Designation: D 2894 – 73

Standard Method for ANALYSIS OF CALCIUM AND BARIUM PETROLEUM SULFONATES BY LIQUID CHROMATOGRAPHY[1]

This Standard is issued under the fixed designation D 2894; 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.

1. Scope

1.1 This method covers the determination of mineral oil, calcium or barium sulfonate, average molecular weight, water, and specific gravity of crude and refined natural and synthetic calcium and barium sulfonates.

NOTE 1—A method for analysis of the same type of materials is described in ASTM Method D 1216, Analysis of Calcium and Barium Petroleum Sulfonates.[2]

NOTE 2—The values stated in U.S. customary units are to be regarded as the standard.

2. Summary of Methods

2.1 The sample is dissolved in ethyl ether and converted to sulfonic acid, using dilute hydrochloric acid. The sulfonic acid and mineral oil, after extraction, are converted to sodium sulfonate and the isolated sodium sulfonate and mineral oil dissolved in chloroform. An aliquot of the chloroform solution is adsorbed on silica gel. The oil is eluted with chloroform and the sulfonate with ethyl alcohol, and both are determined gravimetrically. Average molecular weight is calculated from the average equivalent weight of the isolated sodium sulfonate, which is determined by ashing a portion of the isolated sodium sulfonate. Water is determined by ASTM Method D 95, Test for Water in Petroleum Products and Bituminous Materials By Distillation.[2] Specific gravity is determined by pycnometer.

3. Apparatus

3.1 *Chromatographic Column*, made of glass and consisting of a reservoir and a separator section, and fitted with TFE-fluorocarbon stopcock with a 2-mm bore, as shown in Fig. 1 of ASTM Method D 2548, Analysis of Oil-Soluble Sodium Petroleum Sulfonates by Liquid Chromatography.[2] A column with a detachable reservoir connected by a standard-taper joint may be used.

3.2 *Steam Bath.*

3.3 *Vacuum Desiccator*, shielded.

3.4 *Vacuum Oven*, capable of being maintained at 212 F (100 C) and connected to 22 to 25 in. (259 to 635 mm) Hg vacuum.

3.5 *Muffle Furnace*, capable of operating at 1500 to 1800 F (800 to 1000 C).

3.6 *Water Bath*, capable of being maintained at 77 ± 0.3 F (25 ± 0.2 C).

3.7 *Distillation Apparatus*, as described in Method D 95.

3.8 *Dish*, platinum, 100-ml capacity.

3.9 *Pycnometer*, as shown in Fig. 2 of Method D 1216. To calibrate, weigh to the nearest 1 mg, with cap in place, then fill with distilled water at 60 to 68 F (15 to 20 C) and place in a water bath at 77 ± 0.3 F (25 ± 0.2 C). After 30 min, adjust the water meniscus at the top of the neck so that it is exactly level. To obtain a flat meniscus, add a minute amount of wetting agent to the water surface. Remove the pycnometer from the bath and dry the outside. Replace the cap and weigh to the nearest 1 mg. Record the weight of water contained as W_c.

4. Reagents and Materials

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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

[1] This method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants.

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[2] *Annual Book of ASTM Standards*, Part 18.

[3] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopeia."

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.

4.2 *Acetone.*

4.3 *Chloroform.*

4.4 *Ethyl Alcohol (95 percent)*—Either pure grain or denatured ethyl alcohol conforming to Formula 3A of the U.S. Bureau of Internal Revenue.

4.5 *Ethyl Ether.*

4.6 *Hydrochloric Acid (1+1)*—Add 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1 volume of water.

4.7 *Hydrochloric acid (1+3)*—Add 1 volume of concentrated HCl to 3 volumes of water.

4.8 *Isopropyl Alcohol (99 percent)*—Water content shall be 0.9 percent maximum.

4.9 *Phenolphthalein Indicator Solution (10 g/liter)*—Dissolve 1 g of phenolphthalein in 100 ml of ethyl alcohol (50 percent).

4.10 *Silica Gel*, 60 to 200-mesh.[4]

4.11 *Sodium Hydroxide Standard Solution (1 N)*—Prepare and standardize a 1 *N* aqueous, carbonate-free solution of sodium hydroxide (NaOH).

4.12 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H_2SO_4).

5. Conversion of Calcium or Barium Sulfonate to Sodium Sulfonate

5.1 *Conversion of Calcium or Barium Sulfonate to Sulfonic Acid:*

5.1.1 Transfer approximately 10 g of the sample, weighed to the nearest 0.001 g, into a 250-ml Erlenmeyer flask, designating this weight as *A*. Add 50 ml of ethyl ether and stir to dissolve the sample. Add 100 ml of HCl (1+1) and mix thoroughly until reaction is complete.

5.1.2 Quantitatively transfer the mixture to a 250-ml separatory funnel. Shake well, let settle, and draw the aqueous acid layer into a second 250-ml separatory funnel. Extract the aqueous acid layer with three 50-ml portions of ethyl ether, using the ethyl ether to rinse the Erlenmeyer flask first. Combine all the ethyl ether extracts in the first separatory funnel and wash with 50 ml of HCl (1+3). Combine all the aqueous acid layers and re-extract them with 50 ml of ethyl ether. Combine all the ethyl ether extracts in a 400-ml beaker and evaporate the ethyl ether on a steam bath until approximately 10 ml of solution remain.

5.2 *Conversion of Sulfonic Acid to Sodium Sulfonate*—Add 75 ml of ethyl alcohol (95 percent) to the ethyl ether concentrate and neutralize with 1 *N* NaOH solution to a phenolphthalein end point. Evaporate the ethanolic solution of sodium sulfonate on the steam bath, adding small portions of acetone or isopropyl alcohol (99 percent) to aid in removing water. Using a volumetric flask dissolve the sodium sulfonate and oil residue in enough chloroform to make exactly 100 ml of solution.

6. Preparation of Column

6.1 With the stopcock closed, pour 80 to 100 ml of chloroform in the column, and push a wad of cotton to the bottom with a rod (Note 3). Compress the cotton enough to hold back the silica gel but not enough to impede the flow of solvent.

NOTE 3—A coarse fritted disk made of borosilicate glass may be used in place of the cotton wad.

6.2 Pour 15 ± 1 g of silica gel into the column containing the chloroform. The packed column must be free of air bubbles to avoid channeling. Start the flow of chloroform by opening the stopcock. When the liquid level is within ½ in. (12.7 mm) of the surface of the gel, close the stopcock.

NOTE 4—Never allow the liquid level to fall below the surface of the silica gel.

7. Separation of Mineral Oil and Sodium Sulfonate

7.1 *Adsorption of Sample*—Transfer exactly 25 ml of the chloroform solution of sodium sulfonate and mineral oil (5.2) to the column, being careful to prevent channeling.

7.2 *Elution of Oil*—If a column with a coarse fritted disk is being used, place a small filter funnel containing a plug of cotton under the stopcock of the column.

7.2.1 Tare a 250-ml beaker, to the nearest 0.0001 g, and place it under the column or under the funnel, if used. Open the stopcock and adjust the flow rate to between 1 and 5 drops/s. Maintain the flow rate throughout the elution of the oil and sulfonate.

[4] Silica gel, Grade 62, obtainable from the Davison Chemical Corp., Baltimore, Md., has been found satisfactory for this purpose.