



Designation: D4124 – 09 (Reapproved 2018)

## Standard Test Method for Separation of Asphalt into Four Fractions<sup>1</sup>

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 ( $\epsilon$ ) 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 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.

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 8.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

D140 Practice for Sampling Bituminous Materials

<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 in Miscellaneous Asphalt Tests.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

#### 2.2 Other Documents:

Manual on Hydrocarbon Analysis<sup>3</sup>

### 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<sub>n</sub>H<sub>2n</sub>, 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<sub>5</sub> to *n*-C<sub>10</sub> 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

<sup>3</sup> Available from ASTM as MNL3-6TH-EB.

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).<sup>4</sup> 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).

<sup>4</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

6.2.1 *LC Apparatus* (Fig. 2)—(a) ring stand with clamp, flask (25-mL round bottom or Erlenmeyer flask); (b) metering pump; (c) sealed glass LC column; (d) UV detector with data acquisition system (wavelength range 200 to 500 nm at 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.

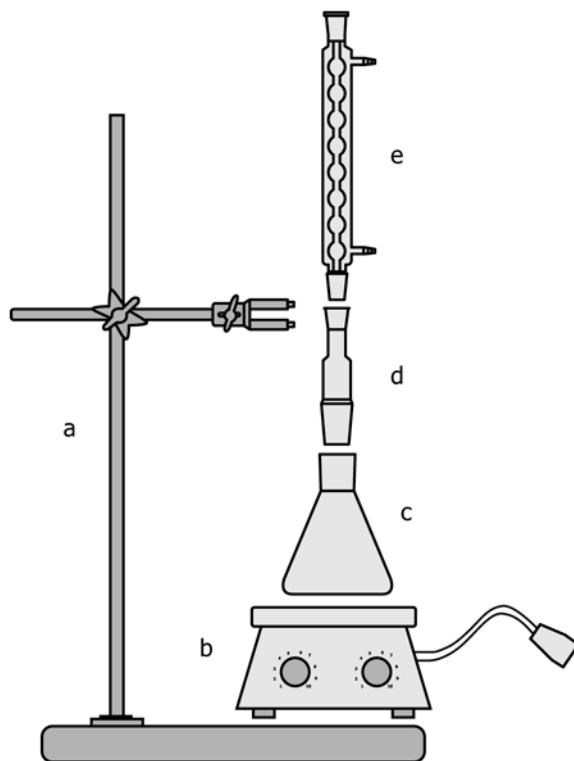
6.2.3 *Metering Pump* (Fig. 2)—Piston and piston chamber will be constructed of materials resistant to deterioration by solvents that will be used to perform the method. Flow rate range of the pump will be 0.1 to 5.0 mL/min  $\pm$  0.1 mL/min flow rate stability.

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 end plates 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 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).

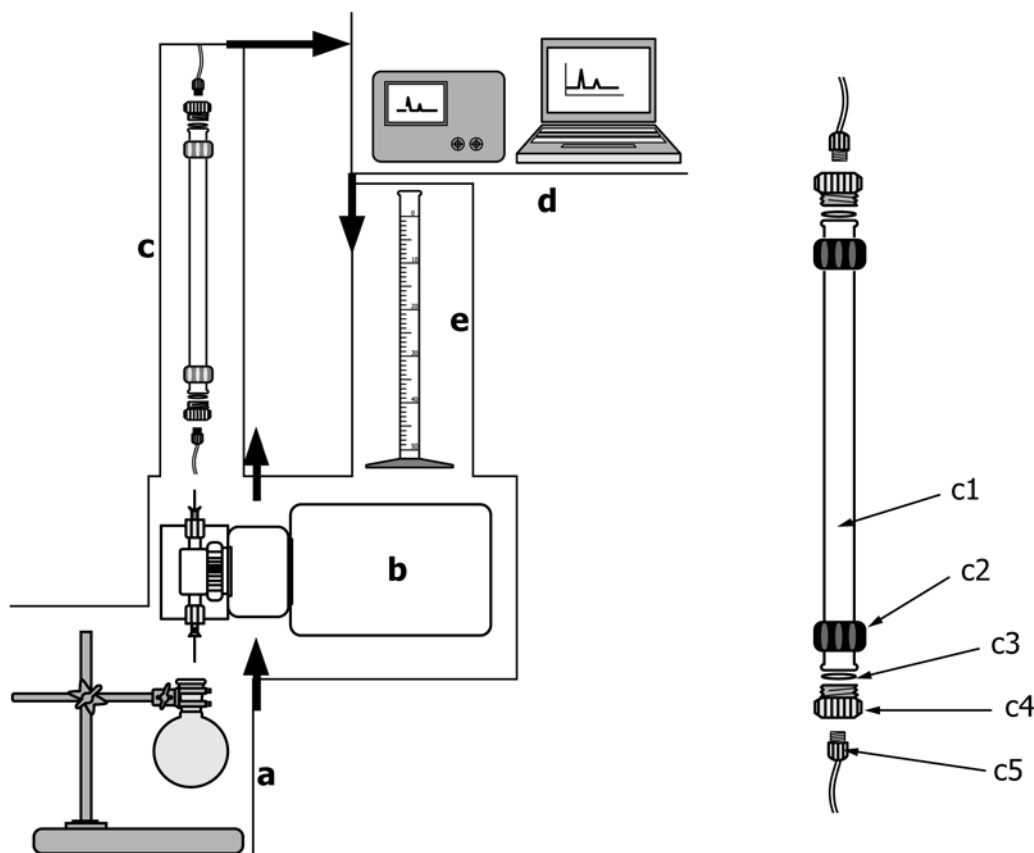
## 6.3 Materials:

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.



NOTE 1—Key: (a) ring stand with 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 with 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) end plate; (c5) tubing nut/ferrule and tubing; (d) UV-VIS spectrophotometric detector (200 to 500 nm at 0.1 nm); (e) graduated cylinders of various sizes for fraction collection.

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

6.3.2 *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 to 15- $\mu$ 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 to 250 g  $\pm$  0.0001 g.

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 ( $\frac{5}{8}$ -in. ID).

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

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

## 7. Absorbent and Reagents

7.1 *Alumina*,<sup>5</sup> 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.<sup>6</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.

<sup>5</sup> 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<sub>2</sub>O<sub>3</sub>) 80-200 mesh CAS 1344-28-1, Cat # EM-AXO612-3.

<sup>6</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.