Designation: D500 – 95 (Reapproved 2016)

Standard Test Methods of Chemical Analysis of Sulfonated and Sulfated Oils[1]

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:

	Section
Moisture:	
Test Method A. Water by Distillation with Volatile Solvent	4 – 9
Test Method B. Moisture and Volatile Matter by Hot-Plate Method	10 – 14
Organically Combined Sulfuric Anhydride:	
Test Method A. Titration Test	15 – 19
Test Method B. Extraction-Titration Test	20 – 24
Test Method C. Ash-Gravimetric Test (in the Presence of True Sulfonates)	25 – 28
Total Desulfated Fatty Matter	29 – 32
Total Active Ingredients	33 – 36
Unsaponifiable Nonvolatile Matter	37 – 41
Inorganic Salts	42 – 46
Total Alkalinity	47 – 49
Total Ammonia	50 – 52
Acidity as Free Fatty Acids or Acid Number:	
Test Method A. In the Absence of Ammonium or Triethanolamine Soaps	53 – 56
Test Method B. In the Presence of Dark Colored Oils but in the Absence of Ammonium or Triethanolamine Soaps (Brine Test)	57 – 60
Test Method C. In the Presence of Ammonium or Triethanolamine Soaps	61 – 63
Water-Immiscible Organic Solvents Volatile with Steam	64 – 70

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.

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.

---

[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, 2016. Published August 2016. Originally approved in 1937. Last previous edition approved in 2009 as D500 – 95(2009). DOI: 10.1520/D0500-95R16.

[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] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

5. Apparatus

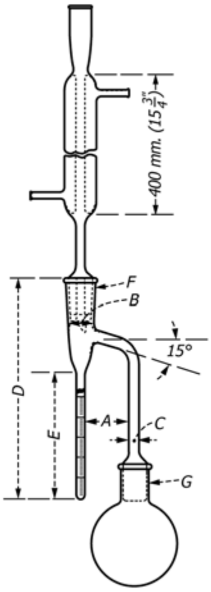
5.1 The apparatus required consists of a glass flask heated by suitable means and provided with a reflux condenser discharging into a trap and connected to the flask. The connections between the trap and the condenser and flask shall be interchangeable ground joints. The trap serves to collect and measure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



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. 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.

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 jellying 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.

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

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 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:

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

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 SO_3 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.*

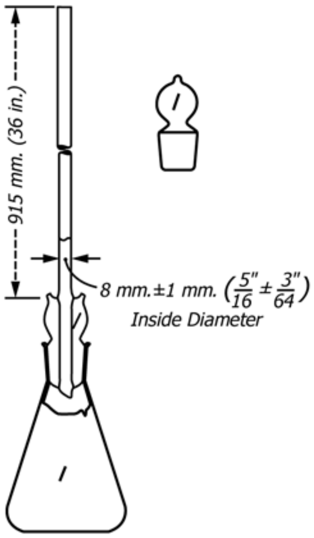


FIG. 2 Apparatus for Determination of Organically Combined Sulfuric Anhydride, Method A

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 (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:

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

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:

$$F = [(S - B)N]/W \tag{4}$$

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:

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

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.

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:

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

where:

A = weight of ash, g, and
B = weight of sample, g.

27.1.2 *In the Presence of Ammonia*—Dissolve 5 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:

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

where:

A = extracted ash, %, and
1.1267 = molecular ratio of $2SO_3$:Na_2SO_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 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:

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

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 to 10 mL of the alcoholic KOH solution in order to stabilize the residue.

35.2 Dry the residue at 108 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:

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

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:

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

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:

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

or

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

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 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 over a hot-water bath until practically free of ether. Heat the beaker at 75 to 80°C until constant weight is obtained.

NOTE 8—A30 % alcoholic solution by volume is the most satisfactory solution from which to extract the unsaponifiable matter.

NOTE 9—If emulsions form, add 5 mL of alcohol, pouring it down the side of the funnel.

NOTE 10—It is important to maintain the volume of ether at not less than 150 mL, otherwise small quantities of unsaponifiable matter may be lost.

NOTE 11—To check whether or not the unsaponifiable matter is free from fatty acids, dissolve the residue in 10 mL of freshly boiled neutral alcohol and titrate with 0.1 *N* alcoholic KOH solution, using phenolphthalein as the indicator. Not more than 0.1 mL should be required for neutralization. If more is required, the determination has not been carried out effectively and must be repeated.

41. Calculation

41.1 Calculate the unsaponifiable matter as follows:

$$U = (R/G) \times P \tag{14}$$

where:

U = unsaponifiable nonvolatile matter, %,
R = weight of residue, g,
G = weight of desulfated fatty matter, g, and
P = desulfated fatty matter, %

INORGANIC SALTS

42. Scope

42.1 This test method covers the determination in a sample of sulfonated or sulfated oil, or both, the inorganic sulfates, chlorides, and all other salts that are insoluble in a mixture of oleic acid and chloroform.

43. Apparatus

43.1 Either a Gooch crucible or filter paper may be used for filtering. Ignite the Gooch crucible in a larger crucible, supported by an asbestos ring and assembled as shown in Fig. 3. If filter paper is used, it may be a 9-cm general purpose ashless filter paper.

43.2 *Thermometer.*

44. Reagents

44.1 *Chloroform ($CHCl_3$).*

44.2 *Ethyl Ether.*

44.3 *Oleic Acid.*

45. Procedure

45.1 The procedure consists of dehydrating the sample, dissolving in a solvent, filtering, igniting, and weighing the residue. In the presence of ammonium salts, the residue is not ignited but only dried to constant weight. The presence of sodium acetate does not interfere with this method.

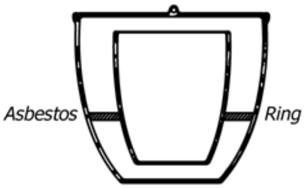


FIG. 3 Gooch Crucible Assembly for Determination of Inorganic Salts

45.1.1 *In the Absence of Ammonium Salts*—Weigh 3 to 5 g of the sample and place in a 250-mL beaker, add an approximately equal amount of oleic acid, and heat the mixture on an oil bath, while stirring constantly with a thermometer, at a temperature of 105 to 110°C until practically free from water. Continue the heating until the temperature of the contents reaches 118 to 120°C and maintain at that temperature for about 5 min. If the dehydrated sample upon cooling does not remain liquid, add more oleic acid. Dissolve the dehydrated sample in 100 mL of $CHCl_3$ warmed to 50 to 55°C and filter through a counterpoised filter paper or a Gooch crucible. Prepare the Gooch crucible by passing a thin emulsion of alkali- and acid-washed asbestos fiber in water through the crucible until a pad of about 2 mm in thickness is formed. Dry the asbestos pad and ignite for 30 min at first gently and finally more strongly. Then pass 75 mL of $CHCl_3$ through the crucible and again ignite the asbestos pad, cool in a desiccator, and weigh. Repeat the process of washing with $CHCl_3$ until there is no further loss in weight. Wash the residue with three 15-mL portions of a solution of oleic acid in $CHCl_3$ (2 %), then with six 15-mL portions of hot $CHCl_3$, and finally with two 15-mL portions of ether or until the residue is free from oil. Take care that the top of the filter is thoroughly washed. Transfer the last traces of the residue to the filter by allowing the solvent to evaporate when the salts become free flowing. Dry the residue at 125 to 130°C for 45 min, cool in a desiccator, and weigh. Ignite the residue at a dull red heat for 15 min, weigh, and repeat the ignition until constant weight is obtained.

45.1.2 *In the Presence of Ammonium Salts*—Proceed as described in 45.1.1 for the determination of inorganic salts in the absence of ammonium salts with the following exceptions: (*1*) in preparing the Gooch crucible, do not ignite but heat it at 105 ± 2°C for 45 min and repeat the heating until constant weight is obtained, and (*2*) heat the residue, whether in a Gooch crucible or on a filter paper as in (*1*) but do not ignite it.

46. Calculation

46.1 The method of calculation depends upon whether or not ammonium salts are present in the sample.

46.1.1 Calculate the inorganic sulfates and chlorides including ammonium salts as follows:

$$\text{Inorganic sulfates and chlorides, including ammonium salts, } \% = (A/B) \times 100 \tag{15}$$

where:

A = weight of dried residue, g, and
B = weight of sample, g.

46.1.2 Calculate the nonvolatile inorganic sulfates and chlorides (in the absence of ammonium salts) as follows:

$$\text{Nonvolatile, inorganic sulfates and chlorides; } \% = (A/B) \times 100 \tag{16}$$

where:

A = weight of ignited residue, g, and

B = weight of sample, g.

NOTE 12—In the absence of ammonium salts, the difference between the percentage of the dried residue and the percentage of the ignited residue shall not be greater than 0.25 %.

TOTAL ALKALINITY

47. Scope

47.1 This test method covers the determination of the total alkalinity existing in a sample of sulfonated or sulfated oil, or both, by titrating a water solution of the sample with mineral acid in the presence of methyl orange as the indicator. This test method covers the determination of the total alkalinity of the fixed alkali, ammonia and triethanolamine bound as soap, free alkali, and the alkalinity of titratable alkaline salts, but not that of nontitratable alkaline salts.

48. Procedure

48.1 Proceed as described in the determination of alkalinity under organically combined sulfuric anhydride, Test Method A (18.1.1).

49. Calculation

49.1 Calculate the total alkalinity as described in 18.1.1.

TOTAL AMMONIA

50. Scope

50.1 This test method covers the determination of the total ammonia in a sample of sulfonated or sulfated oil, or both, by boiling a water solution of the sample with excess alkali and determining by titration the loss in alkali after the boiling.

51. Procedure

51.1 The procedure consists of two determinations: namely, (*a*) the total alkalinity, and (*b*) the loss in alkalinity after boiling with excess NaOH.

51.1.1 *Total Alkalinity*—Determine the total alkalinity as described in the determination of organically combined sulfuric anhydride, Test Method A (18.1.1).

51.1.2 *Alkalinity After Boiling*—Dissolve 10 g of the sample in 100 mL of water in a 500-mL beaker, add 25 mL of 0.5 *N* NaOH solution, and boil the mixture for 30 min or until all the ammonia is expelled as indicated by moistened red litmus paper. Cool the contents of the beaker, add methyl orange indicator solution (0.1 %), and titrate to an approximate end point. Transfer the mixture to a 250-mL glass-stoppered flask and complete the titration (with the addition of salt and ether) as described in the determination of organically combined sulfuric anhydride, Test Method A (18.1.2).

52. Calculation

52.1 Calculate the total ammonia as follows:

$$T = A + \{[(B \times D) - (C \times E)]/W\} \quad (17)$$

or

$$\text{Total ammonia, \%} = 0.0303\,T \quad (18)$$

where:

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

ACIDITY AS FREE FATTY ACIDS OR ACID NUMBER

Test Method A. In the Absence of Ammonium or Triethanolamine Soaps

53. Scope

53.1 This method of analysis covers the determination of the acidity as free fatty acids existing in a sample of sulfonated or sulfated oil or both by titrating the sample dissolved in a solvent. It is not applicable in the presence of ammonium or triethanolamine soaps or salts, or other compounds that do not react neutral to phenolphthalein when dissolved in alcohol.

54. Reagents

54.1 *Alcohol-Ether Mixture*—Mix 50 mL of neutral alcohol with 25 mL of ether.

54.2 *Phenolphthalein Indicator Solution (10 g/L)*—Dissolve 1 g of phenolphthalein in 100 mL of ethanol (95 %).

54.3 *Sodium Hydroxide, Standard Solution* (0.5 *N*)—Prepare and standardize a 0.5 *N* solution of sodium hydroxide (NaOH). Potassium hydroxide (KOH) may be substituted for NaOH.

55. Procedure

55.1 The procedure consists of titrating a solution of the sample in a mixture of alcohol and ether in the presence of phenolphthalein indicator. Dissolve 10 g of the sample in an alcohol-ether mixture, add 5 drops of phenolphthalein indicator solution, and titrate the solution with 0.5 *N* NaOH or KOH solution until the pink color persists after vigorous shaking.

56. Calculation

56.1 Calculate the acidity as free fatty acids, as follows:

$$K = (C \times E)/W \quad (19)$$

where:

K = acidity as free fatty acids or acid number, mg of KOH/g,
C = millilitres of NaOH or KOH solution required for titration of the sample,
E = strength of NaOH or KOH solution, mg of KOH/mL, and
W = weight of sample, g.

Test Method B. In the Presence of Dark Colored Oils but in the Absence of Ammonium or Triethanolamine Soaps (Brine Method)

57. Scope

57.1 This test method covers the determination of the acidity as free fatty acids existing in a sample of sulfonated or sulfated oil or both by titrating a water solution of the sample with phenolphthalein as the indicator. It is not applicable in the presence of ammonia or triethanolamine soaps or acid salts.

58. Reagents

58.1 *Ethyl Ether.*

58.2 *Phenolphthalein Indicator Solution (10 g/L)*—Dissolve 1 g of phenolphthalein in 100 mL of ethanol (95 %).

58.3 *Sodium Chloride* (NaCl).

58.4 *Sodium Hydroxide, Standard Solution (0.5 N)*—Prepare and standardize a 0.5 *N* solution of sodium hydroxide (NaOH).

59. Procedure

59.1 The procedure consists of titrating a water solution of the sample in the presence of salt, ether, and alcohol with phenolphthalein as the indicator. Dissolve 10 g of the sample in 100 mL of water contained in a 250-mL, glass-stoppered, Erlenmeyer flask, warming to obtain solution, if necessary. After cooling, add 30 g of NaCl, 25 mL of ether, and 50 mL of neutral alcohol (Note 13). Add 5 drops of phenolphthalein indicator solution and titrate the contents of the flask with 0.5 *N* NaOH solution until the first pink tinge appears in the water layer, shaking vigorously after each addition of the reagent.

NOTE 13—At this stage, methyl orange indicator solution may be added and the total alkalinity determined as described in the determination of organically combined sulfuric anhydride, Test Method A (18.1.1).

60. Calculation

60.1 Calculate the acidity as free fatty acids as described in the determination of acidity as free fatty acids, Test Method A (Section 56).

NOTE 14—In case the total alkalinity was determined on the same sample the acidity of the free fatty acids is calculated as follows:

$$K = [(C \times E)/W] - A \qquad (20)$$

where:

K = acidity as free fatty acids or acid number, mg of KOH/g,
C = millilitres of NaOH solution required for titration of the sample,
E = strength of NaOH solution, mg of KOH/mL,
A = total alkalinity, and
W = weight of sample, g.

Method C. In the Presence of Ammonium or Triethanolamine Soaps

61. Scope

61.1 This test method covers the determination of the acidity as free fatty acids in the presence of ammonium or triethanolamine soaps, or both, existing in a sample of sulfonated or sulfated oils, or both, by calculation from the total alkalinity and the free-and-alkali-combined fatty acids.

62. Procedure

62.1 The procedure consists of two determinations: namely; (*a*) total alkalinity, and (*b*) free-and-alkali-combined fatty acids.

62.1.1 *Total Alkalinity*—Determine the total alkalinity as described in the determination of organically combined sulfuric anhydride, Test Method A (18.1.1).

62.1.2 *Free-and-Alkali-Combined Fatty Acids*—Extract the total sulfated and sulfonated fatty matter as described in the determination of total active ingredients (35.1 and 35.2), but omit the dehydration of the extract (Note 15). Add exactly 0.5 mL of 0.5 *N* NaOH solution to the extract, evaporate the ether to a volume of about 25 mL, add approximately 50 mL of neutral alcohol, and titrate the mixture with 0.5 *N* NaOH solution to a phenolphthalein end point.

NOTE 15—In the presence of acetates, wash the ether layer carefully with concentrated NaCl solution until 1 or 2 drops of 0.5 *N* NaOH solution added to the final wash water are neutral to phenolphthalein indicator.

63. Calculation

63.1 Calculate the free-and-alkali-combined fatty acids as described in the determination of acidity as free fatty acids, Test Method A (Section 56). Calculate the acidity as free fatty acids in the presence of ammonium or triethanolamine soaps, or both, as follows:

$$K = J - A \qquad (21)$$

where:

K = acidity as free fatty acids or acid number, mg of KOH/g,
J = free and alkali-combined fatty acids, and
A = total alkalinity.

WATER-IMMISCIBLE ORGANIC SOLVENTS VOLATILE WITH STEAM

64. Scope

64.1 This test method covers the determination of water-immiscible organic solvents that are volatile with steam existing in a sample of sulfonated or sulfated oil, or both. Alcohol or other volatile compounds that are mutually soluble in water and solvents interfere in this test method.

65. Apparatus

65.1 *General*—The apparatus required consists of a glass distillation flask heated by suitable means and provided with a reflux condenser discharging into a trap and connected to the flask. The trap serves to collect and measure the condenser solvent and return the water to the flask. Except as specified in 65.2 – 65.5, the apparatus described in Section 5 shall be used.

65.2 *Flask*—A 300-mL glass distillation flask of the shortneck, round-bottom type, made of well-annealed glass.

65.3 *Trap for Solvents Heavier than Water*—For the determination of solvents heavier than water, the trap described in 5.1.4 shall be used.

65.4 *Trap for Solvents Lighter than Water*—For the determination of solvents lighter than water, the trap shall be made of well-annealed glass constructed in accordance with Fig. 4 and shall be graduated as shown from 0 to 5 mL in 0.1-mL divisions. The error of any indicated capacity shall not be greater than 0.05 mL.

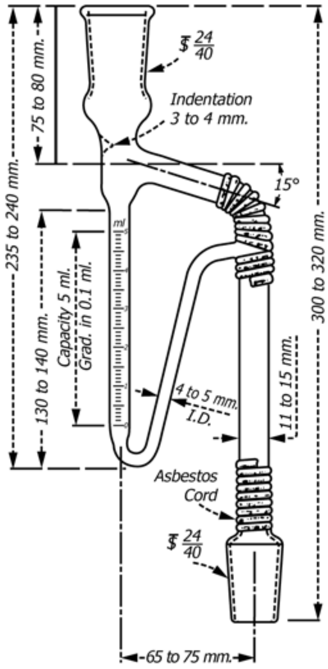


FIG. 4 Trap for Solvents Lighter than Water

65.5 *Pycnometer*—A pycnometer of 2-mL capacity shall be used for determining the specific gravity of solvents.

66. Reagents

66.1 *Calcium Chloride* ($CaCl_2$).

66.2 *Phenolphthalein,* powder.

66.3 *Sodium Carbonate* (Na_2CO_3).

66.4 *Sodium Hydroxide Solution (40 g/L)*—Dissolve 40 g of sodium hydroxide (NaOH) in water and dilute to 1 L. Potassium hydroxide (KOH) may be substituted for NaOH.

67. Calibration

67.1 To calibrate the trap for solvents heavier than water, follow the procedure described in Section 7.

67.2 To calibrate the trap for solvents lighter than water (Fig. 4), close the plain arm of the trap with a one-hole rubber stopper through which is passed a short piece of glass tubing and connect the glass tube by means of rubber tubing to a separatory funnel (Note 16). Fill the funnel with dichloroethyl ether or other liquid heavier than, and nonmiscible with water, open the stopcock of the funnel, and carefully raise the funnel until enough of the liquid overflows into the return tube to reach the 0.3-mL mark on the graduated arm of the trap. From a standard pipet, introduce exactly 1 mL of water into the graduated arm, then add a drop of pine oil (to protect the surface from evaporation), and measure the volume of water in the arm. Raise the level of the solvent in the graduated arm by approximately 1 mL by running in more liquid from the funnel, and again measure the volume of water. Continue this procedure until the whole length of the graduated column of the trap has been calibrated.

NOTE 16—Some traps are provided with an outlet and stopcock below the graduated arm. To calibrate such traps, the heavier-than-water liquid may very conveniently be introduced into the graduated column by connecting the separatory funnel directly to the outlet.

68. Procedure

68.1 Before using, clean the condenser and the receiving tube thoroughly with soap and warm water, 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.

68.2 Transfer about 50 mL of water to the distillation flask. Take enough of the sample for analysis to yield about 4 mL of solvent (Note 17). Introduce the approximate quantity of the sample into a weighing bottle and make weighings from the bottle into the distillation flask, taking care that after removal of the sample no drops of oil are left on the outside of the bottle (Note 18). Rapidly neutralize the solution with NaOH solution (40 g/L) or KOH solution (40 g/L) until slightly alkaline to phenolphthalein. The phenolphthalein should preferably be added as a powder. Add to the mixture in the flask, 2 g of Na_2CO_3, enough $CaCl_2$ to prevent foaming (3 to 5 g will usually suffice), and a few glass beads or pumice stone to prevent bumping. Fill the trap with water, using the trap for solvents heavier than water or the trap for solvents lighter than water, whichever is to be determined, and connect the apparatus.

NOTE 17—In the presence of cresylic acid, use a sample large enough to yield about 2.5 mL of solvent. Before distillation is begun, add approximately 1.5 mL of pine oil, which should be weighed exactly, in order to reduce the specific gravity of the distillate.

NOTE 18—In the case of highly volatile solvents, it is more accurate in weighing out the sample to remove the top of the weighing bottle and quickly to drop the bottle and its contents into the distillation flask.

68.3 Starting with the water at room temperature, heat the distillation flask at a rate such that the refluxing starts 7 to 10 min after the heat has been applied. Make a reading of the amount of solvent collected in the trap 2 h from the time the refluxing started. Make additional readings at the end of each subsequent 1-h period until the analysis is complete, that is, when the volume of solvent increases by not more than 0.1 mL in any two consecutive 1-h periods. Before making each reading, remove the source of heat from the distillation flask, and allow the flask to cool for 3 min (Note 19).

NOTE 19—As an additional precaution, the distillation may be continued for another 15 to 30 min with the water in the condenser tube emptied.

NOTE 20—When present, water-miscible solvents (such as alcohol) that are also miscible with the water-immiscible solvents will be found in the solvent layer. When there is an appreciable difference in the boiling points and specific gravities of the two types of solvents, they may be separated qualitatively by a fractional distillation and the specific gravities of the fractions determined. The amount of water-immiscible solvents may then be calculated from the specific gravities of the fractions and the specific gravity of the solvent layer.

In the case of pine oil or cresylic acid mixed with alcohol, the alcohol may be volatilized by heating over a hot plate, while stirring constantly, to a temperature of about 150°C, and then determining the specific gravity of the residue. The amount of water-immiscible solvent may now be calculated as in the previous procedure. This method may be applied to all such mixtures when there is considerable difference in boiling points and specific gravities and the specific gravity of one of the solvents is known.

When there is a difference in the specific gravities but not in the boiling points and the specific gravity of the water-miscible solvents is known, the water-immiscible solvent may be extracted with ether over water, the ether evaporated, and the specific gravity of the residue determined. In this procedure it is assumed that the boiling point of the water-immiscible solvent is considerably higher than that of ether. In all other cases it will be necessary to determine the water-immiscible solvent by quantitative fractional distillation or by chemical means.

68.4 When the analysis is complete, allow the distillate to stand for at least 40 min until it settles clear, and cools to about room temperature. Read the volume of the solvent in the trap. Immediately after reading, carefully remove about 2.5 mL of the solvent with a pipet and determine the specific gravity in the 2-mL pycnometer (Note 20). In the case of solvents heavier than water, separate the solvent from the water by means of a small separatory funnel.

68.5 For the analysis of samples containing solvents that are both heavier and lighter than water, make the distillation first with the trap for solvents heavier than water in place. Flush out all of the solvent floating on top of the water layer back into the distillation flask, substitute the trap for solvents lighter than water, and continue the distillation to completion.

69. Calculation

69.1 Calculate the percentage of water-immiscible volatile solvent by weight as follows:

$$A = \frac{[(A \times C) - D]}{E} \times 100 \quad (22)$$

where:

A = percentage of water-immiscible volatile solvent by weight,
B = millilitres of solvents in traps,
C = specific gravity of solvents in traps,
D = correction for the addition of pine oil, if added, and
E = weight of sample, g.

70. Reproducibility of Results

70.1 Duplicate determinations by the same or different operators shall not differ from each other by more than 0.1 mL.