



Designation: D4124 – 09

Standard Test Method for Separation of Asphalt into Four Fractions¹

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 Analysis³

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

¹ This test method is under the jurisdiction of ASTM Committee D04 on Road and Paving Materials and is the direct responsibility of Subcommittee D04.47 on Miscellaneous Asphalt Tests.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from ASTM as PCN 03-332030-12.

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*-C₅ to *n*-C₁₀ 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

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 \pm 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 (1/4-in.) tubing fittings.

6.2.5 *Refrigerated/Heating Circulator*—a refrigerated/heating circulator, temperature range between 0°C and 100°C \pm 0.1°C stability, with water circulation through the LC-column water jacket via high pressure hose 15.9-mm (5/8 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*,

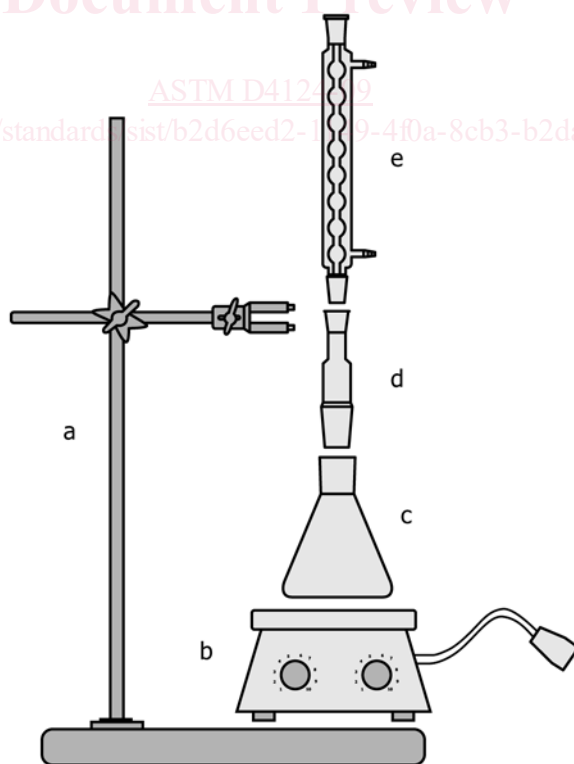
6.3.4 *Graduated Cylinder*,

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

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

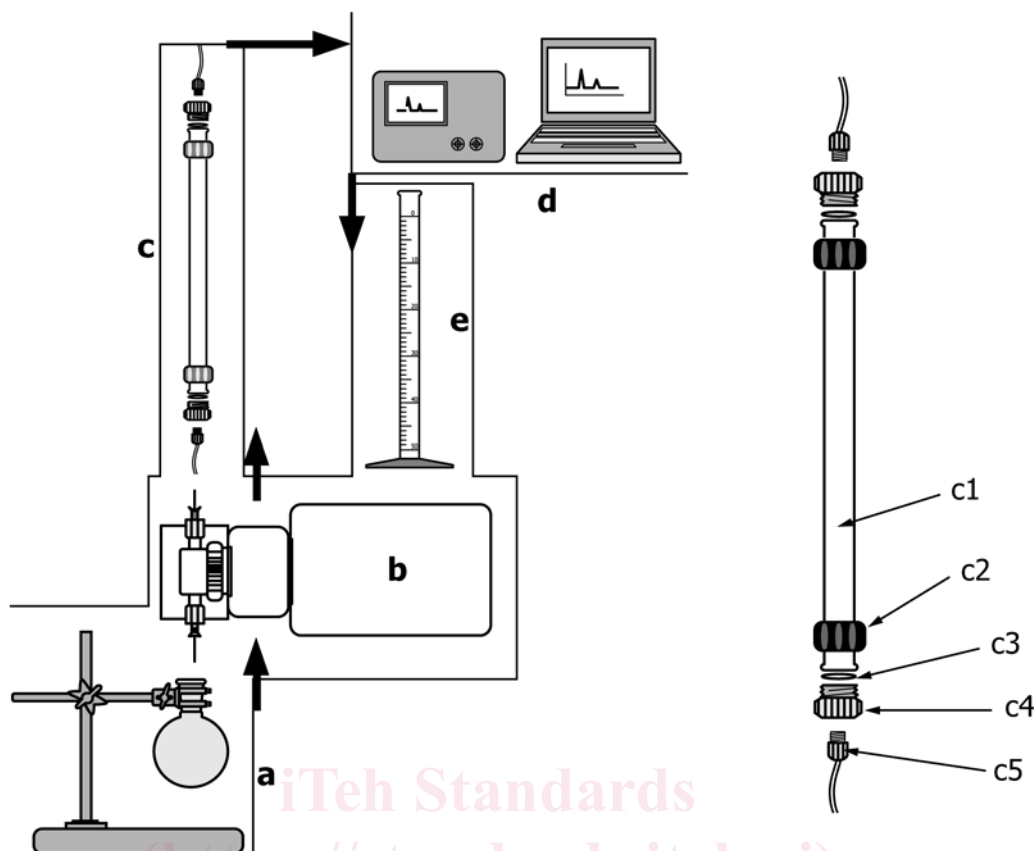
6.3.7 *Rinse Squeeze Bottle*, 0.5-L size, TFE-fluorocarbon.

6.3.8 *Analytical Balance*, 0.0001 g to 250 g \pm 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

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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 (5/8 in. ID).

6.3.15 *Tubing*, clear, resistant to organic solvents, 1.59-mm ID/3.17-mm OD (1/16 in. ID/1/8 in. OD).

6.3.16 *Tubing Fittings*, standard 6.35-mm (1/4 in.) nut with 3.17-mm OD (1/8 in. ID)-hole and 3.17-mm (1/8 in.) ferrule.

7. Absorbent and Reagents

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

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 (Al₂O₃) 80-200 mesh CAS 1344-28-1, Cat # EM-AXO612-3.

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.

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 \pm 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 ($\frac{5}{8}$ 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- μ L 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