



Designation: D500 – 95 (Reapproved 2023)

Standard Test Methods of Chemical Analysis of Sulfonated and Sulfated Oils¹

This standard is issued under the fixed designation D500; 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 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, health, and environmental 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.

1.4 *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 Recom-*

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 and Specifications of Soaps, Synthetics, Detergents and their Components.

Current edition approved July 1, 2023. Published July 2023. Originally approved in 1937. Last previous edition approved in 2016 as D500 – 95 (2016). DOI: 10.1520/D0500-95R23.

mendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

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.

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.

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.

³ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

5. Apparatus

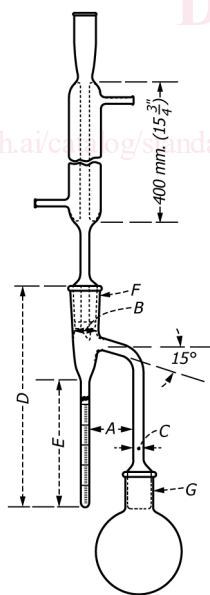
5.1 The apparatus required consists of a glass flask heated by suitable means and provided with a reflux condenser discharging into a trap and connected to the flask. The connections between the trap and the condenser and flask shall be interchangeable ground joints. The trap serves to collect and measure 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 mm to 12.7 mm (¾ in. 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,



A = 45 mm to 55 mm
 B = 22 to 24 mm in inside diameter
 C = 9 to 11 mm in inside diameter
 D = 235 mm to 240 mm
 E = 146 mm 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

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 min to 10 min over a free flame at a temperature of 130 °C to 135 °C.

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 (K₂Cr₂O₇) and 990 mL of sulfuric acid (H₂SO₄, 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:

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.

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

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.

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 mL 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 °C 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 °C 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*.

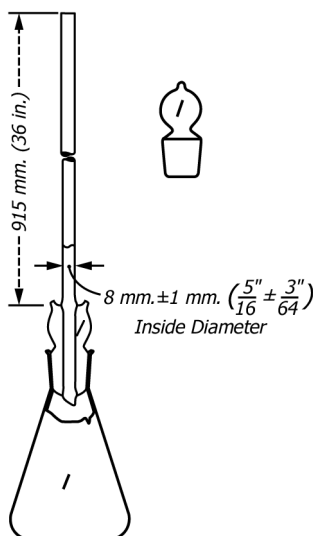


FIG. 2 Apparatus for Determination of Organically Combined Sulfuric Anhydride, Method A

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 millilitre; 1 mL of 1 N NaOH solution is equivalent to 56.1 mg of KOH.

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 (H₂SO₄) solution. Express the strength of the solution as milligrams of KOH per millilitre; 1 mL of 0.5 N H₂SO₄ is equivalent to 28.05 mg of KOH.

17.7 *Sulfuric Acid (1 + 19)*—Carefully mix 1 volume of concentrated sulfuric acid (H₂SO₄, 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 H₂SO₄ 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 H₂SO₄ required for titration of the sample,
- C* = millilitres of NaOH solution required for titration of the sample,
- D* = strength of H₂SO₄, 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 H₂SO₄ (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 H₂SO₄ 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 H₂SO₄, 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 SO₃: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 g 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.

*Method C. Ash-Gravimetric Test
(In the Presence of True Sulfonates)*

25. Scope

25.1 This test method covers the determination of the organically combined sulfuric anhydride existing in a sample of sulfonated or sulfated oil, or both, by extracting the undecomposed sulfonated or sulfated fat and other fatty matter over an acidulated, concentrated salt solution, and ashing the purified extract. This test method is applicable to all types of sulfonated and sulfated oils, including true sulfonic acid oils and those containing sodium acetate or similar partially titratable compounds.

26. Reagents

26.1 *Ethyl Ether.*

26.2 *Hydrogen Peroxide (30 %)*—Concentrated hydrogen peroxide (H_2O_2).

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

26.4 *Sodium Chloride (NaCl)*, solid.

26.5 *Sodium Sulfate (Na_2SO_4)*, anhydrous.

27. Procedure

27.1 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 ashing the purified extract. If the sample contains ammonia, the ammonia shall first be expelled before the determination is made on the sample.

27.1.1 *In the Absence of Ammonia*—Proceed as described in the separation of purified oil (23.1.1), combining the ether layers in the first funnel rather than in the decomposition flask. Carefully remove any water that may settle and dehydrate the ether layer as follows: add 5 g of anhydrous Na_2SO_4 , shake vigorously for 5 min, and filter directly into a 150 mL beaker placed in a bath of warm water. Wash the flask and filter with ether until free from fat (absence of oil stains on the filter paper after drying) and add the filtrate to the beaker. To avoid creeping of the oil, the volume in the beaker should at no time during the filtering and washing exceed 50 mL (one third full). Evaporate the ether solution until the volume has been reduced to about 20 mL and transfer the residue to a tared 50 mL crucible (high form). Immerse the crucible in a 100 mL beaker containing warm water until practically all of the ether has

evaporated. Rinse the beaker with two 10 mL and three 5 mL portions of ether, or until all of the oil has been transferred to the crucible; allow each portion of rinsing ether to evaporate before the next rinsing is made. Burn gently the solvent-free residue, and finally ignite at a dull red heat to constant weight. To prevent creeping of the oil and to hasten evaporation, stir the solution with a glass rod; before the oil is burned, wipe the rod clean with ashless filter paper and add the paper to the crucible. To oxidize traces of carbon or sodium sulfide that might form, moisten the ash with H_2O_2 and again carefully ignite to constant weight. Calculate the percentage of ash as follows:

$$\text{Extracted ash, \%} = (A/B) \times 100 \quad (7)$$

where:

A = weight of ash, g, and

B = weight of sample, g.

27.1.2 In the Presence of Ammonia—Dissolve 5 g to 8 g of the sample in 80 mL of water in a 300 mL beaker. Add 10 mL of 1 *N* NaOH solution and boil the solution gently until wet litmus paper no longer indicates ammonia. Cool the solution, transfer to a 300 mL separatory funnel, and add about 35 g of solid NaCl or enough to make the final solution a 25 % NaCl solution. Add 5 drops of methyl orange solution and complete the neutralization, extraction, etc., in accordance with the procedure described in 27.1.1.

28. Calculation

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

$$\text{Organically combined sulfuric anhydride, \%} = 1.1267 A \quad (8)$$

where:

A = extracted ash, %, and

1.1267 = molecular ratio of $2\text{SO}_3:\text{Na}_2\text{SO}_4$.

TOTAL DESULFATED FATTY MATTER (FOR SULFATED OILS)

29. Scope

29.1 This test method covers the determination of the total desulfated fatty matter in a sample of sulfated oil by decomposition with diluted mineral acids and extraction of the decomposed fat. This test method is not applicable to samples that are not completely decomposed upon boiling with mineral acids.

30. Reagents

30.1 *Ethyl Ether*.

30.2 *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.

31. Procedure

31.1 The procedure consists of decomposing the sample with H_2SO_4 , extracting the fatty matter with ether, evaporating the solvent, and weighing the residue. After cooling, transfer the titrated solution obtained after determining organically

combined sulfuric anhydride in accordance with Test Method A or Test Method B (18.1.2 or 23.1.2) into a 250 mL separatory funnel and shake with 50 mL of ether. Draw off the water layer into another separatory funnel and extract twice with 25 mL portions of ether. Wash the combined ether layers with 15 mL portions of water until the wash water is neutral to methyl orange. Transfer the ether layer to a tared 150 mL beaker, evaporate on the water bath until practically free from solvent, dry in a hot-air oven at 105 °C to 110 °C for 30 min, cool in a desiccator, and weigh. Repeat the heating for 30 min periods until constant weight is obtained.

NOTE 4—Reserve the extracted fatty matter for the subsequent determination of unsaponifiable matter (Sections 37 – 41).

32. Calculation

32.1 Calculate the total desulfated fatty matter as follows:

$$\text{Total desulfated fatty matter, \%} = (A/B) \times 100 \quad (9)$$

where:

A = weight of residue, g, and

B = weight of sample, g.

TOTAL ACTIVE INGREDIENTS

33. Scope

33.1 This test method covers the determination of the total active ingredients in a sample of sulfonated or sulfated oil, or both, as it exists in the original sample by extracting the undecomposed sulfonated or sulfated fat and other fatty matter over an acidified concentrated salt solution. Free alkali or alkali bound as soap is not included.

NOTE 5—In the case of sulfated oils only, this determination may also be estimated by calculation (see 36.3), as it is equivalent to the sum of the desulfated fatty matter and neutralized organically combined sulfuric anhydride.

34. Reagents

34.1 *Ethyl Ether*.

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

34.3 *Sodium Chloride* (NaCl), solid.

34.4 *Sodium Sulfate* (Na_2SO_4), anhydrous.

34.5 *Potassium Hydroxide, Alcoholic Standard Solution (0.5 N)*—Accurately prepare and standardize a 0.5 *N* alcoholic potassium hydroxide (KOH) solution the strength of which shall be expressed as milligrams of KOH per millilitre; 1 mL of 0.5 *N* alcoholic KOH solution is equivalent to 28.05 mg of KOH.

35. Procedure

35.1 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 weighing the purified extract. Proceed as described in the determination of organically combined sulfuric anhydride, Test Method C, in the absence of ammonia (27.1.1), retaining the separated active ingredients in the 150 mL beaker

instead of transferring it to a crucible. Evaporate the filtrate to a total volume of about 20 mL, add exactly 2 mL of alcoholic KOH solution, mix the contents by swirling, and finally evaporate until practically free from ether.

NOTE 6—With highly sulfonated or sulfated oil, it may be necessary to add 5 mL to 10 mL of the alcoholic KOH solution in order to stabilize the residue.

35.2 Dry the residue at 108 °C to 112 °C for 1½ h, cool in a desiccator, and weigh. Repeat the heating for 30 min periods until constant weight is obtained.

36. Calculation

36.1 *Correction for the Alkali Added*—Calculate the correction for the alkali added as follows:

$$\text{Correction for alkali added, g} = 0.0006791 AS \quad (10)$$

where:

A = millilitres of KOH solution added,
 S = strength of KOH solution, mg of KOH/mL, and
 0.0006791 = molecular ratio of (K – H): KOH divided by 1000.

36.2 *Total Active Ingredients*—Calculate the total active ingredients as follows:

$$\text{Total active ingredients, \%} = [(B - C)/D] \times 100 \quad (11)$$

where:

B = weight of residue, g,
 C = alkali correction, and
 D = weight of sample, g.

36.3 *Total Active Ingredients Calculation Method (for Sulfated Oils Only)*—Calculate the total active ingredients by the calculation method that is applicable to sulfated oils only, as follows:

$$T = P + [(\text{NaSO}_4^- / \text{SO}_3) \times Y] \quad (12)$$

or

$$T = P + 1.4875 \times Y \quad (13)$$

where:

T = total active ingredients, %
 P = total desulfated fatty matter, %, and
 Y = percentage of combined SO_3 .

NOTE 7—The factor 1.4875 is based on the assumption that the desulfated fatty matter becomes polymerized at the point where the SO_3 splits off and no hydroxyl groups are formed. If the latter are formed the factor becomes

$$(\text{NaSO}_3 - 1) / \text{SO}_3 = 1.275.$$

Calculated results were in better agreement with actual determinations when the higher factor was used.

UNSAPONIFIABLE NONVOLATILE MATTER (FOR SULFATED OILS)

37. Scope

37.1 This test method covers the determination of the unsaponifiable, nonvolatile (above 80 °C) matter existing in a sample of sulfated oil by saponifying the desulfated fatty matter and extracting the unsaponifiable matter from the soap solution with ethyl ether.

38. Apparatus

38.1 *Saponification Flask*—The apparatus required for the saponification consists of a glass flask provided with an air condenser and identical with the apparatus described in Test Method A for organically combined sulfuric anhydride (16.1.1 and 16.1.2).

39. Reagents

39.1 *Ethyl Ether*.

39.2 *Potassium Hydroxide, Alcoholic Solution (28 g/L)*—Dissolve approximately, but not less than, 28 g of KOH in ethyl alcohol and dilute to 1 L.

39.3 *Potassium Hydroxide Aqueous Solution (28 g/L)*—Dissolve 28 g of potassium hydroxide (KOH) in water and dilute to 1 L.

40. Procedure

40.1 The procedure consists in decomposing the sample with mineral acid, extracting the desulfated fatty matter, saponifying the latter, and extracting the unsaponifiable matter from the soap solution with ethyl ether.

40.1.1 *Desulfated Fatty Matter*—Determine the desulfated fatty matter as described in the determination of total desulfated fatty matter (Section 31).

40.1.2 *Saponification*—Accurately weigh 2 g to 2.5 g of the desulfated fatty matter in the flask, add 25 mL of the alcoholic KOH solution, and simmer the contents (without loss of alcohol) for 1 h with occasional swirling, over an electric hot plate or other source of heat.

40.1.3 *Extraction*—Transfer the contents of the flask to a 250 mL separatory funnel and wash the flask several times with a total of 50 mL of water, pouring it into the separatory funnel. Extract the solution while still warm (about 30 °C) with 50 mL of ether (rinse the saponification flask with the ether before adding it to the separatory funnel), shaking vigorously for about 1 min, and allow the layers to settle and clear. Draw off the lower layer in a second 250 mL separatory funnel and extract in a similar manner with two 50 mL portions of ether.

40.1.4 *Preliminary Water Washing*—Add 20 mL of water to the combined ether layer, turn the separatory funnel and contents over gently about six times, and allow the layers to settle and clear. Draw off the lower layer and discard. Wash the ether layer twice more with 20 mL portions of water, shaking vigorously after each addition.

40.1.5 *Alkali and Water Washing*—Add 20 mL of aqueous KOH solution to the washed ether layer, turn the separatory funnel and contents over gently about six times, and allow the layers to settle and clear. Draw off the lower layer and discard. Wash the ether layer with 20 mL of water, shaking vigorously. Continue washing with 20 mL of KOH solution followed by 20 mL of water, shaking vigorously after each addition, until the alkali layer upon strong acidification with HCl and settling for a few minutes is only faintly opalescent. Finally wash the ether layer with 20 mL portions of water until the wash water is no longer pink to phenolphthalein.

40.1.6 *Solvent Removal*—Transfer the ether layer to a 150 mL beaker (counterbalance the beaker if the amount of unsaponifiable matter is small and important) and evaporate