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## Standard Test Method of Analysis of Oil-Soluble Petroleum Sulfonates by Liquid Chromatography<sup>1</sup>

This standard is issued under the fixed designation D3712; 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 analysis of refined and crude natural and synthetic oil-soluble sulfonate products. Resins, if present, are recovered with the oil phase and carboxylates are recovered as sulfonates.

1.2 This test method covers the determination of mineral oil, sodium sulfonate, inorganic salts, water, basicity or acidity, average molecular weight, and relative density of sodium sulfonate products.

1.3 This test method covers the determination of mineral oil, sulfonate, water, base number, average molecular weight, and relative density of calcium, barium, magnesium, and ammonium sulfonate products.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *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:<sup>2</sup>

**D95** Test Method for Water in Petroleum Products and Bituminous Materials by Distillation

**D2896** Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration

<sup>1</sup> 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.

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This test method was adopted as a joint ASTM-IP standard.

<sup>2</sup> 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.

### 3. Terminology

#### 3.1 Symbols:

3.1.1 Following are definitions of the symbols used in Section 17, and as noted in the sections in parentheses.

A	=	grams of sample of calcium, barium, magnesium, or ammonium sulfonate (8.1.1).
B	=	volume of chloroform solution, mL (10.1).
C	=	grams of sample of sodium sulfonate (10.1.1).
D	=	grams of oil recovered (10.4).
E	=	grams of sodium sulfonate recovered (10.5).
F	=	grams of residue from chloroform blank (10.6).
G	=	grams of residue from alcohol blank (10.6).
H	=	grams of sodium sulfonate (11.1).
I	=	grams of sodium sulfate ash from sodium sulfonate (11.2).
J	=	T/KS.
K	=	valence of cation.
S	=	average equivalent weight of sodium sulfonate (17.1.4).
T	=	average molecular weight of calcium, barium, magnesium, or ammonium sulfonate (17.1.5).
U	=	percentage of sodium sulfonate (17.1.2).
V	=	percentage of calcium, barium, magnesium, or ammonium sulfonate (17.1.3).
W <sub>c</sub>	=	grams of water contained in pycnometer at 25°C (6.9).
W <sub>s</sub>	=	grams of sample contained in pycnometer at 25°C (15.1).
X	=	grams of sodium sulfonate sample for basicity (12.1).
Y	=	volume of standard H <sub>2</sub> SO <sub>4</sub> or NaOH solution used to determine basicity or acidity (12.1).
Z	=	normality of standard H <sub>2</sub> SO <sub>4</sub> or NaOH solution to determine free basicity or acidity (12.1).
AA	=	grams of sodium sulfonate product ashed (13.1).
BB	=	grams of sodium sulfate from inorganic salt determination (13.1).
CC <sub>A</sub>	=	percentage of free acidity of sodium sulfonate product as H <sub>2</sub> SO <sub>4</sub> (17.1.6).
CC <sub>B</sub>	=	percentage of free basicity of sodium sulfonate product as NaOH (17.1.6).
DD	=	percentage of inorganic salts as sodium sulfate (17.1.7).

### 4. Summary of Test Method

4.1 The sample, except a sodium sulfonate product, is dissolved in ethyl ether and converted to sulfonic acid, using dilute hydrochloric acid. The sulfonic acid after extraction is converted to sodium sulfonate and the isolated sodium sulfonate and mineral oil are dissolved in chloroform. An aliquot of the chloroform solution, or a sample of a sodium sulfonate product, dissolved in chloroform, is placed on a silica gel column. The oil is eluted with chloroform, the sulfonate with ethyl alcohol, and both are determined gravimetrically. Average molecular weight is calculated from the average equivalent

weight of the sodium sulfonate, which is determined by ashing a portion of the isolated sodium sulfonate.

4.2 Water is determined by Test Method D95. Base number is determined by Test Method D2896. Relative density is determined by pycnometer.

### 5. Significance and Use

5.1 This test method provides a means of determining sulfonate content and of classifying and characterizing natural and synthetic petroleum sulfonate products by sulfonate content and average molecular weight. Purity of sodium sulfonate products is measured by basicity and inorganic salt contents and the reserve alkalinity of alkaline earth sulfonates by the total base number.

### 6. Apparatus

6.1 *Chromatographic column*, made of glass and consisting of a reservoir and separator section, and fitted with a TFE-fluorocarbon stopcock with a 2-mm bore, as shown in Fig. 1. A column with a detachable reservoir connected by a standard-taper joint can be used.

6.2 *Steam Bath*.

6.3 *Vacuum Desiccator*, shielded.

6.4 *Vacuum Oven*, capable of being maintained at 100°C (212°F) and connected to 559 to 635 mm (22 to 29 in.) Hg vacuum.

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

6.6 *Dish*, platinum, 100-mL capacity.

6.7 *Distillation Apparatus*, as described in Test Method D95.

6.8 *Water Bath*, capable of being maintained at  $25 \pm 0.2^\circ\text{C}$  ( $77 \pm 0.3^\circ\text{F}$ ).

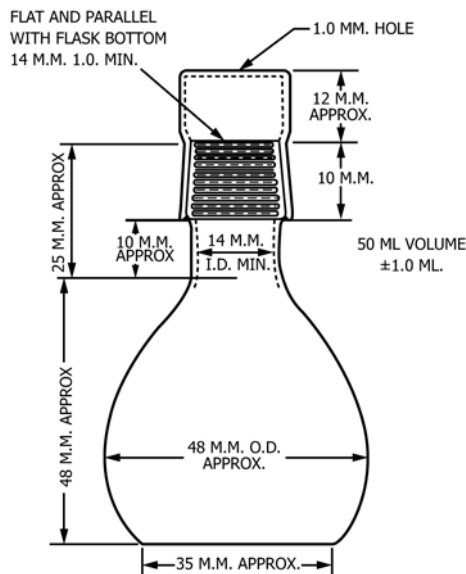


FIG. 2 Pycnometer for Determining Relative Density of Petroleum Sulfonates

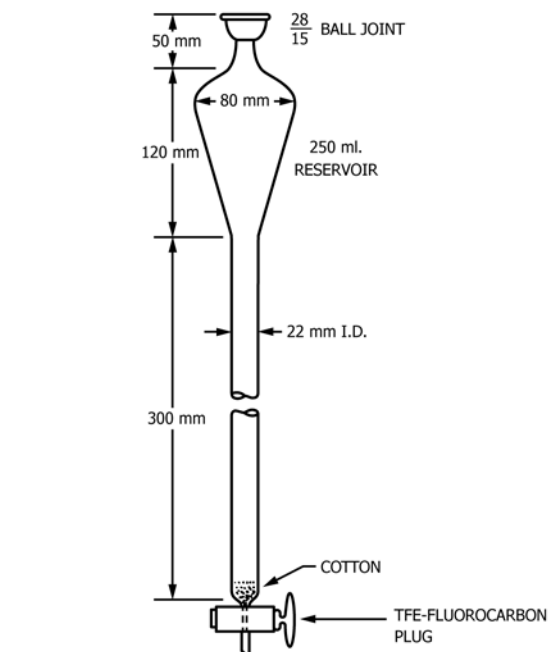


FIG. 1 Chromatographic Column

6.9 *Pycnometer*, as shown in Fig. 2. To calibrate, weigh to the nearest 1 mg with cap in place; then fill with distilled water at 15 to 20°C (60 to 68°F) and place in water bath at  $25 \pm 0.2^\circ\text{C}$  ( $77 \pm 0.3^\circ\text{F}$ ). After 30 min, adjust the water meniscus at the top of the neck so 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 mass of water contained as  $W_c$ .

### 7. Reagents and Materials

7.1 *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.<sup>3</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.

7.2 *Chloroform* (**Warning**—Flammable, Health Hazard.).

7.3 *Ethyl Alcohol (95 %)*—Either pure grain or denatured ethyl alcohol conforming to Formula 3A of the U.S. Bureau of Internal Revenue (**Warning**—Flammable. Denatured alcohol cannot be made nontoxic.).

<sup>3</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.

7.4 *Ethyl Ether* (**Warning**—Extremely flammable. Harmful if inhaled. May cause eye injury. Effects may be delayed. May form explosive peroxides. Vapors may cause flash fire. Moderately toxic. Irritating to skin.).

7.5 *Filter Paper*, slow-filtering, ashless, gravimetric.

7.6 *Hydrochloric Acid (Concentrated)*—(**Warning**—Poison. Corrosive. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled.).

7.6.1 *Hydrochloric Acid, Dilute (1 + 1)*—(See **Warning** in 7.6.) One volume of concentrated hydrochloric acid (HCl) is added to 1 volume of water.

7.6.2 *Hydrochloric Acid, Dilute (1 + 3)*—(See **Warning** in 7.6.) One volume of concentrated hydrochloric acid (HCl) is added to 3 volumes of water.

7.7 *Isopropyl Alcohol (99 Mass %)*—Water content shall be 0.9 mass % maximum. (**Warning**—Flammable.)

7.7.1 *Isopropyl Alcohol, Dilute (1 + 1)*—One volume of 99 mass % isopropyl alcohol is diluted with 1 volume of water.

7.8 *Methyl Orange Indicator Solution*—Dissolve 1.0 g of methyl orange in water and dilute to 1 L.

7.9 *Phenolphthalein Indicator Solution*—Dissolve 1 g of phenolphthalein in 100 mL of 50 mass % ethyl alcohol.

7.10 *Silica Gel, 250 to 74 μm (60 to 200-mesh)*.<sup>4</sup>

7.11 *Sodium Hydroxide Solution, Standard (0.1 mol/L)* (**Warning**—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water.)—Prepare and standardize a 0.1 mol/L aqueous, carbonate-free, NaOH solution.

7.12 *Sodium Sulfate, Anhydrous, Crystalline*.

7.13 *Sodium Sulfate Solution*—Dissolve 240 g of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) in water and dilute to 1 L.

7.14 *Sulfuric Acid* (relative density 1.84)—Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), 36 mol/L. (**Warning**—Poison. Corrosive. Strong oxidizer. Contact with organic material may cause fire. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled. Contact with water liberates large amounts of heat. Spillage may cause fire.)

7.14.1 *Sulfuric Acid Solution, Standard (0.1 mol/L)*—Prepare and standardize a 0.1 mol/L aqueous sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

## 8. Conversion of Calcium, Barium, Magnesium, or Ammonium Sulfonate to Sodium Sulfonate

8.1 *Conversion of Calcium, Barium, Magnesium or Ammonium Sulfonate to Sulfonic Acid*:

8.1.1 Transfer approximately 10 g of 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 dilute HCl (1 + 1) and swirl to mix

thoroughly until reaction is complete. In analyzing barium sulfonate products if barium chloride crystallizes out, add sufficient water to redissolve.

8.1.2 Quantitatively transfer the mixture to a 500-mL separatory funnel. Shake well, let settle, and draw the aqueous acid layer into a 250-mL separatory funnel. Extract the aqueous acid layer in the 250-mL separatory funnel with three 50-mL portions of ethyl ether, using the ethyl ether washes to rinse the Erlenmeyer flask first. Combine all the ethyl ether extracts in the 500-mL separatory funnel and wash with 50 mL of dilute HCl (1 + 3). Combine all the aqueous acid layers and reextract them with 50 mL of ethyl ether.

## 8.2 Conversion of Sulfonic Acid to Sodium Sulfonate:

8.2.1 Collect all of the ether washes in the 500-mL separatory funnel and shake with successive 50-mL portions of Na<sub>2</sub>SO<sub>4</sub> solution containing 2 to 3 drops of methyl orange indicator until a washing does not appear pink. Discard the salt washes.

8.2.2 Drain off as much of the aqueous layer as possible from the washed ether solution. Lay the separatory funnel on its side and introduce about 10 g of anhydrous Na<sub>2</sub>SO<sub>4</sub>. Stopper the funnel, making sure that the funnel mouth is free of Na<sub>2</sub>SO<sub>4</sub> crystals and shake the mixture vigorously for 3 to 4 min, to remove the last traces of water, venting the funnel frequently. Place a 250-mL Erlenmeyer flask on a steam bath and filter the ether solution through a small plug of cotton, placed in the vortex of a filter funnel, into the Erlenmeyer flask, keeping approximately 50 mL of solution in the Erlenmeyer flask while evaporating. Rinse the funnel and filter with 50 mL of ethyl ether, adding the rinsing to the main ether solution. Evaporate the ethyl ether until approximately 10 mL of solution remains. Add 50 mL of 99 mass % isopropyl alcohol, several drops of phenolphthalein indicator solution, and titrate with 0.1 mol/L standard NaOH solution to the red color change. Place the flask on a steam bath and evaporate to dryness. Dissolve the sodium sulfonate and oil residue in chloroform; transfer quantitatively into a 100-mL volumetric flask, adjust to volume, and proceed directly with Section 10. The solution may turn acidic on standing in the laboratory. Should this occur, add sufficient 0.1 N NaOH solution to the aliquot taken until the solution is pink.

## 9. Preparation of the Column

9.1 With the stopcock closed, pour 80 to 100 mL of chloroform into the column, and push a wad of cotton to the bottom with a rod (**Note 1**). Compress the cotton enough to hold back the silica gel but not enough to impede the flow of solvent.

**NOTE 1**—A coarse-fritted disk made of borosilicate glass can be used in place of the cotton wad.

9.2 Pour 15 ± 1 g of silica gel into the column containing the chloroform. The 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 13 mm (½ in.) of the surface of the gel, close the stopcock. Never allow the liquid level to fall below the surface of the silica gel.

<sup>4</sup> The sole source of supply of silica gel, Grade 62, known to the committee at this time is W.R. Grace and Co., Davison Chemical Corp., Baltimore, MD 21203. 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,<sup>1</sup> which you may attend.