g of alumina, which constitutes a dry packing density of 0.90-g/cc for calcined alumina. Insure that a ½-in. gap is present above the top of the bed of alumna and below the lip of the column. Attach the upper endplate snuggly into the collar ensuring not to strip the threads of the endplate.

11.3 Table 1, Footnote A lists a schedule for selecting column size, mass of alumina and volume of elution solvents based on the initial mass of sample to be separated, given a 1.0 % sample loading (that is, mass of sample per mass of alumina).

11.4 Begin the separation of petrolenes into three fractions by pumping *n*-heptane up onto the column to pre-wet the column. Once solvent begins to elute from the column (approximately 70 mL will be required to completely wet the column), collect the eluting solvent in a 10-mL graduated cylinder. Adjust the flow rate to 3.0-mL/min by timing the volume change of solvent eluting from the column with a stop watch. After adjusting the column flow, replace the 10-mL graduated cylinder with a 100-mL graduated cylinder to collect excess solvent prior to introducing the sample onto the column. Activate the refrigerated/heating circulator directly after beginning the introduction of the wetting solvent (*n*-heptane) onto the column. Set the water bath temperature of the refrigerated/heating circulator to 25°C (77°F) and allow the temperature of the column to stabilize during the column pre-wetting step.

11.5 When the column has been pre-wetted, the flow rate adjusted to the recommended flow rate, and the temperature of the column stabilizes, introduce the sample (11.1) onto the column by transferring the petrolene solution from the 25-mL Erlenmeyer flask to the column by placing the up-take tubing end (attached to the in-take of the metering pump) into the Erlenmeyer flask containing the sample solution. Use a ring stand or lab mounting bracket to secure the tubing end in place inside of the Erlenmeyer flask (Note 6). Allow the sample solution to pump up into the column, and as the last portions of solution are taken up by the pump, rinse down the sides of the Erlenmeyer flask and the end of the tubing with approximately 5 to 10 mL of *n*-heptane from a squirt bottle to rinse the entire sample onto the column. Replace the 100-mL graduated cylinder at the collecting end of the column with a 500-mL graduated cylinder to collect the elution containing the saturates fraction. Determining the cut point for the eluting fractions requires close attention, especially during the collection of the saturates and the naphthene aromatics fractions.

NOTE 6— The flask containing the sample solution should be clamped to a ring stand at a 30° angle, and the up-take tubing, which may be secured in place with a thermometer clamp, so that the very end of the tubing is positioned and held in place at the lowest point inside the flask.

TABLE 1 Separation Schedule

Column Feed Volumes		Volume of Elution Collected/Fraction	
Eluant Solvent[A]	mL	Eluate Fraction	mL[B]
n-Heptane	150	Saturates (S)	183
Toluene	33		
Toluene	67	Naphthene-aromatics	142
Methanol/toluene 50/50	75	(NA)	
Trichloroethylene	150	Polar-aromatics (PA)	150
Column hold-up	...		

[A] The current method may be scaled linearly to accommodate separations of larger sample sizes. Solvent volumes listed in Table 1 are representative of a separation of a sample of mass: 1.0 g, loaded onto a column at 1 % mass of sample per mass of column stationary-phase packing (alumina ~ 100-g). Thus, doubling, tripling, etc., the sample size will require doubling, tripling, etc., the mass of alumina and the volumes of eluting solvents listed in Table 1.

[B] Approximate eluate volumes since cut points may be adjusted (10.3.10) and hold-up can vary.

11.6 With the initial introduction of the sample solution onto the column, activate the UV-detector (see Note 7) and monitor the change in absorbance at wavelengths of 350-nm and 400-nm as a function of time (Fig. 3).

NOTE 7—This practice will provide a common reference point for the occurrence of the naphthene aromatics and polar aromatics fractions based on their retention times when measured relative to the point of sample introduction if the separation of materials derived from different crude sources is to be compared.

11.7 Once the sample has been introduced onto the column, temporarily shut off the pump and replace the 50-mL Erlenmeyer flask which contained the sample solution with the first elution solvent, (HPLC grade *n*-heptane, (see Warning below)). Secure the 500-mL graduated Erlenmeyer flask containing the elution solvent to a ring stand or lab mounting bracket, then place the up-take end of the tubing into the flask (that is, secure tubing with a thermometer clamp to hold the tubing in place inside the flask), then re-engage the pump. Throughout this separation procedure note the decrease in the volume of solvents pumped from the 500-mL graduated Erlenmeyer flasks and subsequent increase in elution solvents that are collected in the graduated cylinders to gauge the volumes of solvent that are introduced onto the column. Prior to introducing an elution solvent onto the column, it is recommended that the graduated Erlenmeyer flasks be filled with an excess volume of solvent required to elute a given fraction. For example, the elution of saturates will require the collection of approximately 183 mL of solvent (150 mL of *n*-heptane plus 33 mL of toluene). To monitor the solvent collection, fill a 500-mL graduated Erlenmeyer flask to the 500-mL mark with *n*-heptane and note the decrease in solvent volume until 150 mL of solvent have been removed from the flask. Temporarily stop the pump, remove the flask containing *n*-heptane and replace the *n*-heptane with a second 500-mL graduated Erlenmeyer flask filled to the 500-mL mark with toluene, re-engage the pump and monitor the removal of approximately 33 mL of toluene, which indicates that the saturates fraction have been successfully collected. Introduce new elution solvents to the column in accordance with the schedule in Table 1. **Warning:** At no time should the column packing be allowed to dry out due to the lack of solvent being pumped onto the column.

11.8 The saturates fraction is essentially eluted once the 150 mL of *n*-heptane and 33 mL of toluene have been introduced onto the column. The cut point between the saturates and naphthene aromatics is made by observing the movement of a fluorescent band (and faint brownish discoloration of the alumina coinciding with the fluorescent band), which may be monitored with a 366-nm fluorescent lamp when shined on the column. This band will move up the column packing as soon as the second elution solvent, toluene, is introduced onto the column. Collect the eluate containing saturates in a 500-mL graduated cylinder.

11.9 See Note 8. Make the cut point switch to collect the naphthene aromatics while the fluorescent band is approximately 2 in. below the top of the alumina bed. The complete introduction of toluene (100 ml), followed by the introduction

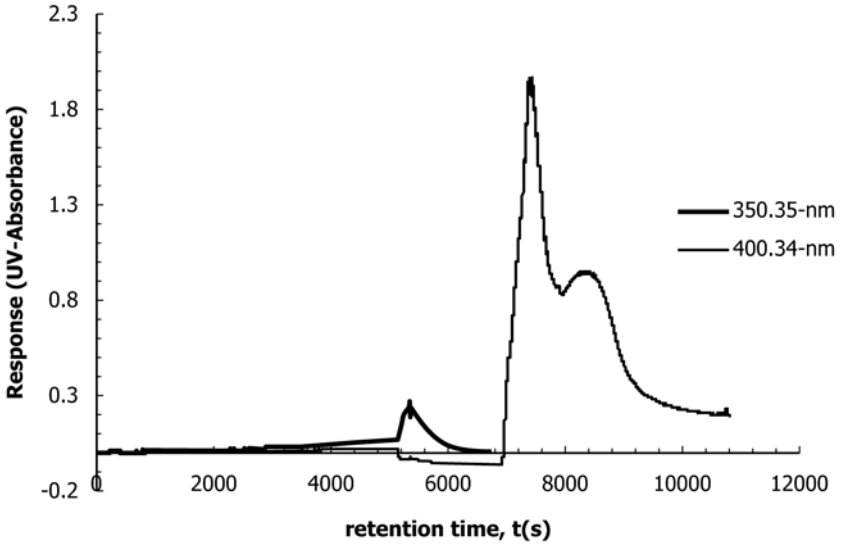


FIG. 3 Chromatogram Depicting Retention Peaks for Naphthene Aromatics and Polar Aromatics Fractions

of 75 mL of a 50:50 toluene:methanol elution solvent, constitutes the separation of the naphthene aromatics fraction and the initiation of the movement of the polar aromatics up the column. Collect the naphthene aromatics fraction in a 250-mL graduated cylinder.

11.10 See Note 8. The eluate containing the saturates fraction is clear in color, while the eluate containing the naphthene aromatics is yellow in color. The cut point between the naphthene aromatics and polar aromatics fractions is much more obvious than the cut point between the saturates and naphthene aromatics fractions as observed by the appearance of a dark band migrating up the column below the fluorescent band and a dark opaque eluate exiting the column. Make the cut point between the naphthene aromatics and polar aromatics fractions as soon as this dark band reaches the very top of the alumina bed. The tubing used to collect the eluate material should be clear enough that once the dark band appears, representing the polar aromatics, switch to the third graduated cylinder. Collect the polar aromatics fraction in a 250-mL graduated cylinder.

NOTE 8—The determination of cut points may be further monitored with the use of a UV detection system, with the exception of the saturates fraction, which are not detectable by UV light. As depicted in Fig. 3, the first peak represents the elution of the naphthene aromatics fraction, which is detected at a wave length of 350-nm, and the second peak represents the elution of the polar aromatics fraction, which is detected at a wave length of 400-nm. Cut points may be made directly after observing the beginning of the rapid increase in the UV-absorbance signal after elution of the naphthene aromatics fraction.

11.11 Recover the three fractions by quantitatively transferring, separately, each of the three eluate solutions from the graduated cylinders to a 1-L pear-shaped flask clamped to a ring stand. Transfer the 1-L pear-shaped flask to a rotary evaporator and distill off all but 10 to 15 mL of the solvent to retain a liquid concentrate. Quantitatively transfer each concentrate to tared 25-mL Borosilicate screw-cap vials. Remove the remaining solvent present in each concentrate by placing the vials on a 35°C heated nitrogen gas-stream evaporator for 24 to 48 h. After solvent removal via the nitrogen gas-stream evaporator, remove the samples from the nitrogen gas-stream evaporator and further dry each sample to a constant mass on an oil-bath rotary evaporator (22-mm Hg vacuum, 120°C, 30 min to 1 h). Allow samples to cool, subtract the vial tare weights and record the mass of each fraction as, M_s : mass (g) of recovered saturates, M_{NA}: mass (g) of recovered naphthene aromatics, and M_{PA}: mass (g) of recovered polar aromatics.

12. Calculation and Report

12.1 Calculate the mass percentages recovered for each fraction collected, and the total recovered material, based on the mass of the original sample, $M_{asphalt}$, as follows:

$$M_{asphaltenes}\,(dry) + M_{asphaltenes}\,(residual) = M_{asphaltenes} \tag{1}$$

$$\left(\frac{M_{asphaltenes}}{M_{asphalt}}\right)\cdot 100\,\% + \left(\frac{M_{petrolenes}}{M_{asphalt}}\right)\cdot 100\,\% = \%\ asphalt\,(recovered) \tag{2}$$

$$\left(\frac{M_{s}}{M_{petrolene}}\right)\cdot 100\,\%\ \left(\frac{M_{NA}}{M_{petrolene}}\right)\cdot 100\,\% + \left(\frac{M_{PA}}{M_{petrolene}}\right)\cdot 100\,\% = \%\ petrolene\,(recovered) \tag{3}$$

$$\left(\frac{M_{S}}{M_{asphalt}}\right)\cdot 100\,\%\ \left(\frac{M_{NA}}{M_{asphalt}}\right)\cdot 100\,\% + \left(\frac{M_{PA}}{M_{asphalt}}\right)\cdot 100\,\% + \left(\frac{M_{asphaltenes}}{M_{asphalt}}\right)\cdot 100\,\% = \%\ total \tag{4}$$

12.1.1 $M_{asphalt}$: mass (g) of asphalt initially separated.
12.1.2 $M_{asphaltenes}$: mass (g) of recovered asphaltenes.
12.1.3 $M_{asphaltenes}(dry)$: mass (g) of loose dried recovered asphaltenes.
12.1.4 $M_{asphaltenes}(residual)$: mass (g) of recovered residual asphaltenes.
12.1.5 $M_{petrolene}$: mass (g) of recovered petrolene.
12.1.6 M_S: mass (g) of recovered saturates.
12.1.7 M_{NA}: mass (g) of recovered naphthene aromatics.
12.1.8 M_{PA}: mass (g) of recovered polar aromatics.

12.2 Report fraction mass percentages to the nearest 0.1-%mass.

13. Precision and Bias

13.1 Precision and bias information will be added in the near future. Table 2 lists data, which includes asphaltene and petrolene (maltenes) mass percentages, and saturates, naphthene aromatics and polar aromatics mass percentages collected from a single laboratory study for separation of an AC-30, SHRP Grade 64-22, Source-Boscan asphalt conducted in duplicate.

TABLE 2 Repeatability Analyses (Single Laboratory), (Asphalt Cement, AC-30, SHRP Grade 64–22, Source-Boscan)

%Fraction	Sample Mass Percentage	
	Run 1	Run 2
Asphaltenes	23.7	25.0
Maltenes	76.2	72.5
% Asphalt Recovery	99.9	97.5
Fraction/petrolene Saturates	10.0	10.3
Naphthene aromatics	31.0	30.1
Polar aromatics	54.0	57.3
% Petrolene Recovery	96.6	97.8

13.2 Since a precision estimate for this standard has not been developed, this test method is to be used for research or informational purposes only. Therefore, this standard should not be used for acceptance or rejection of a material for purchasing purposes.

14. Keywords

14.1 aromatics; asphaltenes; napthene; petrolenes (maltenes); polar aromatics; saturates

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