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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography[1]

This standard is issued under the fixed designation D 2549; 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 and determination of representative aromatics and nonaromatics fractions from hydrocarbon mixtures that boil between 232 and 538°C (450 and 1000°F). Alternative procedures are provided for the separation of 2 g or 10 g of hydrocarbon mixture.

NOTE 1—Some components may not be eluted from the chromatographic column for some types of samples under the conditions used in this method.

NOTE 2—Test Method D 2007 is an alternative method of separating high-boiling oils into polar compounds, aromatics, and saturates fractions.

1.2 An alternative procedure is provided to handle samples boiling below 232°C (450°F), but whose 5 % point is above 178°C (350°F) as determined by Test Method D 2887. This procedure is given in Annex A1.

1.3 The values stated in acceptable SI units are to be regarded as the standard. The values given in parentheses are provided for information purposes only.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 2007 Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other PetroleumDerived Oils by the Clay-Gel Adsorption Chromatographic Method[2]

D 2425 Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry[2]

D 2786 Test Method for Hydrocarbon Types Analysis of Gas-Oil Saturate Fractions by High Ionizing Voltage Mass Spectrometry[3]

D 2887 Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography[3]

D 3239 Test Method for Aromatic Types Analysis of Gas-Oil Aromatic Fractions by High Ionizing Voltage Mass Spectrometry[3]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *aromatics fraction*—the portion of the sample desorbed with the polar eluants. The aromatics fraction may contain aromatics, condensed naphthenic-aromatics, aromatic olefins, and compounds containing sulfur, nitrogen, and oxygen atoms.

3.1.2 *nonaromatics fraction*—the portion of the sample eluted with *n*-pentane. The nonaromatics fraction is a mixture of paraffinic and naphthenic hydrocarbons if the sample is a straight-run material. If the sample is a cracked stock, the nonaromatics fraction will also contain aliphatic and cyclic olefins.

4. Summary of Test Method

4.1 A weighed amount of sample is charged to the top of a glass chromatographic column packed with activated bauxite and silica gel. *n*-Pentane is added to the column to elute the nonaromatics. When all of the nonaromatics are eluted, the aromatics fraction is eluted by additions of diethyl ether, chloroform, and ethyl alcohol.

4.2 The solvents are completely removed by evaporation, and the residues are weighed and calculated as the aromatics and nonaromatics fractions of the sample.

5. Significance and Use

5.1 The determination of compound types by mass spectrometry requires, in some instances, a preliminary separation of the petroleum sample into representative aromatics and nonaromatics fractions, as in Test Methods D 2425, D 2786, and D 3239. This test method provides a suitable separation technique for this application.

6. Apparatus

6.1 *Chromatographic Columns*, as shown in Fig. 1. Different chromatographic columns are provided for the analysis of 2 and 10-g samples.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

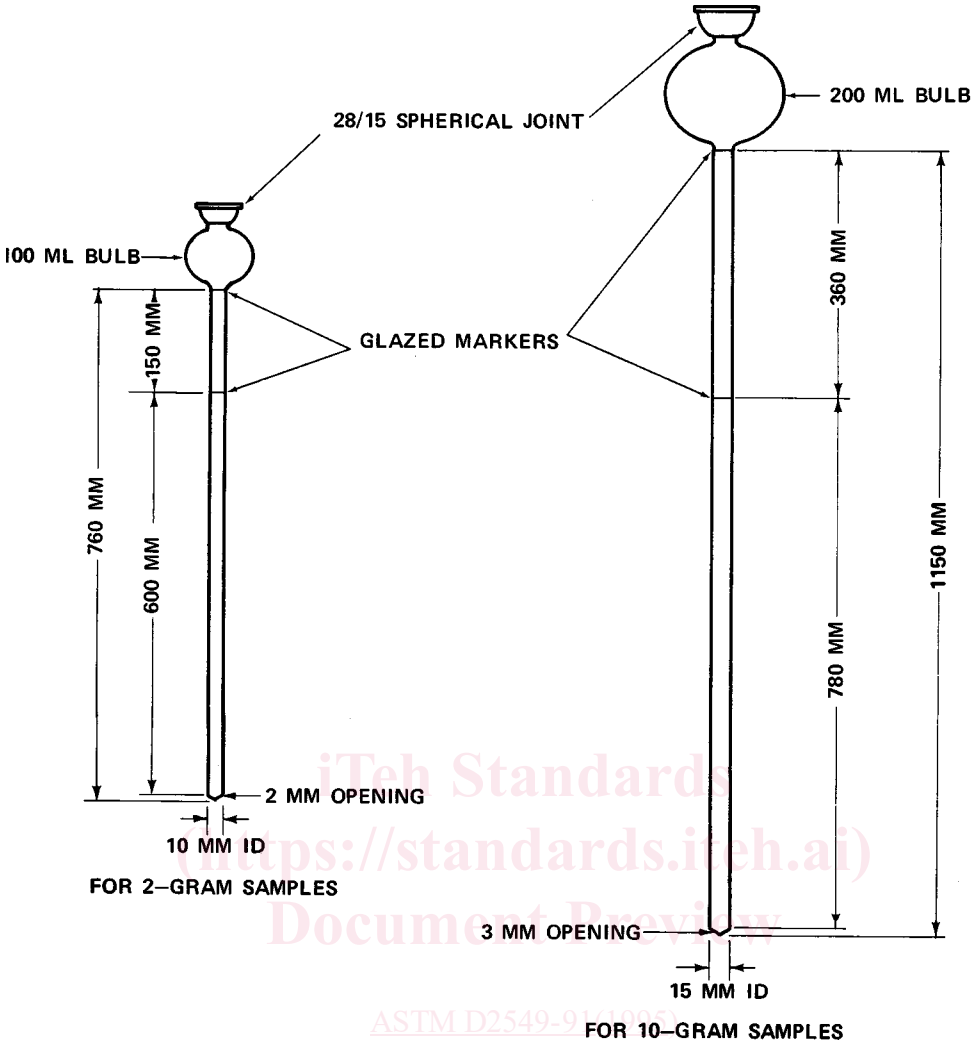

FIG. 1 Chromatographic Columns

6.2 *Beakers*, 100, 250, and 600-mL, inverted-rim type.[4]
6.3 *Steam Bath*.
6.4 *Electric Vibrator*, for packing column.
6.5 *Weighing Bottles or Erlenmeyer Flasks*, 25 and 50 mL.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in this test. Unless otherwise indicated, it is intended that all reagents shall 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 *Bauxite*,[6] 20 to 60-mesh. Before use, activate the bauxite by heating at 538°C (1000°F) for 16 h. Transfer the activated material to an airtight container while still hot and protect thereafter from atmospheric moisture.

7.3 *Chloroform* (**Warning**—Toxic. May be fatal if swallowed. See Annex A2.1.).

7.4 *Cleaning Solution*—Chromic- sulfuric acid (**Warning**—Causes severe burns. A recognized carcinogen, strong oxidizer, contact with organic material may cause fire. See Annex A2.2.).

7.5 *Diethyl Ether*, anhydrous, (**Warning**—Extremely flammable). The ethyl ether used in this test method should be free of peroxides as determined byu the procedure in "Reagent Chemical, American Chemical Society Specifications."

7.6 *Ethyl Alcohol*, denatured, conforming to Formula 2B of the U.S. Bureau of Internal Revenue (**Warning—**Flammable.).

7.7 *Pressuring Gas*, dry air or nitrogen, delivered to the top of the column at a regulated gage pressure of 0 to 2 psi (13.8 kPa) (**Warning—**Compressed gas.).

7.8 *n-Pentane*, commercial grade, aromatic-free. Some

[4] Beakers available from Kontes Glass Co., Vineland, NJ, by ordering "Anti-Creep" beakers and referring to Drawing No. 9413-A.

[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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[6] Bauxite available from Porocel Corp., Little Rock, AR.

samples of waxy stocks may not dissolve completely in *n*-pentane, in which case cyclohexane, commercial grade, aromatic-free, may be substituted for *n*-pentane (**Warning—** Extremely flammable liquid.).

7.9 *Silica Gel*,[7] 100 to 200-mesh.

8. Procedure

NOTE 3—The procedural details differ depending on the initial boiling point of the sample. If the 5 % point is above 178°C (350°F), but below 232°C (450°F) use procedure described in Annex A1. If above 232°C continue as written depending on amount of sample to be analyzed. Instructions specific for 2-g samples are given in 8.4.1-8.4.13, and instructions specific for 10-g samples are given in 8.5.1 and 8.5.8.

8.1 Select the appropriate column, depending on whether 2 or 10 g of sample are to be analyzed. Clean the column with chromic-sulfuric acid, (**Warning—**Causes severe burns. See Annex A2.2.) followed by distilled or demineralized water, acetone, and dry air or nitrogen.

8.2 Introduce a small plug of glass wool into the column, pressing it firmly into the lower end to prevent the flow of silica gel from the column.

8.3 Clamp the column in a vertical position. Add small increments of silica gel, while vibrating the column along its length, until the tightly packed silica gel extends to the lower mark on the chromatographic column. Continue to vibrate the column and add bauxite until the bauxite layer extends to the upper mark on the chromatographic column. Vibrate the column for an additional 3 min after filling is completed.

8.4 If 2 g of sample are to be analyzed, continue as in 8.4.1, otherwise continue as in 8.5.

8.4.1 If the sample is viscous, warm it with intermittent mixing or shaking until it is completely fluid. Transfer a representative sample (approximately 2 g) to a 25-mL weighing bottle or flask. Determine the weight of the sample to the nearest 1 mg by weighing the flask before and after sample transfer. Add 10 mL of *n*-pentane (**Warning—** Extremely flammable liquid.) to the flask and dissolve the sample. If the sample does not dissolve completely in cold *n*-pentane, warm it in warm water or over a steam bath. If the sample does not dissolve in warm *n*-pentane, take a fresh sample and substitute cyclohexane for the *n*-pentane.

8.4.2 Add 10 mL of *n*-pentane to the top of the column to prewet the adsorbent. When the liquid level reaches the top of the bauxite bed, transfer the sample solution from the weighing flask to the top of the column. Rinse the flask with three successive 3-mL washes of *n*-pentane. Add each wash to the top of the column. Then rinse the walls of the column bulb with two 3-mL portions of *n*-pentane, allowing the liquid level to reach the top of the bauxite bed before adding the next portion. Finally add 35 mL of *n*-pentane to the column bulb.

8.4.3 Place a 50-mL graduate beneath the column to collect the eluate. The elution rate should be approximately 1 mL/min.

NOTE 4—Gas pressure (**Warning—**Compressed gas.) can be applied to the top of the column as necessary to maintain the elution rate at approximately 1 mL/min. If the correct pressure setting is known from previous runs, gas pressure may be applied after addition of the last increment of *n*-pentane. Otherwise, gas pressure should be applied when *n*-pentane begins to elute from the column and should be adjusted to give a flow rate of approximately 1 mL/min.

8.4.4 When the *n*-pentane level reaches the top of the bauxite bed, add 80 mL of diethyl ether (**Warning—**Extremely flammable.). Connect the pressuring gas to the top of the column and adjust the pressure to maintain an elution rate of 1 to 2 mL/min.

8.4.5 Collect 50 mL of *n*-pentane eluate in the graduate. Rinse the tip of the column with 1 to 2 mL of *n*-pentane, adding this to the 50 mL in the graduate (Note 5). Label the 50-mL graduate as *n*-pentane eluate.

NOTE 5—The *n*-pentane will have reached the adsorbent bed before the required volume of eluate has been collected in the 50-mL receiver. Continue collection in this receiver after the addition of ether until the proper volume has been collected before changing to the 100-mL graduate.

8.4.6 When the ether level reaches the top of the bauxite bed, release the gas pressure and add 100 mL of chloroform (**Warning—**Toxic. May be fatal if swallowed.) to the top of the column. Reconnect the gas pressuring system and continue the elution. When 80 mL of eluate have been collected in the graduate, rinse the column tip with 1 mL of ether and add the rinse to the 100-mL graduate. Change the receiver to a 250-mL graduate. Label the 100-mL graduate as ether-eluted fraction.

8.4.7 When the chloroform level reaches the top of the bauxite bed, release the gas pressure and add 75 mL of ethyl alcohol (**Warning—**Flammable liquid.). Reconnect the gas pressuring system and continue the elution until the alcohol level reaches the top of the bauxite bed. Release the gas pressure. Rinse the column tip with 1 mL of chloroform adding this to the graduate. Label the 250-mL graduate as chloroform-alcohol-eluted fraction.

8.4.8 Weigh a 100-mL inverted-rim beaker to the nearest 1 mg. Quantitatively transfer the *n*-pentane eluate to this beaker and allow the *n*-pentane to evaporate at room temperature. Cyclohexane, if used as the elution solvent, is evaporated on a steam bath. Evaporation is accelerated in both cases by directing a controlled stream of dry nitrogen downward onto the surface of the liquid.

8.4.9 When all the solvent appears to be evaporated, stop the nitrogen flow, allow the beaker to come to room temperature, and dry the outside of the beaker to remove any condensed moisture. Reweigh the beaker to the nearest 1 mg.

NOTE 6—Complete solvent evaporation is indicated by a tendency of the oil to creep up the side of the beaker.

8.4.10 Repeat the evaporation step for 5-min periods until the weight loss between successive evaporations is less than 20 mg. Heat from a steam bath is generally required during the final evaporation steps to remove completely the elution solvent. The weight of the residue in the beaker is the quantity of the nonaromatics fraction.

8.4.11 Weigh a 250-mL inverted-rim beaker to the nearest 1 mg. Quantitatively transfer the chloroform-alcohol-eluted fraction to this beaker and evaporate on a steam bath with a controlled stream of dry nitrogen directed downward onto the surface of the liquid. When the solvent is evaporated, remove

[7] Silica gel available from W.R. Grace and Co., Davison Chemical Div., Baltimore, MD 21203, by specifying Code 923.