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Standard Test Methods of Chemical Analysis of Sulfonated and Sulfated Oils¹

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1. Scope

1.1 These test methods cover the chemical analysis of sulfonated and sulfated oils. The analytical procedures appear in the following order:

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1.2 The values stated in inch-pound units are to be regarded as the standard. The metric equivalents of inch-pound units may be approximate.

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.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 [Specification for Reagent Water](#)

3. Purity of Reagents

3.1 *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 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.

¹ These test methods are under the jurisdiction of ASTM Committee D12 on Soaps and Other Detergents and is the direct responsibility of Subcommittee D12.12 on Analysis of Soaps and Synthetic Detergents.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *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.

3.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193.

MOISTURE

Method A. Water by Distillation with Volatile Solvent

4. Scope

4.1 This test method covers the determination of water existing in a sample of sulfonated or sulfated oil, or both, by distilling the sample with a volatile solvent. The method is applicable only to sulfonated and sulfated oils that do not contain the following: mineral acids, free sulfonic acids, or free sulfuric acid esters; or alkali hydroxides, carbonates or acetates; or alcohol, glycerin, diethylene glycol, acetone, or other water-miscible volatile compounds.

5. Apparatus

5.1 The apparatus required consists of a glass flask heated by suitable means and provided with a reflux condenser discharging into a trap and connected to the flask. The connections between the trap and the condenser and flask shall be interchangeable ground joints. The trap serves to collect and measure the condensed water and to return the solvent to the flask. A suitable assembly of the apparatus is illustrated in Fig. 1.

5.1.1 *Flask*, 500-mL, of either the short-neck, round-bottom type or the Erlenmeyer type.

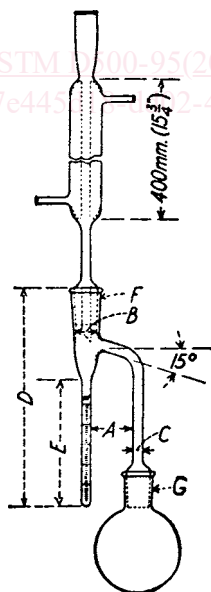
5.1.2 *Heat Source*—The source of heat may be either an oil bath (stearic acid, paraffin wax, etc.), or an electric heater provided with a sliding rheostat or other means of heat control.

5.1.3 *Condenser*—A water-cooled glass reflux condenser (Fig. 1), having a jacket approximately 400 mm (15¾ in.) in length with an inner tube 9.5 to 12.7 mm (⅜ to ½ in.) in outside diameter. The end of the condenser to be inserted in the trap shall be ground off at an angle of 30° from the vertical axis of the condenser. When inserted into the trap, the tip of the condenser shall be about 7 mm (¼ in.) above the surface of the liquid in the trap after the distillation conditions have been established. Fig. 1 shows a conventional sealed-in type of condenser, but any other condenser fulfilling the detailed requirements above may be used.

5.1.4 *Trap*—A trap made of well-annealed glass constructed in accordance with Fig. 1 and graduated as shown to contain 5 mL at 20°C. It shall be subdivided into 0.1-mL divisions, with each 1-mL line numbered (5 mL at top). The error in any indicated capacity may not be greater than 0.05 mL.

6. Reagents

6.1 *Oleic Acid*, heated previous to use for 5 to 10 min over a free flame at a temperature of 130 to 135°C.



A = 45 to 55 mm
 B = 22 to 24 mm in inside diameter
 C = 9 to 11 mm in inside diameter
 D = 235 to 240 mm
 E = 146 to 156 mm
 F and G are interchangeable joints, standard taper 24/40.

FIG. 1 Apparatus for Water Determination by Distillation with Volatile Solvent, Method A

6.2 Xylene.

7. Calibration

7.1 To calibrate the apparatus add approximately 1 g of water to a mixture of 80 g of xylene and 10 g of oleic acid. Conduct the distillation as described in 8.2-8.4. When all the water has distilled, cool the apparatus, add another g of water, and repeat the distillation. Continue the calibration up to the capacity of the receiving tube.

8. Procedure

8.1 Clean the condenser and the receiving tube thoroughly with soap and warm water before using. Rinse well, then treat with hot cleaning solution (a mixture of 10 mL of saturated potassium dichromate ($K_2Cr_2O_7$) and 990 mL of sulfuric acid (H_2SO_4 , sp gr 1.84)), and finally thoroughly wash and dry.

8.2 Take enough of the sample to be tested for analysis to yield about 4 mL of water. Introduce the approximate quantity into a weighing bottle and make the weighings from the bottle into the flask, taking care that after removal of the sample no drops of oil are left on the outside of the weighing bottle. Add 80 g of xylene and oleic acid equivalent to about two and one-half times the weight of the bone-dry sample to prevent foaming and jelling of the contents of the flask. Introduce glass beads to prevent bumping and mix the contents of the flask thoroughly by swirling, taking care to avoid any loss of material. Fill the trap with xylene and immediately connect the flask with the distillation apparatus. Insert a loose cotton plug in the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube.

8.3 Heat the flask and regulate the heating so that the condenser tube immediately below the water jacket is just barely hot. In this way a minimum of water will condense farther up the condenser where it may be difficult to volatilize any moisture condensed on the walls.

8.4 Continue the distillation at the specified rate until practically no water is visible on any part of the apparatus except within the graduations of the trap. This operation usually requires less than 1 h. Increase the rate of distillation in order to remove all traces of condensed water in the condenser tube, and continue the distillation until the water level in the trap remains unchanged after a 10-min interval. Dislodge any droplets adhering to the side of the receiver with a thin copper wire twisted into a loop. Immerse the receiving tube in warm water at about 40°C for 15 min or until the xylene layer becomes clear, then read and record the temperature and the exact volume of the water in the trap.

9. Calibration

9.1 The volume of condensed water measured in the trap may be converted into its equivalent weight in grams by means of Table 1. Calculate the percentage of water as follows:

$$\text{Water, \%} = (A/B) \times 100 \quad (1)$$

where:

A = weight of water, g, and

B = weight of sample, g.

Method B. Moisture and Volatile Matter by Hot-Plate Method

10. Scope

10.1 This test method covers the determination of the percentage of water and other compounds volatile at about 100°C existing in a sample of sulfonated or sulfated oil, or both, by rapid evaporation. The test method is applicable only to sulfonated and sulfated oils that do not contain the following: mineral acids, free sulfonic acids or free sulfuric acid esters, ammonia, acetic acid or similar volatile acids, alkali hydroxides, carbonates, acetates or similar salts that may react with oleic acid at elevated temperatures liberating volatile acids, or glycerin, diethylene glycol, xylene, or other compounds of similar volatility.

TABLE 1 Specific Gravity of Water^A

| Temperature, °C | Specific Gravity |
|-----------------|------------------|
| 4 | 1.00000 |
| 35 | 0.99406 |
| 36 | 0.99371 |
| 37 | 0.99336 |
| 38 | 0.99299 |
| 39 | 0.99262 |
| 40 | 0.99224 |
| 41 | 0.99186 |
| 42 | 0.99147 |
| 43 | 0.99107 |
| 44 | 0.99066 |
| 45 | 0.99025 |

^A This table is taken from *Smithsonian Tables*, compiled from various authors.

11. Apparatus

- 11.1 The apparatus required consists of a glass-stoppered weighing flask, a glass beaker, and a suitable thermometer.
- 11.1.1 *Weighing Flasks*—Any suitable glass-stoppered weighing flask of 10 to 15-mL capacity.
- 11.1.2 *Beaker*—A Griffin low-form glass beaker with an approximate capacity of 150 mL and a diameter of about 5 cm.
- 11.1.3 *Heat Source*—The source of heat may be either an electric hot plate with or without asbestos paper or board cover, or an open flame under a suitable asbestos board and a wire gauze (to spread the heat).
- 11.1.4 *Thermometer*, graduated from 90 to 150°C, about 3 in. in length, and substantially constructed.

12. Reagents

- 12.1 *Desiccating Agent*—Any suitable desiccating agent may be used.

NOTE 1—Recent investigations seem to indicate that calcium chloride is unreliable as a laboratory desiccating agent.

- 12.2 *Oleic Acid*.

13. Procedure

13.1 Weigh approximately 5 g of oleic acid into the beaker and insert the thermometer. Heat the oleic acid gradually, while stirring with the thermometer, until the temperature reaches 130°C. Place the beaker in an oven at 105 to 110°C for 15 min, cool in a desiccator, and weigh. Repeat the heating over the hot plate and in the oven until two successive weighings differ by less than 1.5 mg.

13.2 Place about 6 g of the sample in the weighing flask and determine the weight accurately. Transfer the sample to the beaker (containing the oleic acid and the thermometer) and weigh the flask again. Heat the mixture exactly as in the taring of the beaker as described in 13.1. The loss in weight is equivalent to the moisture in the sample.

14. Calculation

- 14.1 Calculate the percentage of moisture and volatile matter in the sample as follows:

$$\text{Moisture and volatile matter, \%} = (A/B) \times 100 \quad (2)$$

where:

- A = loss of weight, g, and
B = weight of sample, g.

ORGANICALLY COMBINED SULFURIC ANHYDRIDE

Method A. *Titration Test (For Sulfated Oils)*

15. Scope

15.1 This test method covers the determination of the organically combined sulfuric anhydride existing in a sample of sulfated oil by boiling the sample with sulfuric acid and determining the acidity of the reaction mixture. This method is applicable only to oils that split off their combined SO₃ upon boiling with mineral acids and that do not contain compounds that cannot be accurately titrated in water solution with methyl orange as the indicator.

16. Apparatus

16.1 The apparatus required consists of a glass flask provided with a glass stopper and an air condenser. The connection between the flask and the condenser shall be a ground joint. Perforated glass beads shall be used to prevent bumping.

16.1.1 *Flask*—An Erlenmeyer flask (Fig. 2) made of a borosilicate glass, having a capacity of approximately 300 mL and provided with a glass stopper.

16.1.2 *Condenser*—The condenser required consists of a glass tube, 915 mm (36 in.) in length, and 8 mm (⁵/₁₆ in.) in outside diameter. The lower end of the tube shall be flared and ground to fit the mouth of the Erlenmeyer flask.

16.1.3 *Glass Beads*—Perforated glass beads, made of chemically-resistant glass, approximately 4 mm (⁵/₃₂ in.) in diameter. Before using, the glass beads shall be boiled thoroughly in several portions of water or until the wash water reacts neutral to methyl orange indicator.

17. Reagents

- 17.1 *Ethyl Ether*.

17.2 *Methyl Orange Indicator Solution (1 g/L)*—Dissolve 0.1 g of methyl orange in 100 mL of water.

- 17.3 *Sodium Chloride (NaCl)*, solid.

17.4 *Sodium Hydroxide, Standard Solution (1 N)*—Accurately prepare and standardize a 1 N sodium hydroxide (NaOH) solution. Express the strength or concentration of the solution as milligrams of KOH per milliliter; 1 mL of 1 N NaOH solution is equivalent to 56.1 mg of KOH.

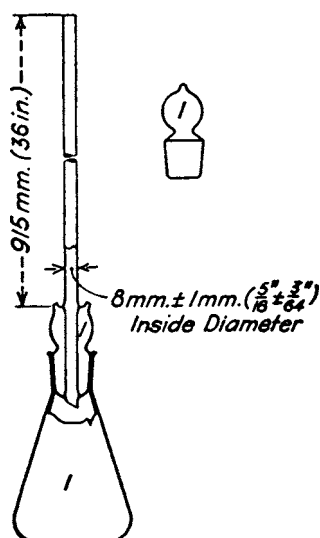


FIG. 2 Apparatus for Determination of Organically Combined Sulfuric Anhydride, Method A

17.5 *Sodium Hydroxide, Standard Solution (0.5 N)*—Accurately prepare and standardize a 0.5 N NaOH solution. Express the strength of the solution as milligrams of KOH per millilitre; 1 mL of 0.5 N NaOH solution is equivalent to 28.05 mg of KOH.

17.6 *Sulfuric Acid, Standard (0.5 N)*—Accurately prepare and standardize a 0.5 N sulfuric acid (H_2SO_4) solution. Express the strength of the solution as milligrams of KOH per millilitre; 1 mL of 0.5 N H_2SO_4 is equivalent to 28.05 mg of KOH.

17.7 *Sulfuric Acid (1 + 19)*—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) into 19 volumes of water while stirring.

18. Procedure

18.1 The procedure consists of two determinations: namely, (a) the alkalinity of the sample, designated as *A*, and (b) the increase in acidity after boiling the sample with sulfuric acid, designated as *F*.

18.1.1 *Alkalinity, A*—Dissolve 10 g of the sample in 100 mL of water in the 300-mL glass-stoppered Erlenmeyer flask, warming to obtain solution if necessary. After cooling, add 30 g of NaCl, 25 mL of ether, and 5 drops of methyl orange indicator solution; then add 0.5 N H_2SO_4 with frequent but gentle shaking until the mixture is slightly acid. Shake the contents of the flask vigorously, and complete the titration by adding first 0.5 N NaOH solution several drops at a time until the solution is alkaline and then the acid 1 or 2 drops at a time until the end point is reached. Shake the solution vigorously after each addition of reagent. Drain burets for 3 min before taking readings. Calculate the alkalinity, *A*, as follows:

$$A = [(B \times D) - (C \times E)]/W \quad (3)$$

where:

- A* = total alkalinity, mg of KOH/g,
- B* = millilitres of H_2SO_4 required for titration of the sample,
- C* = millilitres of NaOH solution required for titration of the sample,
- D* = strength of H_2SO_4 , mg of KOH/mL,
- E* = strength of NaOH solution, mg of KOH/mL, and
- W* = weight of sample, g.

18.1.2 *Increase in Acidity upon Boiling, F*—Weigh 10 g of the sample into the Erlenmeyer flask and boil under the air condenser with H_2SO_4 (1+19) for 1½ h or until both the oil and water layers are perfectly clear, using glass beads to prevent bumping. The volume of H_2SO_4 added shall be sufficient to neutralize the total alkalinity, *A*, of the sample plus 25 mL in excess. Regulate the heating so that the solution boils rather vigorously but with very little evaporation taking place. At the end of the heating period allow the contents to cool, wash the condenser with a spray of water from a wash bottle, and disconnect the condenser. Add 30 g of NaCl, 25 mL of ether, 50 mL of water, and 5 drops of indicator solution and titrate the solution with 1 N NaOH solution to the same end point as in the total alkalinity titration, 18.1.1. During the titration stopper the flask frequently and shake the contents of the flask thoroughly. Drain the burets for 3 min before readings are taken.

NOTE 2—Reserve the titrated solution for the subsequent determination of total desulfated fatty matter (Sections 29-32).

18.1.2.1 Make a blank determination simultaneously with the sample, using the same amount and strength of the H_2SO_4 , approximately the same weight of glass beads, and heating and titrating under the same conditions as the sample.

18.1.2.2 Calculate the increase in acidity upon boiling, *F*, as follows:

$$F = [(S - B)N]/W \quad (4)$$

where:

- F = increase in acidity (Note 3) upon boiling, mg of KOH/g,
 S = millilitres of NaOH solution required for titration of the sample,
 B = millilitres of NaOH solution required for titration of the blank,
 N = strength of NaOH solution, mg of KOH/mL, and
 W = weight of sample, g.

NOTE 3—The increase in acidity, F , may be negative, in which case retain the sign obtained from the above equation in Section 19.

19. Calculation

19.1 Calculate the percentage of organically combined sulfuric anhydride as follows:

$$\text{Organically combined sulfuric anhydride, \%} = 0.1426(A + F) \quad (5)$$

where:

- 0.1426 = one tenth of the molecular ratio of SO_3 :KOH,
 A = total alkalinity, mg of KOH/g, and
 F = increase in acidity upon boiling, mg of KOH/g. Retain the sign of F as obtained in 18.1.2.

Method B. Extraction-Titration Test (For Sulfated Oils)

20. Scope

20.1 This test method covers the determination of the organically combined sulfuric anhydride existing in a sample of sulfated oil by extracting the undecomposed sulfated fat and other fatty matter over an acidulated, concentrated salt solution, boiling the residue with sulfuric acid after evaporating the solvent, and titrating the products of reaction. This method is applicable only to sulfated oils that split off their combined SO_3 upon boiling with mineral acids, including samples containing sodium acetate or other compounds that cannot be accurately titrated in water solution with methyl orange as the indicator.

21. Apparatus

21.1 The apparatus shall be the same as described for Test Method A in Section 16.

22. Reagents

22.1 The solutions shall be the same as described for Test Method A in Section 17.

23. Procedure

23.1 The procedure consists of isolating and purifying the fatty matter as it exists in the original oil by dissolving the sample in a solvent, acidifying and washing with saturated brine, and determining the increase in acidity upon boiling the isolated product with sulfuric acid. This increase in acidity is designated as F .

23.1.1 *Separation of Purified Oil*—Weigh 5 to 10 g of the sample, depending upon the concentration of the fatty matter, into a 250-mL separatory funnel containing 50 mL of concentrated NaCl solution, some solid NaCl, 5 drops of methyl orange indicator solution, and 50 mL of ether. Shake the mixture and neutralize with H_2SO_4 (1+19) until the lower layer is distinctly pink (about 0.2 mL in excess). Highly sulfated oils at this stage may form three layers instead of two. In such cases, use a fat solvent consisting of a mixture of 2 parts of ether and 1 of alcohol. Allow the mixture in the separatory funnel to settle for at least 5 min, draw off the lower layer into another separatory funnel, and wash the ether layer with 25-mL portions of NaCl solution until practically neutral to methyl orange, that is, until 1 drop of 0.5 N NaOH solution turns the wash water strongly alkaline. Allow all separations to settle for at least 5 min. Combine the water layers, and extract with two 25-mL portions of ether. Combine the last two ether extractions and wash with NaCl solution until free from acid, as in the case of the ether layer in the first funnel. Combine all the ether layers in the decomposition flask and evaporate the ether.

23.1.2 *Increase in Acidity upon Boiling, F* —Determine the increase in acidity upon boiling in accordance with the procedure described for Test Method A in 18.1.2. Reserve the titrated solution for the subsequent determination of total desulfated fatty matter (Sections 29-32). Make a blank determination as described for Test Method A in 18.1.2. Calculate the increase in acidity F in accordance with 18.1.2.

24. Calculation

24.1 Calculate the percentage of organically combined sulfuric anhydride as follows:

$$\text{Organically combined sulfuric anhydride, \%} = 0.1426 \times F \quad (6)$$

where:

- 0.1426 = one tenth the molecular ratio of SO_3 :KOH, and
 F = increase in acidity upon boiling.