Designation: D 4124 – 01

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

This standard is issued under the fixed designation D 4124; 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 These test methods cover the separation of four defined fractions from petroleum asphalts. The four fractions are defined as saturates, naphthene aromatics, polar aromatics, and nC$_7$-asphaltenes. These methods 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 the 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 and 15.

2. Referenced Documents

2.1 *ASTM Standards:*

C 670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials[2]

C 802 Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods for Construction Materials[2]

D 140 Practice for Sampling Bituminous Materials[3]

D 3279 Test Method for *n*-Heptane Insolubles[3]

2.2 *Other Documents:*

Manual on Hydrocarbon Analysis[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *asphaltenes or n-heptane insolubles*—insoluble matter that can be separated from asphalt following digestion of the asphalt in *n*-heptane under the specified conditions in these test methods.

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

3.1.3 *petrolenes*—the *n*-heptane-soluble matter recovered following separation of the asphaltenes from the digested mixture under the specified conditions in these test methods.

3.1.4 *polar aromatics*—material desorbed from calcined CG-20 alumina absorbent, after the saturates and naphthene aromatics have been removed, using toluene and trichloroethylene eluants under the conditions specified.

3.1.5 *saturates*—material that, on percolation in a *n*-heptane eluant, is not absorbed on calcined CG-20 alumina absorbent under the conditions specified.

METHOD A

4. Summary of Test Method

4.1 The sample containing the four defined fractions is first separated into *n*-heptane-insoluble asphaltenes and the *n*-heptane-soluble petrolenes. Petrolenes are then adsorbed on calcined CG-20 alumina and further fractionated into the saturate, naphthene aromatic and polar aromatic fractions by downward solvent elution in a glass chromatographic column. Eluted fractions are recovered by solvent removal prior to final weighing. The three eluted fractions plus the *n*-heptane-precipitated (nC$_7$) asphaltenes comprise the four fractions 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. 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 *Glass Chromatographic Column*, [5] 1000 mm long and 31 mm in inside diameter with features as specified in Fig. 1.

6.2 *Utilities*—Steam bath, vacuum source, nitrogen source, and drying oven (Rotavapor solvent stripper and electric heating mantles optional).

[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] *Annual Book of ASTM Standards*, Vol 04.02.

[3] *Annual Book of ASTM Standards*, Vol 04.03.

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

[5] Can be custom-made by any professional glassblower.

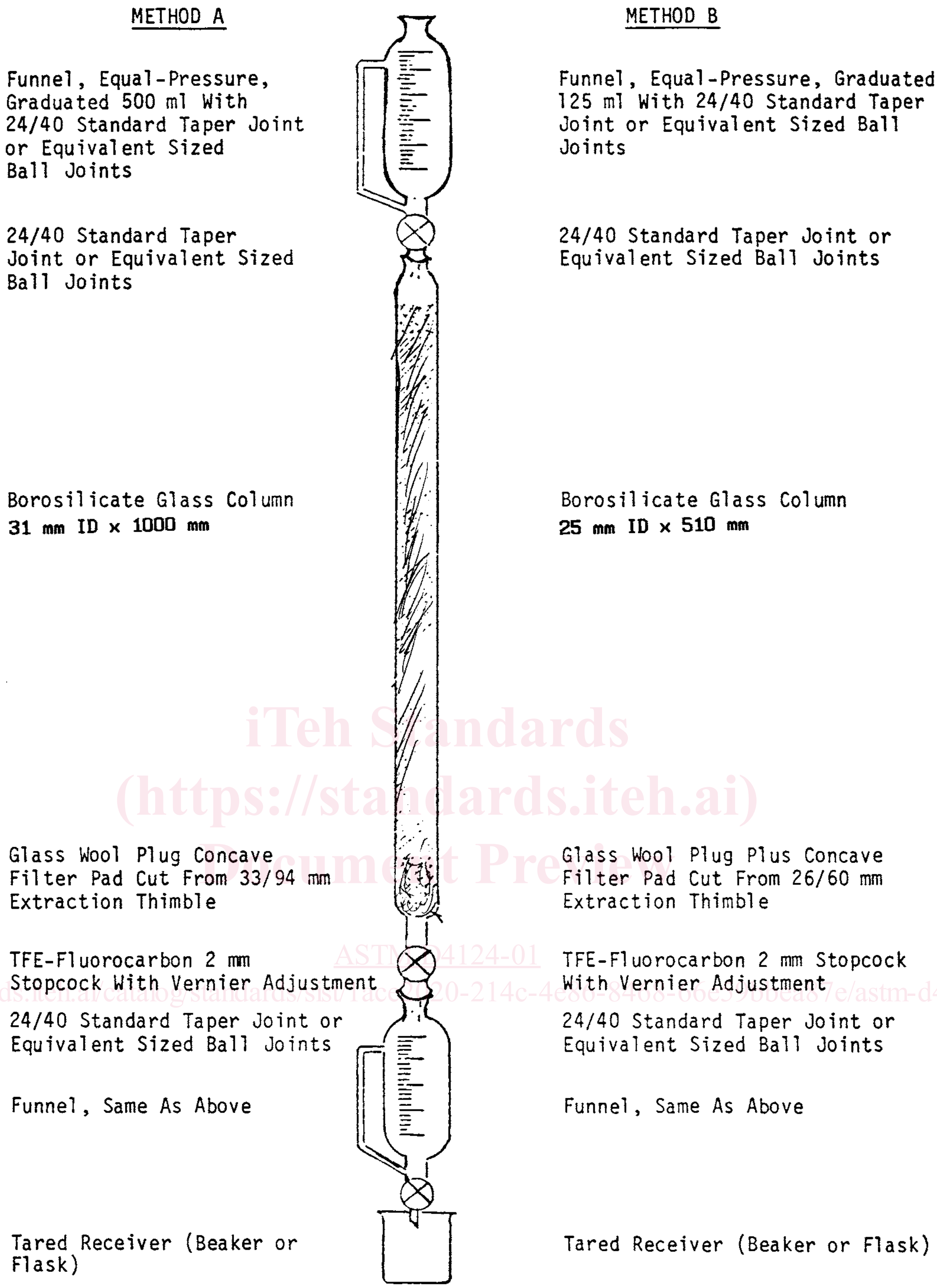
METHOD A
METHOD B
Funnel, Equal-Pressure, Graduated 500 ml With 24/40 Standard Taper Joint or Equivalent Sized Ball Joints
Funnel, Equal-Pressure, Graduated 125 ml With 24/40 Standard Taper Joint or Equivalent Sized Ball Joints
24/40 Standard Taper Joint or Equivalent Sized Ball Joints
24/40 Standard Taper Joint or Equivalent Sized Ball Joints
Borosilicate Glass Column 31 mm ID x 1000 mm
Borosilicate Glass Column 25 mm ID x 510 mm
Glass Wool Plug Concave Filter Pad Cut From 33/94 mm Extraction Thimble
Glass Wool Plug Plus Concave Filter Pad Cut From 26/60 mm Extraction Thimble
TFE-Fluorocarbon 2 mm Stopcock With Vernier Adjustment
TFE-Fluorocarbon 2 mm Stopcock With Vernier Adjustment
24/40 Standard Taper Joint or Equivalent Sized Ball Joints
24/40 Standard Taper Joint or Equivalent Sized Ball Joints
Funnel, Same As Above
Funnel, Same As Above
Tared Receiver (Beaker or Flask)
Tared Receiver (Beaker or Flask)

FIG. 1 Chromatographic Column for Separation of Asphalt by Elution-Adsorption (Method A or B)

6.3 *Beakers*, graduated; *Erlenmeyer flasks*, 400-mL; *Round-Bottom Flasks*, 500-mL, if Rotavapor is used for solvent removal.

6.4 *Funnels*, two, pressure-equalizing, 500-mL.

6.5 *Funnel, Büchner*, 12.5-cm.

6.6 *Funnel, Separatory*, 1-L, TFE-fluorocarbon stopcock preferred.

6.7 *Flask, Suction*, 2-L.

6.8 *Flask, Erlenmeyer*, 2-L, with foil-covered rubber stopper.

6.9 *Rinse Squeeze Bottle*, 0.5 L size, polyethylene or TFE-fluorocarbon.

6.10 *Evaporating Dishes*, porcelain, 16 and 28-cm.

6.11 *Analytical Balance*.

6.12 *Filter Paper*, slow to medium filter speed, qualitative grade, 12.5-cm diameter.

6.13 *Extraction Thimble*, 33/94 mm.

6.14 *Stirrer*, air-powered.

6.15 *Stirring Rod* with suitable foil-covered rubber stopper to fit 2-L Erlenmeyer flask.

6.16 *Glass Wool*, borosilicate.

6.17 *Electric Heat Lamp or Hot Plate*.

7. Reagents and Absorbent

7.1 *Alumina,*[6] CG-20 chromatographic grade, calcined at 413°C for 16 h and stored in an evacuated desiccator or airtight bottles.

7.2 *n-Heptane* (Note 1), 99 minimum mol % (pure grade).

NOTE 1—*n*-Heptane should be totally free of moisture. Pretreatment of *n*-heptane with 5A molecular sieves or by refluxing over calcium hydride may be necessary to remove residual moisture in the solvent.

7.3 *Methanol*, anhydrous, reagent grade.

7.4 *Toluene*, reagent grade.

7.5 *Trichloroethylene*, boiling point 86.5 to 87.5°C.

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. All working areas should be kept free of sparks, flames, or other sources of high temperature.

9. Sampling and Sample Preparation

9.1 Bulk samples taken in accordance with Practice D 140 shall be representative and free of foreign substances. Samples for testing in 10.1.1 can be transferred by chilling to facilitate fracturing the sample or by heating the sample until it has become sufficiently fluid to pour. **Caution:** In no case shall the samples be heated more than 110°C above the expected softening point. Transfer of a representative portion from the bulk sample to a smaller container may be necessary for determination of sample mass to the nearest 0.01 g in 10.1.1.

10. Procedure

10.1 *Separation of Asphaltenes and Petrolenes*:

10.1.1 Weigh to the nearest 0.01 g and place into a 2-L Erlenmeyer flask a sufficient quantity of asphalt (Note 2) so that it yields about 10 g of petrolenes as indicated by the following equation:

$$\text{Sample mass, g} = 1000/100 - \%\ \text{asphaltenes} \quad (1)$$

For paving asphalts, this would be 11 to 13 g of asphalt and slightly more for airblown asphalts. Unless the asphalt is in granular form, warm the flask gently with a heat lamp or hot plate and disperse the asphalt over the bottom and lower sides of the flask before adding the *n*-heptane solvent in the ratio of 100 mL of solvent per 1 g of sample.

NOTE 2—The quantity of asphalt required for 10 g of petrolenes can easily be predetermined in accordance with Test Method D 3279.

10.1.2 Install an air-powered stirrer assembly into the flask prior to placing flask and its contents on a steam bath. The stirring rod should rotate inside a foil-covered rubber stopper that is used to seal the Erlenmeyer flask to reduce the evaporation of *n*-heptane. Maintain the solvent temperature near its boiling point and stir the contents of the flask at a moderate rate until there is no visual evidence of undispersed asphalt adhering to the sides of the flask. Begin timing and continue stirring for an additional 1 h. Normally 1 h is sufficient time for straight reduced asphalts but for airblown or chemically modified asphalts the digestion time should be extended to 1.5 h. After digestion, remove the flask and stirring assembly from the steam bath. Rinse the stirring assembly as it is removed from the flask with *n*-heptane from a squeeze bottle. Cover the flask with a foil-covered rubber stopper and set aside overnight at ambient temperature so the precipitated asphaltenes can settle to the bottom of the flask.

10.1.3 Set up a 12.5-cm diameter Büchner funnel appropriately fitted with a slow to medium filter speed, qualitative-grade filter paper and a 2-L suction flask. The 1-L separatory funnel should be suspended about 25 mm above the center of the filter paper.

10.1.4 Decant as much of the clear heptane-petrolene solution as possible from the mixture prepared in 10.1.2 and place it directly in the separatory funnel.

10.1.5 Wet the filter paper in the Büchner funnel with *n*-heptane from a squeeze bottle and apply sufficient suction to the flask to secure the filter paper firmly to the funnel surface before beginning the filtration step. Add petrolene solution from the separatory funnel at a closely controlled rate and in such a manner that all of the filtering takes place in the center of the paper. The filter paper should be wetted periodically from the squeeze bottle to ensure a tight seal with the funnel surface. After the filtering is completed, it is advisable to empty or replace the suction flask before proceeding with the final phase of filtration process.

10.1.6 Test the filtrate from 10.1.5 for insolubles by placing a drop of the filtrate on a filter paper. Refilter if a ring appears.

10.1.7 Transfer the contents remaining in the Erlenmeyer flask directly to the Büchner funnel, using additional solvent from the squeeze bottle and repeatedly wash the asphaltene cake until the filtrate becomes colorless. Take care to ensure that no insolubles creep over the edges of the filter paper into the filtrate. Next, transfer the filter paper and its contents to a 500-mL beaker and add 150 mL of *n*-heptane. Heat the contents in the beaker for about 30 min with occasional stirring to remove *n*-heptane-soluble materials entrained in the asphaltene cake. Filter the hot solution through the same Büchner funnel fitted with a tared, fresh piece of filter paper, using the prescribed procedures. Continue washing the asphaltene cake until the filtrate is colorless. Test the filtrate for insolubles as in 10.1.6 and repeat this task if a ring appears.

10.2 *Solvent Evaporation*:

10.2.1 Transfer the asphaltene cake on the filter papers (10.1.5 and 10.1.7) to a 16-cm evaporating dish and dry in a 104°C oven until a constant mass is achieved. Record the net mass of asphaltenes recovered and store if desired in a screw-cap bottle.

[6] F-20 grade alumina originally referenced in this standard is no longer available from Alcoa, the manufacturer. The CG-20 alumina now referenced is the replacement supplied by the manufacturer. The test results are very sensitive to the quality and grade of alumina used. Currently there is no data available indicating difference in test results between the F-20 and the CG-20 alumina. If users of this method have historical data, it may be useful to do a comparison between data derived from tests using the two aluminas.