Designation: ~~D2549 – 02 (Reapproved 2017)~~ D2549 – 23

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 D2549; 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~~ Scope*

1.1 This test method covers the separation and determination of representative aromatics and nonaromatics fractions from hydrocarbon mixtures that boil between 232 °C and 538 °C (450 °F 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 D2007 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 D2887. This procedure is given in Appendix X1.

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

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:*[2]

D2007 Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method

D2425 Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry

D2786 Test Method for Hydrocarbon Types Analysis of Gas-Oil Saturates Fractions by High Ionizing Voltage Mass Spectrometry

D2887 Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0C on Liquid Chromatography.

Current edition approved ~~Dec. 1, 2017~~March 1, 2023. Published ~~December 2017~~March 2023. Originally approved in 1966. Last previous edition approved in ~~2012~~2017 as D2549 – 02 ~~(2012).~~(2017). DOI: ~~10.1520/D2549-02R17.~~10.1520/D2549-23.

[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.

***A Summary of Changes section appears at the end of this standard**

D3239 Test Method for Aromatic Types Analysis of Gas-Oil Aromatic Fractions by High Ionizing Voltage Mass Spectrometry
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *aromatics ~~fraction—~~fraction, n—*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.

3.2.2 *nonaromatics ~~fraction—~~fraction, n—*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 D2425, D2786, and D3239. 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 g and 10 g samples.

6.2 *Beakers,* 100 mL, 250 mL, and 600 mL, inverted-rim type.

6.3 *Steam Bath.*

6.4 *Electric Vibrator,* for packing column.

6.5 *Weighing Bottles or Erlenmeyer Flasks,* 25 mL 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.[3] 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.

[3] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, DC. For ~~Suggestions~~suggestions on the testing of reagents not listed by the American Chemical Society, see ~~*Annual*~~*Analar 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.

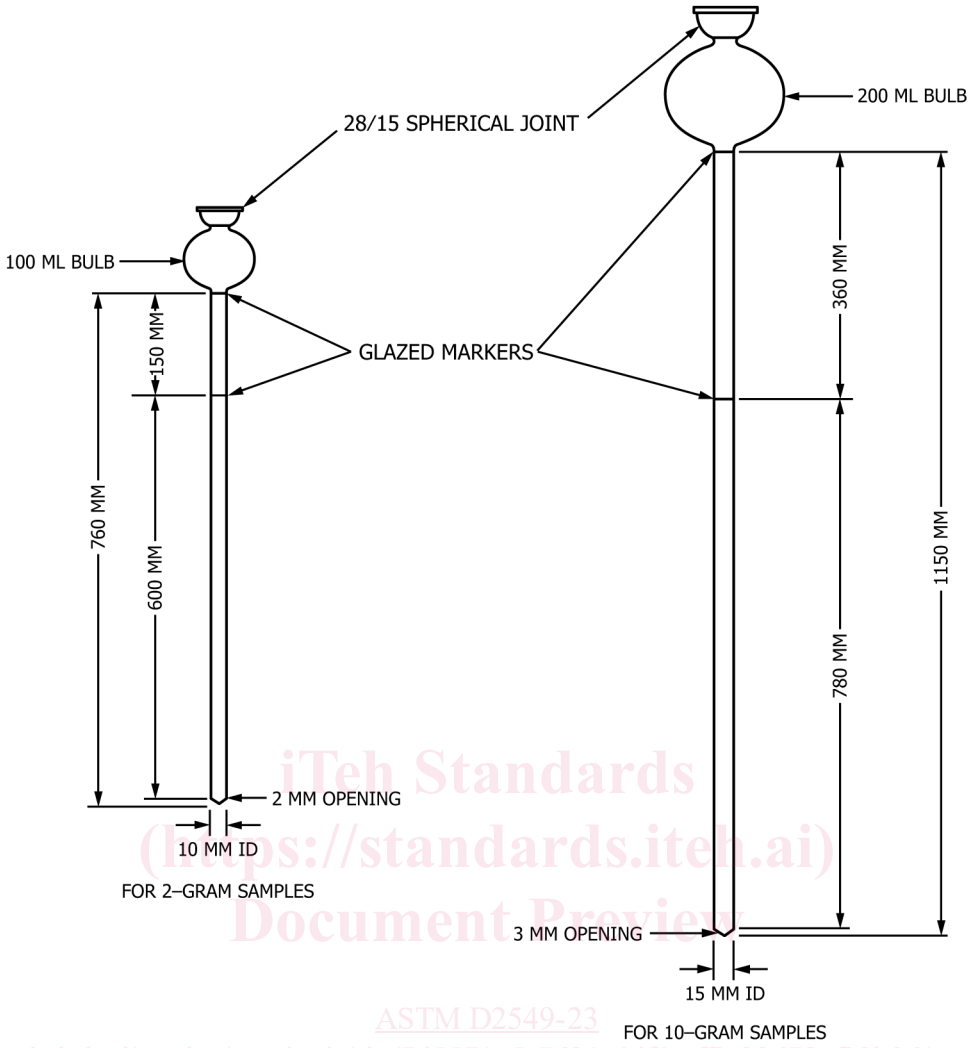

FIG. 1 Chromatographic Columns

7.2 *Bauxite,*[4] 20 mesh 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.~~Warning)~~ ~~—Toxic. May be fatal if swallowed.)~~

7.4 *Cleaning Solution*—Chromic-sulfuric ~~acid.~~acid (**Warning—** Causes severe burns. A recognized carcinogen, strong oxidizer, contact with organic material may cause fire~~Warning);— Causes severe burns. A recognized carcinogen, strong oxidizer, contact with organic material may cause fire.)~~ or other glassware detergents that are a homogeneous blend of sodium linear alkylaryl sulfonate, alcohol sulfate, phosphates, and carbonates. (**Warning—**Toxic if swallowed.)

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

[4] The sole source of supply of the bauxite known to the committee at this time is Porocel Corp., Little Rock, AR. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee[1], which you may attend.

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

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

7.8 *n-Pentane,* commercial grade, aromatic-free. Some 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.~~Warning—~~)~~Extremely flammable liquid.)~~

7.9 *Silica Gel,*[5] 100 mesh 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 Appendix X1. 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 g or 10 g of sample are to be analyzed. Clean the column with either chromic-sulfuric acid (**Warning—**Causes severe burns~~Warning—~~),~~Causes severe burns),~~ or a glassware detergent 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 mass 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.~~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.~~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.

[5] The sole source of supply of the silica gel known to the committee at this time is W.R. Grace and Co., Davison Chemical Div., Baltimore, MD 21203, by specifying Code 923. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee[1], which you may attend.

8.4.4 When the *n*-pentane level reaches the top of the bauxite bed, add 80 mL of diethyl ~~ether~~ether. (**Warning—**Extremely flammable.~~Warning—)Extremely flammable).~~ Connect the pressuring gas to the top of the column and adjust the pressure to maintain an elution rate of 1 mL ⁄min 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 mL 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.~~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~~alcohol. (**Warning—**Flammable liquid.~~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 mass 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 mass 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 the beaker from the steam bath, cool to room temperature, and add quantitatively the ether-eluted fraction. Evaporate the ether at room temperature as described in 8.4.8 – 8.4.10. Determine the mass of the residue (aromatics fraction) to the nearest 1 mg.

8.4.12 The mass of the aromatics plus the nonaromatics fraction recovered must equal at least 95 % of the sample charged. If 95 % recovery is not obtained, repeat the test. Recoveries greater than 100 % indicates incomplete removal of solvent or the condensation of moisture in the beakers.

8.4.13 Transfer the aromatics and nonaromatics fractions into suitable size vials for storage pending further analysis.

8.5 If 10 g of sample are to be analyzed, continue as in 8.5.1.

8.5.1 Warm the sample with intermittent mixing or shaking until it is completely fluid. Transfer a representative sample (approximately 8 g to 10 g) to a 50 mL weighing bottle or flask. Determine the mass of the sample to the nearest 1 mg by weighing the flask before and after sample transfer. Add 20 mL of *n*-pentane 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 *n*-pentane.

8.5.2 Add 45 mL of *n*-pentane to the top of the prepacked large column to prewet the adsorbent. When the *n*-pentane 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 level of each portion to reach the top of the bauxite bed before adding the next portion. Finally add 70 mL of *n*-pentane to the column bulb.

8.5.3 Place a 200 mL graduate beneath the column to collect the eluate. The elution rate should be approximately 3 mL/min.

NOTE 7—Air or nitrogen pressure may be applied to the top of the column as necessary to accomplish and maintain a satisfactory elution rate. Three to five pounds of pressure generally is sufficient. If the correct pressure setting is known from previous runs, gas pressure can 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 3 mL/min.

8.5.4 When the *n*-pentane level reaches the top of the bauxite bed, add 100 mL of diethyl ether. Connect the pressuring gas to the top of the column and adjust the pressure to maintain an elution rate of 3 mL/min to 5 mL/min.

8.5.5 Collect 130 mL of eluate in the graduate. Rinse the tip of the column with 1 mL to 2 mL of *n*-pentane, adding this to the 130 mL in the graduate. Change the receiver to a 100 mL graduate (Note 8). Label the 200 mL graduate as *n*-pentane eluate.

NOTE 8—The *n*-pentane will have reached the absorbent bed before the required volume of eluate has been collected in the 200 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.

8.5.6 When the ether level reaches the top of the bauxite bed, release the gas pressure and add 100 mL of chloroform to the top of the column. Reconnect the gas pressuring system and continue with the elution. When 100 mL of eluate have been collected in the graduate, rinse the column tip with 1 mL of ether and then change the receiver to a 500 mL graduate. Label the 100 mL graduate as ether-eluted fraction.

8.5.7 When the chloroform level reaches the top of the bauxite bed, release the gas pressure and add 175 mL of ethyl alcohol. Reconnect the gas pressuring systems 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 500 mL graduate as chloroform-alcohol-eluted fraction.

8.5.8 Weigh a 250 mL inverted rim beaker to the nearest 1 mg. Quantitatively transfer the *n*-pentane eluate to this beaker and evaporate the solvent on a steam bath. Evaporation can be accelerated by directing a controlled stream of dry nitrogen downward onto the surface of the liquid. Complete the workup of the nonaromatics fraction as described in 8.4.9 and 8.4.10.

8.5.9 Weigh a 600 mL inverted rim beaker to the nearest 1 mg (Note 9). Complete the workup of the aromatics fraction as described in 8.4.11 – 8.4.13.

NOTE 9—The 600 mL inverted-rim beakers from some sources can exceed the capacity of the standard analytical balance, in which case a 250 mL inverted rim beaker can be used, and the chloroform-alcohol-eluted fraction evaporated in increments.

9. Calculation

9.1 Calculate the percentage of the aromatics fraction and the nonaromatics fraction as follows:

$$\text{Aromatics fraction, wt \%} = [A/(A+B)] \times 100 \quad (1)$$

$$\text{Nonaromatics fraction, wt \%} = [B/(A+B)] \times 100 \quad (2)$$

where:

A = mass of aromatics fraction recovered, and
B = mass of nonaromatics fraction recovered.

10. Precision and Bias

10.1 The following criteria should be used for judging the acceptability of results (95 % probability):

10.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under

constant operating conditions on identical test material would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty: 0.4 % by mass for 10 g of sample; and 1.4 % by mass for 2 g of sample.

10.1.2 *Reproducibility*—The difference between ~~two,~~two single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty: 1.6 % by mass for 10 g of sample; and 1.5 % by mass for 2 g of sample.

NOTE 10—The procedure for analyzing 2 g of sample gives recoveries of aromatics fractions that are on average 0.35 % by mass lower than the procedure for analyzing 10 g of sample.

10.2 *Bias*—Bias cannot be determined because there are no reference materials suitable for determining the bias in this test method.

NOTE 11—The precision of the procedure in Appendix X1 has not been determined.

11. Keywords

11.1 aromatics fraction; elution chromatography; high-boiling oils; nonaromatics fraction

APPENDIX

(Nonmandatory Information)

X1. LOWER BOILING SAMPLE PROCEDURE

X1.1 Scope

X1.1.1 This procedure covers the separation and determination of representative aromatics and nonaromatics fractions from hydrocarbon mixtures whose 5 % boiling point is below 232 °C (450 °F), but above 178 °C (350 °F).

X1.2 Summary of Method

X1.2.1 A Kuderna-Danish apparatus is used to evaporate solvents from the aromatic and nonaromatic fractions.

X1.3 Significance and Use

X1.3.1 This procedure extends the range of this test method to separate the samples whose boiling range is specified in Test Methods D2425, D2786, and D3239, all of which refer to this method to provide fractions for analyses.

X1.4 Apparatus

X1.4.1 *Kuderna-Danish Evaporator:*