Designation: D460 – 91 (Reapproved 2014)

Standard Test Methods for Sampling and Chemical Analysis of Soaps and Soap Products[1]

This standard is issued under the fixed designation D460; 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.

These methods are identical in substance with the standard methods of the American Oil Chemists' Society which were developed by the Committee on Soap Analysis A-1 of that Society, and with those of the American Chemical Society.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover the sampling and chemical analysis of cake, powdered, flake, liquid, and paste soaps, and soap products.

1.2 The test methods appear in the following order:

1.3 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered standard.

1.4 *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.* For specific hazard statements, see Section 10. 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]

D216 Method for Distillation of Natural Gasoline

D459 Terminology Relating to Soaps and Other Detergents

D1193 Specification for Reagent Water

[1] These test methods are under the jurisdiction of ASTM Committee D12 on Soaps and Other Detergents and are the direct responsibility of Subcommittee D12.12 on Analysis and Specifications of Soaps, Synthetics, Detergents and their Components.

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[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.

E1 Specification for ASTM Liquid-in-Glass Thermometers

3. Significance and Use

3.1 Soap and soap products are widely used. These test methods are suitable for setting specifications and performing quality control on soap and soap products.

SAMPLING

4. General Requirements

4.1 The seller shall have the option of being represented at the time of sampling, and when he so requests shall be furnished with a duplicate sample.

5. Cake Soaps, Flake and Powdered Soap Products When Packed in Cans or Cartons

5.1 One cake (can or carton) shall be taken at random from not less than 1 % of the seller's shipping containers, provided each package contains not less than 50 lb (22.7 kg). In the case of smaller containers, a cake (can or carton) shall be taken at random from each lot of containers totaling not more than 5000 lb (2268 kg), or fraction thereof. The gross sample shall in all cases consist of not less than three cakes (cans or cartons) taken at random from separate containers. To illustrate, if a total shipment consists of 70 000 lb, all in 1400 containers weighing 50 lb each, then 14 containers are chosen at random and one cake taken from each for a total sample of 14 cakes. If a total shipment of 70 000 lb includes containers weighing less than 50 lb, then the shipment must be divided into 14 lots of containers weighing approximately 5000 lb each, and one cake taken from each lot, again for a total sample size of 14 cakes. The gross sample shall in all cases consist of not less than three cakes (cans or cartons) taken at random from separate containers. In the case of very large lots where the sample drawn as above will amount to more than 20 lb (9.1 kg), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lb. The individual cakes (cans or cartons) shall be sealed at once in moisture-proof containers such as polyethylene bags, or tightly wrapped in paraffined paper and sealed by rubbing the edges with a heated iron. The inspector shall accurately weigh each wrapped cake (can or carton), and record its weight and the date of weighing on the wrapper. The wrapped cakes (cans or cartons) shall be placed in an airtight container, which should be nearly filled, and which shall then be sealed, marked, and sent to the laboratory for test. Samples shall be kept cool until tested.

6. Flake and Powdered Soap Products When in Bulk

6.1 A grab sample of not less than 0.5 lb (227 g) shall be taken at random from not less than 1 % of the seller's shipping containers, provided each package contains not less than 100 lb (45.4 kg). In the case of smaller containers, a grab sample of not less than 0.5 lb shall be taken at random from each lot of containers totaling not more than 10 000 lb (4536 kg) or fraction thereof. The gross sample shall in all cases consist of not less than three grab samples of 0.5 lb each taken at random from separate containers. In the case of very large lots where the sample drawn as above will amount to more than 20 lb (9.1 kg), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lb. The inspector shall rapidly mix the gross sample and place it in an airtight container, which shall be filled, sealed, marked, accurately weighed, its weight and the date of weighing recorded on the package, and sent to the laboratory for test. Samples shall be kept cool until tested.

7. Liquid Soap

7.1 A sample of not less than 0.5 pt (236.6 mL) shall be taken at random from not less than 1 % of the seller's shipping containers, provided each package contains not less than 10 gal (37.9 L). In the case of smaller containers, a sample of not less than 0.5 pt shall be taken at random from each lot of containers totaling not more than 1000 gal (3785.4 L) or fraction thereof. The gross sample shall in all cases consist of not less than three samples of 0.5 pt each taken at random from separate containers. Before drawing the sample from the container selected, the contents of the container shall be thoroughly agitated. The inspector shall thoroughly mix the gross sample, place it in clean, dry cans or bottles, which shall be completely filled and securely stoppered with clean corks or caps, then sealed, marked, and sent to the laboratory for test.

8. Paste Soap Products

8.1 *When Packed in Cans or Cartons of 5 lb (2.27 kg) or Less*—One can or carton shall be taken at random from not less than 1 % of the seller's shipping containers, provided each package contains not less than 50 lb (22.7 kg). In the case of smaller containers, a can or carton shall be taken at random from each lot of containers totaling not more than 5000 lb (2268 kg) or fraction thereof. The gross sample shall in all cases consist of not less than three cans or cartons taken at random from separate containers. In the case of very large lots where the sample drawn as above will amount to more than 20 lb (9.1 kg), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lb. The samples shall be wrapped, sealed, marked, and sent to the laboratory for test.

8.2 *When Packed in Bulk*—A *trier* sample[3] of not less than 0.5 lb (227 g) shall be taken at random from not less than 1 % of the seller's shipping containers, provided each package contains not less than 50 lb. In the case of smaller containers, a *trier* sample[3] of not less than 0.5 lb shall be taken at random from each lot of containers totaling not more than 5000 lb or fraction thereof. The gross sample shall in all cases consist of not less than three 0.5-lb samples, each taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 10 lb (4.5 kg), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 10 lb. The inspector shall promptly place the gross sample in a clean, dry, airtight and

[3] A trier sample is obtained by inserting a *trier* into the material. A trier is a half-round steel cylinder ½ to ¾ in. (12.7 to 19.1 mm) in diameter, 6 to 36 in. (152 to 914 mm) in length, pointed on one end and having a grip handle on the other end. After insertion, the trier is turned two or three times, and upon removal a core of the material being sampled is obtained.

watertight container, which shall be filled, sealed, marked, and sent to the laboratory for test.

9. Preparation of Samples

9.1 *Cake Soap*—Grind all bars through a suitable food chopper. In the case of large samples, it is permissible to quarter the bars and grind one quarter from each bar. However, each ground sample should consist of at least 3 lb (1.36 kg). Mix all ground samples thoroughly on a clean, dry, nonabsorbent, impervious surface with a spatula. Divide into four quarters and discard the two opposite quarters. Combine, remix, and requarter the remaining two quarters. Continue in this manner until the sample is reduced to approximately 2 lb (0.91 kg). Place this portion in a clean, dry sample container. Close tightly and label completely for identification. This is the sample for analysis and must be preserved in a cool dry place.

9.2 *Powdered and Chip Soaps*—Rapidly disintegrate and mix the sample of powdered, flake, or chip soap. If desired, quarter down to about 1 lb (454 g). Weigh at once all portions for analysis, preserving the remainder in an airtight container in a cool place.

9.3 *Liquid Soap*—No preparation of the sample of liquid soap, other than a thorough mixing, is necessary unless it is received during very cold weather, when it should be allowed to stand at least 1 h after it has warmed to room temperature (20 to 30°C) before it is tested, particularly for its lathering qualities.

9.4 *Paste Soap Products*—Mix the sample of paste soap products thoroughly by kneading and quarter down to about 1 lb (454 g). Weigh at once all portions for analysis, preserving the remainder in an airtight container in a cool place.

METHODS FOR CHEMICAL ANALYSIS

10. Hazards

10.1 **Precaution**—All reagents and chemicals should be handled with care. Before using any chemical, read and follow all safety precautions and instructions on the manufacturer's label. Clean up any spill immediately. Consult the Material Safety Data Sheet for specific handling and disposal information.

10.2 Use of glass wool in place of asbestos cloth is recommended where applicable.

11. Purity of Reagents

11.1 *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.[4] 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.

11.2 Unless otherwise indicated, references to water shall be understood to mean Type III reagent water conforming to Specification D1193.

12. Duplicate Tests

12.1 When a determination shows nonconformity with the specifications a duplicate test shall be made.

[4] *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.

MOISTURE

13. Choice of Test Method

13.1 The oven method described in Section 14 is generally applicable to all soaps, but certain exceptions to this method must be made if accurate results are desired. These exceptions include the following:

13.1.1 For soaps containing appreciable amounts of sodium silicate, the distillation method (Sections 15 – 18) is preferred.

13.1.2 Soaps of linseed and other oxidizing oils absorb oxygen, and if the oven method is used may gain weight near the end of the test. Therefore, either an inert atmosphere or vacuum oven should be used. The distillation method is also applicable to these types of soap.

13.1.3 Soaps containing appreciable amounts of glycerin, such as cold-made and semiboiled (including paste soaps), usually give high results by the oven method. The distillation method is preferred for most accurate results on these types of soaps.

Method A—Matter Volatile at 105°C (Oven Method)

14. Procedure

14.1 Weigh 5 ± 0.01 g of the sample in a porcelain or glass dish about 6 to 8 cm in diameter and about 2 to 4 cm in depth, and dry to constant weight in an air oven at a temperature of 105 ± 2°C. Constant weight is attained when successive heating for 1-h periods shows a loss (or gain) of not more than 0.1 %.

Method B—Distillation Method

15. Apparatus

15.1 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.

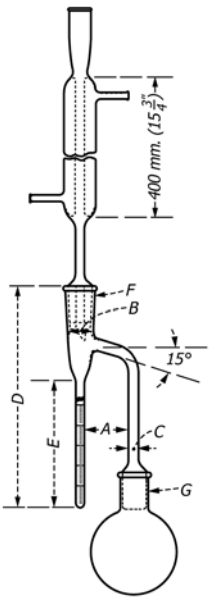
15.1.1 *Flask,* 500-mL, of either the shortneck, round-bottom type or the Erlenmeyer type.

15.1.2 *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.

15.1.3 *Condenser*—A water-cooled glass reflux condenser (Fig. 1), having a jacket approximately 400 mm in length with an inner tube 9.5 to 12.7 mm in outside diameter. The end of the condenser to be inserted in the trap may 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 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.

15.1.4 *Trap*—For greatest accuracy several trap sizes are allowable, depending upon the percentage of moisture expected:

Moisture Expected, %	Size of Trap, mL
0 to 5, incl	5
Over 5 to 17, incl	10
Over 17 to 30, incl	10
Over 30 to 50, incl	25
Over 50 to 70, incl	25
Over 70 to 85, incl	25



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

FIG. 1 Assembly at Distillation Apparatus

Traps made of well-annealed glass, constructed essentially as shown in Fig. 1 and graduated to contain one of the following specified volumes at 20°C shall be used:

15.1.4.1 *5-ml Trap,* 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.

15.1.4.2 *10-mL Trap,* subdivided from 0 to 1 mL in 0.1-mL divisions and from 1 to 10 mL in 0.2-mL divisions.

15.1.4.3 *25-mL Trap,* subdivided from 0 to 1 mL in 0.1-mL divisions and from 1 to 25 mL in 0.2-mL divisions.

NOTE 1—The condenser and trap should be thoroughly cleaned before use.

16. Solvent

16.1 *Toluene*—Saturate the toluene with water by shaking with a small quantity of water and distill. Use the distillate for the determination.

17. Procedure

17.1 For soaps containing from 5 to 25 % moisture and volatile matter, use 20 ± 0.04 g of the sample. For soaps containing more than 25 % moisture and volatile matter, use 10 ± 0.02 g of the sample. Carefully transfer the weighed sample to the 500-mL flask. Add approximately 10 g of anhydrous, fused sodium acetate to prevent violent frothing, and then follow with 100 mL of xylene (or toluene) which has been saturated with water. Attach the flask to the trap which is connected to the condenser. Prior to starting the determination, fill the receiver with saturated xylene (or toluene) by pouring in through the reflux condenser. So that the refluxing will be under better control, wrap the flask and tube leading to the receiver with asbestos cloth. Heat the oil bath with a gas burner or other source of heat, or apply heat directly to the flask with an electric heater and distill slowly. The rate at the start should be approximately 100 drops per min. When the greater part of the water has distilled over, increase the distillation rate to 200 drops per min until no more water is collected. Purge the reflux condenser during the distillation with 5-mL portions of xylene (or toluene) to wash down any moisture adhering to the walls of the condenser. The water in the receiver may be made to separate from the xylene (or toluene) by using a spiral copper wire. Move the wire up and down in the condenser occasionally, thus causing the water to settle at the bottom of the receiver. Reflux for at least 2 h, and shut off the heat at the end of this period. Adjust the temperature of the distillate to 20°C and read the volume of water.

18. Calculation

18.1 Calculate the percentage of moisture in the soap, as follows:

$$\text{Moisture, \%} = [(V \times 0.998)/W] \times 100 \quad (1)$$

where:

V = millilitres of water at 20°C, and
W = grams of sample used.

TOTAL MATTER INSOLUBLE IN ALCOHOL

19. Reagent

19.1 *Ethyl Alcohol (95 %)*—Freshly boiled, reagent grade, ethyl alcohol, 95 % or higher, neutral to phenolphthalein, and containing only volatile denaturants[5] plus 5 mL of water.

20. Procedure

20.1 Digest 2 to 10 ± 0.01 g of the sample with 200 mL of freshly boiled ethyl alcohol in a covered vessel on a steam bath until the soap is dissolved. Filter through a tared filter paper neutral to phenolphthalein. Tare the filter paper by heating at 100 to 105°C for 30 min., cooling and weighing. Or filter through a weighed Gooch crucible with suction, protecting the solution from carbon dioxide and other acid fumes during the operation by covering with a watch glass. Wash the residue on the paper or in the crucible with hot neutral ethyl alcohol until free from soap, and reserve the filtrate and washings. Dry the filter paper or crucible with the residue at 100 to 105°C for 3 h, cool, and weigh the total matter insoluble in alcohol.

NOTE 2—The matter insoluble in alcohol will contain most of the alkaline salts, such as carbonates, borates, silicates, phosphates, and sulfates, as well as starch, and may be used for the approximate determination of these constituents. These salts are not entirely insoluble in alcohol, so for accurate determinations separate portions of the soap should be used. For determination of carbonates, see Sections 61 – 68; phosphates, Sections 69 – 76; sulfates, Sections 80 and 81; silicates, Sections 59 and 60; borax, Sections 56 – 58; and starch, Sections 87 and 88.

NOTE 3—In the case of soap products containing a high level of matter insoluble in alcohol, see 25.4 for an approximate determination of soap content.

FREE ALKALI OR FREE ACID

21. Procedure

21.1 Heat the reserved filtrate from the determination of total matter insoluble in alcohol (Section20) to incipient boiling, add 0.5 mL of a 1 % solution of phenolphthalein, titrate with standard acid or alkali solution, and calculate to sodium hydroxide (NaOH) (or potassium hydroxide (KOH)) if alkaline, or to oleic acid, if acid.

NOTE 4—In the analysis of soaps known to contain little or no alkaline salts, it is unnecessary to filter the hot alcoholic soap solution as described in Section 20. However, the filtration should be carried out in all cases where alkaline salts such as silicates, phosphates, borates, and similar salts are present, since these are known to affect the free alkali determination. Free alkali values in soap or surfactant mixtures containing borax are unreliable due to solubility of borax in hot alcohol. In this case, see Sections 56 – 58 to determine the percentage of borax present, titrate an equivalent amount of borax with the standard acid, and subtract this titer from the one obtained in 21.1 before calculating alkalinity as NaOH or KOH.

MATTER INSOLUBLE IN WATER

22. Procedure

22.1 Proceed as in the determination of matter insoluble in alcohol (starting with a fresh sample of soap and omitting the drying and weighing of matter insoluble in alcohol) (Section 20). After filtering and thoroughly washing the residue, change the receivers, extract the residue with water at 60°C and wash the filter thoroughly. (When the matter insoluble is all inorganic, boiling water may be used for the extraction and washing.) Reserve the water solution. Dry the filter and residue at 100 to 105°C for 3 h, cool, and weigh the matter insoluble in water. The nature of this matter may be determined by further examination.

TOTAL ALKALINITY OF MATTER INSOLUBLE IN ALCOHOL, ALKALINE SALTS

23. Procedure

23.1 Titrate the water solution obtained in the determination of matter insoluble in water (Section 22) with standard acid, using methyl orange as indicator. Calculate the alkalinity to sodium oxide (Na_2O) and, if desired, to any other basis agreed upon by the purchaser and the seller.

COMBINED ALKALI, TOTAL ANHYDROUS SOAP

24. Reagents

24.1 *Ethyl Alcohol, Neutral*, carbon dioxide (CO_2)-free.

24.2 *Ethyl Ether.*

24.3 *Methyl Orange Indicator.*

24.4 *Phenolphthalein Indicator Solution.*

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

24.6 *Sulfuric Acid (1 + 1)*—Gradually pour 10 g of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) onto 10 g of cracked ice made from distilled water, gently swirling the mixing vessel, or gradually pour the acid down the sides of the mixing vessel into an equal weight of water, swirling gently, while submersing the vessel in an ice bath.

25. Procedure

25.1 Dissolve 5 to 10 ± 0.01 g of the sample, depending upon the anhydrous soap content, in 100 mL of water in a 250-mL Erlenmeyer flask. The flask may be heated to not more than 60°C to effect solution. When the solution is complete, add H_2SO_4 (1 + 1) in slight excess, insert a small funnel in the neck of the flask, and heat the flask to a temperature not exceeding 60°C until the fatty acids separate as a clear layer. Transfer to a separatory funnel, draw off the acid layer into a second separatory funnel, and shake the acid aqueous liquid with three 30-mL portions of ethyl ether. Dissolve the fatty acids in the ether used for washing the aqueous liquid, and shake with 10-mL portions of water until they are no longer acid to methyl orange. Unite the water portions used for washing and shake with 30 mL of ether. Wash this ether until the wash water is neutral to methyl orange. Reserve the acid water for the determination of chlorides (Sections 53 and 54).

25.2 Unite the ether solutions (if necessary, filter, washing the paper with ether) in a suitable weighed vessel, add 100 mL of neutral ethyl alcohol, add phenolphthalein, and titrate to

[5] Fisher Scientific A962, (Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219), or its equivalent, is suitable for this purpose.

exact neutrality with 0.5 *N* NaOH solution. Evaporate the alcohol and ether solution on a steam bath, and dry to constant weight as in the determination of matter volatile at 105°C, and calculate the percentage of soda soap. This naturally includes any mineral oil and neutral fat which, if determined separately, must be deducted from the result to obtain *A*, the percentage of the true anhydrous soap. See also 43.2. Calculate the combined sodium oxide (Na_2O) and deduct from the weight of soda soap to give the acid anhydrides. Calculate the weight percentage of combined sodium oxide as follows:

$$Na_2O, \text{ weight } \% = 3.099MN/W \quad (2)$$

If the original soap was potash soap, titrate directly with 0.5 *N* KOH solution, or make the proper calculation to reduce to K_2O as follows (Note 4):

$$K_2O, \text{ weight } \% = 4.710MN/W \quad (3)$$

If the weight percent soap, *A*, need be converted to percent total fatty acids, calculate as follows:

$$F = A - MNZ/W \quad (4)$$

where:

F = weight percent total fatty acids,
M = mL of standardized NaOH solution,
N = normality of the standardized NaOH per 24.5,
A = weight percent sodium or potassium soap,
W = sample weight in grams per 25.1, and
Z = 2.20 for soda soap, and 3.81 for potash soap.

In case the soap shows an excess of free acid, proper corrections must be made in calculating the combined alkali in the original soap. (A blank test should be made on the NaOH or KOH solution for neutral salts and the proper corrections made if necessary.)

25.3 In the case of soaps containing a large amount of soluble silicates and soap products containing a high percentage of finely divided material insoluble in water, the foregoing procedure cannot be applied as given. In such cases the filtrate obtained in the determination of total matter insoluble in alcohol (Section 20) may be used after neutralizing any free acid or alkali. Evaporate the alcohol on a steam bath, take up with water, and proceed according to the procedure described in 25.1 and 25.2.

25.4 In the case of soap products containing a high percentage of matter insoluble in alcohol where approximate results will suffice, such as cleansers, soap powders, scouring compounds, pastes, etc., and where agreed upon by the purchaser and the seller, the alcoholic solution obtained after filtering off and washing the matter insoluble in alcohol (Section 20) may be evaporated directly in a weighed vessel on a steam bath, then dried at 105°C to constant weight, and the result reported as soap.

COMBINED SODIUM AND POTASSIUM OXIDES

NOTE 5—The total combined alkali present in the soap is determined by the method described in Section 25, and calculated as sodium oxide (Na_2O). Determine the combined potassium oxide (K_2O) by the following method, calculate it to the equivalent Na_2O, and subtract this from the total combined alkali calculated as Na_2O; the remainder is the combined Na_2O.

26. Reagents

26.1 *Ammonium Chloride Solution*—Dissolve 100 g of ammonium chloride (NH_4Cl) in 500 mL of water, add 5 to 10 g of pulverized potassium chloroplatinate (K_2PtCl_6), and shake at intervals for 6 to 8 h. Allow the mixture to settle overnight and filter. (The residue may be used for the preparation of a fresh supply of NH_4Cl solution.)

26.2 *Ethyl Alcohol* (80 %).

26.3 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

26.4 *Hydrochloric Acid (1 + 1)*—Mix equal volumes of HCl (sp gr 1.19) and water.

26.5 *Platinum Solution*—Prepare a solution containing the equivalent of 1 g of metallic platinum (2.1 g of chloroplatinic acid (H_2 $PtCl_6$)) in each 10 mL of solution. For materials containing less than 15 % of K_2O, a solution containing 0.2 g of metallic platinum (0.42 g of H_2PtCl_6) in each 10 mL of solution is recommended.

27. Preparation of Sample

27.1 Weigh 10 ± 0.01 g of the sample and sinter it in an evaporating dish below a dull red heat. Leach the ash with hot water, filter into a 100-mL volumetric flask, and wash the paper with three 5 to 10-mL portions of hot water. Complete the ashing after returning the filter paper and residue to the original dish and sintering as before. Excessive heating shall be avoided. Removal of most of the alkali present by thoroughly washing the ash with hot water before completion of the ashing will aid in preventing overheating of the greater portion of the sample. Add a few drops of HCl (1 + 1) to the ash and wash the contents of the dish into the volumetric flask. Acidify the solution in the volumetric flask with HCl, dilute to 100 mL, mix thoroughly, and pass through a dry filter.

28. Procedure

28.1 Acidify an accurately measured 10-mL aliquot of the solution obtained as described in Section 27 with a few drops of HCl and add 10 mL of the platinum solution. Evaporate the solution on a water bath to a thick paste which will become solid on cooling to room temperature. Avoid exposure to ammonia fumes while heating the solution. Treat the residue with approximately 6 mL of ethyl alcohol and add 0.6 mL of HCl (sp gr 1.19). Filter on a Gooch crucible and wash the precipitate thoroughly with ethyl alcohol both by decantation and on the filter, continuing the washing until after the filtrate is colorless. Then wash the residue five or six times with 25-mL portions of the NH_4Cl solution to remove the impurities from the precipitate. Wash again thoroughly with ethyl alcohol, dry the precipitate at 100°C for 30 min, and weigh.

29. Calculation

29.1 Calculate the percentage of K_2O as follows:

$$K_2O, \% = A \times 19.376 \quad (5)$$

where *A* = grams of K_2PtCl_6 weighed.

FREE ALKALI AND POTASSIUM CARBONATE IN POTASH PASTE SOAPS

30. Reagents

30.1 *Ethyl Alcohol, Neutral* (*Absolute*)—Freshly boiled absolute ethyl alcohol, neutral to phenolphthalein, conforming to either Formula No. 3A or 30 of the U.S. Bureau of Internal Revenue.

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

30.3 *Phenolphthalein Indicator Solution (10 g/L)*—Prepare a solution of 1 g phenolphthalein in 100 mL of neutral ethyl alcohol (95 %).

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

30.5 *Sulfuric Acid, Standard Solution* (0.5 *N*)—Prepare and standardize a 0.5 *N* sulfuric acid (H_2SO_4) solution.

31. Procedure

31.1 Weigh 10 ± 0.01 g of the sample into a 250-mL beaker and dissolve in 100 mL of freshly boiled water. Add a measured amount of 0.5 *N* H_2SO_4 sufficient to make the solution acid to methyl orange indicator, and bring to incipient boiling until fatty acids separate out in a clear layer. Excessive boiling should be avoided to preclude the possibility of volatilization of any low molecular weight fatty acids that may be present.

31.2 Add 0.5 mL of phenolphthalein indicator solution, and while stirring the contents of the beaker, titrate with NaOH solution until the solution is almost neutral but still slightly on the acid side to phenolphthalein.

31.3 Evaporate to dryness on a steam bath and dissolve in 200 mL of neutral alcohol (absolute). Titrate with NaOH solution to neutrality to phenolphthalein.

31.4 Determine carbon dioxide (CO_2) on a separate sample by the train-absorption method (Section 64) or the evolution-volumetric method (Section 65).

32. Calculation

32.1 Calculate the percentages of potassium carbonate (K_2CO_3) and free potassium hydroxide (KOH) as follows:

$$K = C \times 3.140 \tag{6}$$

$$K_2CO_3,\ \% = (K/W_1) \times 100$$

$$V_k = K/0.03455$$

$$V_t = V_1 - (V_2 + V_3)$$

$$\text{Free } KOH,\ \% = [(V_t - V_k) \times 0.02805 \times 100]/W_2$$

where:

K = grams of K_2CO_3 equivalent to C,
C = grams of CO_2 (31.4),
W_1 = grams of sample used for determination of CO_2 (31.4),
V_k = millilitres of 0.5 *N* H_2SO_4 equivalent to K_2CO_3,
V_t = millilitres of 0.5 *N* H_2SO_4 equivalent to free KOH + K_2CO_3,
V_1 = millilitres of 0.5 *N* H_2SO_4 used to acidify sample (31.1),
V_2 = millilitres of 0.5 *N* NaOH solution required for titration of aqueous solution (31.2),
V_3 = millilitres of 0.5 *N* NaOH solution required for titration of alcoholic solution (31.3), and
W_2 = grams of sample used for titration procedure (31.1).

UNSAPONIFIED PLUS UNSAPONIFIABLE MATTER

NOTE 6—In the case of superfatted soaps, free fatty acids, which are the superfatting agents in highest percentage, plus this unsaponified and unsaponifiable matter, constitute the major portion of the superfatting agents used.

33. Apparatus

33.1 *Extraction Cylinder*—The extraction cylinder shall be a 250-mL graduated glass-stoppered cylinder about 39 mm in diameter and about 35.5 cm (14 in.) in length.

34. Reagents

34.1 *Ethyl Alcohol* (95 %)

34.2 *Ethyl Alcohol* (50 %)

34.3 *Ethyl Alcohol* (10 %)

34.4 *Petroleum Ether*—The solvent used shall be of the pentane type, containing a minimum amount of isopentane, isohexane, and hexane, and boiling in the range 35 to 60°C.[6]

Distillation test:[A]	
Initial boiling point	35 to 38°C
Dry flask end point	52 to 60°C
Distilling under 54°C, min	95 %
Distilling under 40°C, max	60 %
Specific gravity at 15.5/15.5 °C (60/60°F)	0.630 to 0.660
Color	water white
Doctor test	sweet
Evaporation residue, 100 mL, max	0.0011 g
Copper-strip corrosion test[B]	noncorrosive
Unsaturated compounds[C]	trace only permitted
Residue in distilling flask	neutral to methyl orange
Blotter-strip odor test[D]	odorless within 12 min
Aromatic compounds[E]	no nitrobenzene odor
Saponification value	less than 1.0 mg KOH/100 mL

[A] Distillation test shall be made in accordance with ASTM Method D216. As a check on the evaporation residue, 250 mL of the petroleum ether and 0.25 g of stearin or other hard fat (previously brought to constant weight by heating) when dried as in the actual determination shall not show an increase in weight exceeding 0.003 g.

[B] Copper-strip corrosion test shall be made by inserting a small polished copper strip into the petroleum ether in the distilling flask. There should be no appreciable darkening of the copper.

[C] Unsaturated compounds shall be determined by the method for determining olefins as described in *Industrial and Engineering Chemistry*, Analytical Edition, March 15, 1938, p. 154.

[D] Odor test: Immerse 1 in. of a strip of white unglazed blotting paper, approximately 1 by 4 by 0.166 in. in size, in the petroleum ether for 30 s, remove the strip, and allow to dry at room temperature in still air for 12 min.

[E] Aromatic compounds: Add 5 drops of petroleum ether to 40 drops of sulfuric acid (H_2SO_4, sp gr 1.84) and 10 drops of nitric acid (HNO_3, sp gr 1.42) in a test tube, warm for 10 min, allow to cool for 30 min, transfer to a shallow dish, and dilute with water.

34.5 *Sodium Hydroxide, Standard Solution* (0.1*N*)—Prepare and standardize a 0.1 *N* NaOH solution.

[6] J. T. Baker Analyzed Reagent 9268, (J. T. Baker, Inc. Phillipsburg, NJ) or its equivalent, is suitable for this purpose.

34.6 *Sodium Hydroxide, Standard Solution* (0.04 *N*)—Prepare and standardize a 0.04 *N* sodium hydroxide (NaOH) solution.

35. Procedure

35.1 Weigh 5 ± 0.2 g of the sample and place it in a 250-mL Erlenmeyer flask or beaker that contains 0.1 g of sodium bicarbonate ($NaHCO_3$) to promote phase separation during the extractions, and dissolve in 100 mL of redistilled ethyl alcohol (50 %). Warm and shake to effect solution, keeping the temperature under 60°C, and filter off any undissolved residue on a Gooch crucible with a glass wool pad, or on a funnel using a glass wool pad deposited on a perforated porcelain disk. Wash three times with hot alcohol (50 %). Wash with a small amount of petroleum ether to remove any traces of unsaponified and unsaponifiable matter. Transfer the entire alcohol-water-and-ether filtrate to the extraction cylinder and make up to the 160-mL mark with redistilled, ethyl alcohol (50 %). Add 50 mL of petroleum ether, shake vigorously for 1 min (Note 5), and allow to settle until both layers are clear. The volume of the upper layer should be about 40 mL. Draw off the petroleum ether layer as closely as possible by means of a slender glass siphon into a separatory funnel of 500-mL capacity.

35.2 Repeat the extraction at least six times using 50 mL of petroleum ether each time (Note 8). To avoid extraction of free fatty and rosin acids, wash the combined ether extracts first with a mixture of 15 mL of 0.1 *N* NaOH solution and 15 mL of ethyl alcohol (95 %), and then three times with 25-mL portions of ethyl alcohol (10 %), shaking vigorously each time. Transfer the petroleum ether extract to a beaker and evaporate the petroleum ether on a steam bath by the aid of a current of air.

NOTE 7—Thorough and vigorous shaking is necessary in order to secure accurate results. The two phases must be brought into the most intimate contact possible; otherwise low and disagreeing results may be obtained. If any emulsion occurs, break it with 10 g of sodium sulfate.

NOTE 8—This method will not remove all the unsaponifiable matter in soaps to which lanolin has been added. More extractions are required when substances of this nature are present.

35.3 Test the residue for solubility by treating with 50 mL of petroleum ether at room temperature. Filter, and wash free from the insoluble residue, if any. Evaporate and dry in the same manner on a steam bath, and finally in an air oven at 100 to 101°C for 30 min. Weigh, and return to the oven, reweighing at 15-min intervals until constant weight is reached. Take up the residue in 50 mL of warm ethyl alcohol, neutralized to phenolphthalein, titrate to the same color as the original neutral alcohol with 0.04 *N* NaOH solution, and calculate to oleic acid. Deduct this figure from the gross weight previously found and report as "unsaponified and unsaponifiable matter."

35.4 Make a blank test on the petroleum ether by evaporating 250 mL of the ether with about 0.25 g of stearin or some other hard fat previously brought to constant weight by heating and drying as in the actual determination. The blank must not exceed a few milligrams.

NOTE 9—Any blank from the petroleum ether must be deducted from the weight before calculating the unsaponified and unsaponifiable matter.

UNSAPONIFIABLE MATTER

36. Apparatus

36.1 *Extraction Cylinder*—See Section 33.

37. Reagents

37.1 See 34.1 and 34.4.

37.2 *Potassium Hydroxide Solution (50 %)*—Dissolve 500 g of potassium hydroxide (KOH) in 500 mL of water.

38. Procedure

38.1 Transfer 5 ± 0.2 g of the sample to a 200-mL Erlenmeyer flask. Add 30 mL of redistilled ethyl alcohol (95 %) and 5 mL of KOH solution, and boil for 1 h under a reflux condenser. Transfer to the extraction cylinder and wash to the 40-mL mark with redistilled ethyl alcohol (95 %). Complete the transfer, first with warm and then with cold water, until the total volume is 80 mL, and finally with a small quantity of petroleum ether. Cool the cylinder to room temperature and add 50 mL of petroleum ether; then proceed with the extraction as outlined in the procedure for unsaponified plus unsaponifiable matter (Section 35; see also Note 5 and Note 6), except that the alkaline wash may be omitted. Weigh the residue and correct for fatty acids in the usual manner. Report the result as unsaponifiable matter.

UNSAPONIFIED MATTER

39. Calculation

39.1 From the total unsaponified plus unsaponifiable matter determined in Section 35, deduct the unsaponifiable figure obtained in Section 38 and report the difference as "unsaponified matter."

ROSIN (McNICOLL METHOD)[7]

40. Apparatus

40.1 The apparatus required consists of a glass flask connected, preferably by a ground-glass joint, to a reflux condenser.

40.1.1 *Esterification Flask,* 150-mL of either the round-bottom or Erlenmeyer type.

40.1.2 *Reflux Condenser*—Any suitable water-cooled glass reflux condenser may be used.

41. Reagents

41.1 *Naphthalene-β-Sulfonic Acid Solution*—Dissolve 40 g of reagent[8] in 1 L of absolute methyl alcohol.

41.2 *Phenolphthalein Indicator*—Prepare a 0.5 % solution of phenolphthalein in neutral redistilled alcohol.

[7] Cox and Evers, "Report of British Standards Committee," *Analyst*, Vol 62, No. 741, 1937, pp. 865 to 870; also D. McNicoll, "The Estimation of Rosin Acids in Fatty Mixtures," *Journal*, Soc. Chemical Industry, Vol 40, 1921, p. 124 T.

[8] Eastman grade or equivalent reagent has been found satisfactory for this purpose.

41.3 *Potassium Hydroxide, Standard Alcoholic Solution* (0.2 *N*)—Accurately standardize a 0.2 *N* solution of potassium hydroxide (KOH) in neutral redistilled alcohol (due to volatility of alcohol, this solution should be restandardized frequently).

42. Procedure

42.1 *Preparation of Fatty and Rosin Acids*—For the preparation of the sample for this determination, follow the procedure described in Section 45.

42.2 *Esterification and Titration*—Weigh about 2 ± 0.001 g of the fatty acids into the esterification flask. Add 25 mL of naphthalene-β-sulfonic acid solution. Add a few glass beads to ensure smooth boiling, attach the reflux condenser, and boil for 30 min; also, run a blank test using 25 mL of the reagent. At the end of the boiling period cool the contents of the flask, add 0.5 mL of phenolphthalein indicator, and titrate immediately with 0.2 *N* alcoholic KOH solution.

43. Calculation

43.1 Calculate the percentage of rosin as follows (see Note 10):

$$R = [(S - B) \times N \times 0.346 \times 100]/W \quad (7)$$

$$R_1 = R - 1.0$$

$$R_2 = (R_1 \times F)/100$$

$$R_s = R_2 \times 1.064$$

where:

R = percentage of rosin in fatty acids,
R_1 = corrected percentage of rosin in fatty acids, (see Note 11),
R_2 = percentage of rosin on basis of original sample,
R_s = percentage of rosin soda soap on basis of original sample,
S = millilitres of KOH solution required for titration of the sample,
B = millilitres of KOH solution required for titration of the blank,
N = normality of KOH solution,
W = grams of sample
F = percentage of total fatty acids in soap, (see 25.2).

NOTE 10—In all cases where the rosin content is found to be less than 5 % the actual presence or absence of rosin should be checked qualitatively by the Liebermann-Storch test, as follows:

Transfer 1 to 2 mL of the sample of fatty acids to a test tube, treat with 5 to 10 mL of acetic anhydride, and warm on a steam bath. After cooling, pour 1 to 2 mL into a white porcelain dish and allow a drop or two of sulfuric acid (H_2SO_4, sp gr 1.53) to run down the side of the vessel. (The H_2SO_4 (sp gr 1.53) is prepared by diluting 34.7 mL of H_2SO_4 (sp gr 1.84) with 35.7 mL of water.) If rosin is present, a fugitive violet coloration changing to a brownish tinge is immediately produced at the margin of contact of the reagents. The test should be checked with a sample of fatty acids to which a small amount of rosin has been added.

NOTE 11—Cooperative studies have shown that the McNicoll method gives results approximately 1 % higher than the amount of rosin present. Consequently, the committee recommends deducting 1 % from the percentage of rosin found in the fatty acids.

43.2 If true fatty acid soap is desired, subtract the rosin soap from the total anhydrous soap determined in 25.2, as follows:

$$T = A - R_s \quad (8)$$

where:

T = percentage of true fatty acid soap,
A = percentage of total anhydrous soap, and
R_s = percentage of rosin soda soap.

PREPARATION OF TOTAL FATTY MATTER (FATTY AND ROSIN ACIDS, AND UNSAPONIFIED AND UNSAPONIFIABLE FATTY MATTER)

44. Reagent

44.1 *Sulfuric Acid (1 + 4)*——Slowly mix 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 4 volumes of water.

45. Preparation for Rosin and Titer Tests, Iodine and Acid Numbers

45.1 Dissolve about 50 g of the sample in 500 mL of hot water. (If soaps to be tested contain alcohol, the alcohol should be completely removed by evaporation from the soap solution.) Add 100 mL of H_2SO_4 (30 %), heat gently until the fatty matter collects in a clear layer. Siphon off the aqueous acid layer, add 300 mL of hot water, boil gently for a few minutes, and siphon off the aqueous acid layer. Repeat the washing of the acids in this manner until the final washing is neutral to methyl orange indicator (usually 3 to 6 washings). Complete this acidification and washing in a very short period of time, and keep the beaker covered to prevent oxidation of the acids. After the last washing, remove the last traces of water from the beaker with a pipet, filter the fatty acids through one or two thicknesses of filter paper, and dry at a temperature of 105°C for 45 to 60 min or heat rapidly to 130°C and allow to cool. Do not hold at 130°C, but if water is present, decant the clear fatty acids into another beaker, and again reheat them momentarily to 130°C. These acids may then be used for the titer and rosin determinations.

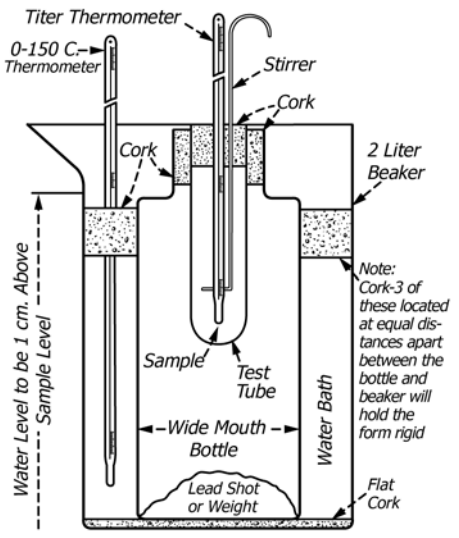


FIG. 2 Apparatus Assembly for Titer Test

45.2 In preparing the acids for the iodine and acid number determinations, the washed acids should be filtered through one or two thicknesses of filter paper at a temperature not exceeding 15°C above the titer point of the fatty acids. If the acids are not perfectly clear and dry, refilter.

TITER TEST

46. Apparatus

46.1 The apparatus required, shall be assembled as shown in Fig. 2 and shall consist of the following:

46.1.1 *Water Bath*—A 2-L Griffin low-form beaker.

46.1.2 *Wide-Mouth Bottle*—A wide-mouth 450-mL bottle, 190 mm in height, having a neck 38 mm in inside diameter, fitted with a cork to carry the test tube (46.1.3) and with sufficient weights or lead in the bottom of the bottle to hold it steady when placed in the water bath.

46.1.3 *Test Tube*—Test tube 100 mm in length, and 25 mm in diameter with or without rim. The tube may have an etched line extending around it at a distance of 57 mm from the bottom to indicate the height to which it is to be filled.

46.1.4 *Stirrer*—A stirrer 2 to 3 mm in outside diameter with one end bent in the form of a loop 19 mm in diameter. Glass, Nichrome, stainless steel, or Monel metal wire may be used. The upper end of the stirrer may be formed to accommodate hand stirring or for attachment to a mechanical stirrer.

46.1.5 *Laboratory Thermometer*—A laboratory thermometer having a range from 0 to 150°C.

46.1.6 *Thermometer*—An ASTM Titer Test Thermometer, having a range from −2 to +68°C and conforming to the requirements for Thermometer 36°C[9] as prescribed in Specifications E1.

47. Procedure

47.1 Transfer the fatty acids (see Section 45), when cooled somewhat, to the test tube, filling it to the 57-mm line, and place the tube in the wide-mouth bottle. Set the bottle assembly in the water bath (the water should reach the neck of the bottle), as shown in Fig. 2, and adjust the temperature of the bath to 20°C for fatty acids with titers of 35°C and over, and to 15 to 20°C below the expected titer for all fatty acids with titers below 35°C.

47.2 Insert the titer test thermometer in the center of the sample and suspend it at such a height that the immersion mark coincides with the top of the sample.

47.3 When the titer test thermometer reads 10°C above the expected titer, stir with the stirring rod in a vertical manner at the rate of 100 completed up-and-down motions per minute. The stirrer should travel about 3.8 cm. Read the thermometer every 15 s, and continue stirring until the temperature remains constant (or begins to rise) for 30 s. Discontinue stirring immediately and note the rise in temperature. Report as the titer of the fatty acids, the highest temperature reached by the thermometer.

47.4 Duplicate determinations should not differ by more than 0.2°C.

ACID NUMBER OF FATTY ACIDS

48. Procedure

48.1 For the preparation of the sample for this determination follow the procedure described in Section 45. In a 250-mL Erlenmeyer flask dissolve 2 g of the fatty acids, accurately weighed in 20 to 30 mL of neutral ethyl alcohol (95 %) near the boiling point. Titrate with standard alkali, using phenolphthalein as indicator.

49. Calculation

49.1 Calculate the acid number of the fatty acid, expressed as milligrams of KOH per gram of fatty acid, as follows:

$$\text{Acid number} = (AN \times 56.1)/B \quad (9)$$

where:

A = millilitres of KOH solution required for titration of the sample,
N = normality of the KOH solution, and
B = grams of sample used.

IODINE NUMBER (WIJS METHOD)

50. Reagents

50.1 *Potassium Dichromate, Standard Solution* (0.1 *N*)—Dissolve 4.903 g of potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 1 L at the temperature at which titrations are to be made.

NOTE 12—Occasionally $K_2Cr_2O_7$ is found containing sodium dichromate ($Na_2Cr_2O_7$), although this is rare. If the character of the $K_2Cr_2O_7$ is not certain, the purity can be ascertained by titration against freshly resublimed iodine. However, this is usually unnecessary.

50.2 *Potassium Iodide Solution (150 g/L)*—Dissolve 150 g of potassium iodide (KI) in water and dilute to 1 L.

50.3 *Sodium Thiosulfate, Standard Solution* (0.1 *N*)—Dissolve 24.8 g of sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$) in freshly boiled water and dilute to 1 L at the temperature at which the titrations are to be made. To standardize, place 40 mL of $K_2Cr_2O_7$ to which has been added 10 mL of the solution of KI in a glass-stoppered flask, add 5 mL of concentrated hydrochloric acid (HCl, sp gr 1.19), dilute with 100 mL of water, and allow the $Na_2S_2O_3{\cdot}5H_2O$ solution to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and while shaking constantly, continue to add the $Na_2S_2O_3{\cdot}5H_2O$ solution until the blue color just disappears.

50.4 *Starch Paste*—Boil 1 g of starch in 200 mL of water for 10 min, and cool to room temperature.

NOTE 13—An improved starch solution may be prepared by autoclaving 2 g of starch and 6 g of boric acid dissolved in 200 mL of water at 15-psi pressure for 15 min. This solution has good keeping qualities.

50.5 *Wijs Iodine Solution*[10]—Dissolve 13.0 g of resublimed iodine in 1 L of glacial acetic acid and pass in washed and dried

[9] Thermometers made to these specifications conform also with the requirements for the titer test thermometer of the American Oil Chemists Society and the Association of Official Agricultural Chemists, except for the special marking.

[10] Stock Wijs solution can be readily purchased from a number of chemical supply houses at nominal costs.

chlorine gas until the original thiosulfate titration of the solution is not quite doubled. There should be no more than a slight excess of iodine, and no excess of chlorine. When the solution is made from iodine and chlorine, this point can be ascertained by not quite doubling the titration (see Note 14). For preparation of the Wijs solution use glacial acetic acid of 99.0 to 99.5 % strength. For glacial acids of somewhat lower strength, freezing and centrifuging or draining, as a means of purification, is recommended. Preserve the solution in amber, glass-stoppered bottles, sealed with paraffin until ready for use. Mark on the bottles the date on which the solution is prepared; do not use Wijs solution that is more than 30 days old.

NOTE 14—For preparation of the solution, McIlhiney[11] gives the following details:

The preparations of the iodine monochloride solution presents no great difficulty, but it must be done with care and accuracy in order to obtain satisfactory results. There must be in the solution no appreciable excess either of iodine or more particularly of chlorine, over that required to form the monochloride. This condition is most satisfactorily attained by dissolving in the whole of the acetic acid to be used the requisite quantity of iodine, using a gentle heat to assist the solution, if it is found necessary; then setting aside a small portion of this solution, while pure and dry chlorine is passed into the remainder until the halogen content of the whole solution is doubled. Ordinarily, it will be found that by passing the chlorine into the main part of the solution until the characteristic color of free iodine has just been discharged there will be a slight excess of chlorine which is corrected by the addition of the requisite amount of the unchlorinated portion until all free chlorine has been destroyed. A slight excess of iodine does little or no harm, but an excess of chlorine must be avoided.

51. Procedure

51.1 Weigh accurately from 0.10 to 0.50 g (depending on the iodine number) of the fatty acids prepared as described in Section 44 into a clean, dry, 450-mL (16-oz) glass-stoppered bottle containing 15 to 20 mL of carbon tetrachloride. Add 25 mL of the iodine solution from a pipet, allowing each sample to drain for the same length of time. The excess of iodine should be from 50 to 60 % of the amount added, that is, from 100 to 150 % of the amount absorbed. Let the bottle stand in a dark place for 30 min at a temperature of 25 ± 2°C, then add 20 mL of KI solution and 100 mL of water. Titrate the iodine with 0.1 *N* $Na_2S_2O_3 \cdot 5H_2O$ solution, added gradually while shaking constantly, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake vigorously, so that any iodine remaining in solution in the carbon tetrachloride may be taken up by the KI solution. Make two determinations on blanks employing the same procedure as used for the sample except that no fat should be used in the blanks. Slight variations in temperature quite appreciably affect the titer of the iodine solution, since acetic acid has a high coefficient of expansion. It is therefore essential that the blanks and determinations on the sample be made at the same time.

[11] McIlhiney et al, "Report of the Sub-Committee on Shellac Analysis," *Journal*, Am. Chemical Soc., Vol 29, 1907, p. 1222.

52. Calculation

52.1 Calculate the iodine number of the sample test (centigrams of iodine absorbed by 1 g of sample, that is, percentage iodine absorbed), as follows:

$$\text{Iodine value} = [(B - A)N \times 12.69]/C \quad (10)$$

where:

A = millilitres of $Na_2S_2O_3$ solution required for titration of the sample,
B = millilitres of $Na_2S_2O_3$ solution required for titration of the blank,
C = grams of sample used, and
N = normality of the $Na_2S_2O_3$ solution.

CHLORIDES

53. Reagents

53.1 *Magnesium Nitrate Solution (200 g/L)*—Dissolve 200 g of chloride-free magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) in water and dilute to 1 L.

53.2 *Potassium Chromate Indicator Solution*—Dissolve 5 g of potassium chromate (K_2CrO_4) in water and add a solution of $AgNO_3$ until a slight red precipitate is produced, filter the solution, and dilute to 100 mL.

53.3 *Silver Nitrate, Standard Solution* (0.1 *N*)—Prepare and standardize a 0.1 *N* silver nitrate ($AgNO_3$) solution.

54. Procedure

54.1 Neutralize with chloride-free alkali the acid water obtained in the determination of combined alkali (Section 24). Titrate with 0.1 *N* $AgNO_3$ solution, using K_2CrO_4 indicator.

54.2 In case the total anhydrous soap is not to be determined, it will be more convenient to use the following method: Dissolve 5 ± 0.01 g of the sample in 300 mL of water, boiling if necessary to effect solution. Add an excess of neutral, chloride-free $Mg(NO_3)_2$ solution (about 25 mL of the $Mg(NO_3)_2 \cdot 6H_2O$ solution). Without cooling or filtering, titrate with $AgNO_3$ solution, using K_2CrO_4 indicator.

55. Calculation

55.1 Calculate the percentage of sodium chloride (NaCl) or potassium chloride (KCl), as the character of the soap indicates, as follows:

$$\text{Chlorides, \%} = [A \times N \times B]/C \quad (11)$$

where:

A = millilitres of $AgNO_3$ required for titration of the sample,
N = normality of the $AgNO_3$ solution,
B = 5.85 for NaCl or 7.46 for KCl, and
C = grams of sample used.

BORAX

56. Reagents

56.1 *Calcium Carbonate* ($CaCO_3$), precipitated.

56.2 *Glycerin,* neutral.

56.3 *Hydrochloric Acid (1 + 1)*—Mix equal volumes of concentrated hydrochloric acid (HCl, sp gr 1.19) and water.

56.4 *Phenolphthalein Indicator Solution.*

56.5 *Silica* $(SiO)_2$, fine powder.

56.6 *Sodium Carbonate* (Na_2CO_3).

56.7 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare and standardize a 0.1 *N* sodium hydroxide (NaOH) solution.

57. Procedure

57.1 Weigh 10 ± 0.02 g of the sample (or 5 ± 0.01 g if more than 5 % of borax is present) into a platinum dish and add 2.15 g of fusion mixture consisting of 200 g of Na_2CO_3 and 15 g of silica in fine powder. To this mixture add 15 mL of alcohol (94 % or higher), mix with the aid of a glass rod, and after washing the rod with a little alcohol, evaporate the mass to dryness on a water bath. Ignite until the combustible material is destroyed, cover the dish with a piece of platinum foil, and fuse.

57.2 Completely disintegrate the fusion by boiling with water and transfer the solution to a 250-mL round-bottom flask. Acidify the mixture with 20 mL of HCl (1 + 1), heat nearly to boiling, and add a moderate excess of dry precipitated $CaCO_3$. Connect the flask with a reflux condenser and boil vigorously for 10 min. Filter out the precipitate through a folded filter, washing several times with hot water, but keeping the total volume of the liquid below 100 mL.

57.3 Return the filtrate to the flask, add a pinch of $CaCO_3$, and again boil under a reflux condenser. Remove the flame and connect the top of the condenser with a water pump; apply suction until the boiling has nearly ceased. Cool the mixture to room temperature, add 50 mL of glycerin, and titrate the solution with 0.1 *N* NaOH free of carbonate, using phenolphthalein as indicator. After the end point is reached, add 10 mL more of glycerin and again titrate. Repeat this process until the addition of glycerin causes no further action on the end point.

58. Calculation

58.1 Calculate the percentage of borax as follows:

$$\text{Borax, as } Na_2B_4O_7\cdot 10H_2O,\ \% = \left[(AN \times 0.09536)/B\right] \times 100 \quad (12)$$

where:

A = millilitres of NaOH solution required for titration of the sample,
N = normality of the NaOH solution, and
B = grams of sample used.

SILICA PRESENT AS ALKALINE SILICATES

59. Reagents

59.1 *Hydrochloric Acid (sp gr 1.19)*—Concentrated (HCl).

59.2 *Hydrofluoric Acid (48 %)*—Concentrated (HF).

60. Procedure

60.1 When the material contains no mineral matter that is insoluble in water, ignite a sample of the soap containing not to exceed 0.2 g of silica in a platinum dish at a low temperature. When charred, extract the soluble salts with water, return the paper and charred residue to the dish, and complete the ignition. Unite the residue in the dish and the water extract, carefully acidify with HCl, finally adding the equivalent of from 5 to 10 mL of HCl in excess. The dish or casserole containing the solution should be covered with a watch glass while adding acid so as to avoid loss by spray.

60.2 When the material contains mineral matter insoluble in water, or a determination of highest accuracy is not necessary, take a portion of the solution after titrating the matter insoluble in alcohol (see Section 23) containing not more than 0.2 g silica and add 5 to 10 mL of HCl.

60.3 Evaporate the acidified solution (washing off and removing the cover glass if used) to dryness on a steam bath or hot plate at a temperature not exceeding 120°C. Cool, moisten with HCl, let stand 5 to 10 min, breaking up all lumps with a stirring rod. Add about 25 mL of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

60.4 Evaporate the filtrate to dryness and repeat the above treatment, filtering on a second paper. Carefully ignite the two papers and contents in a weighed platinum crucible, first at a low temperature until the paper is consumed, and then over a blast lamp. Cool in a desiccator, weigh, and repeat until constant weight is obtained. If extreme accuracy is desired, moisten the weighed contents of the crucible with water, add 10 mL of HF and four drops of strong sulfuric acid (H_2SO_4), evaporate to dryness over a low flame, ignite at the temperature of the blast lamp for about 2 min, cool in a desiccator, and weigh. The difference between this weight and the previous weight is the weight of the silica (SiO_2). To calculate sodium silicate having the ratio, 1 Na_2O:3.25 SiO_2, multiply the weight of SiO_2 by 1.308.[12]

CARBON DIOXIDE (CARBONATES)

61. Choice of Method

61.1 Whenever the determination of carbon dioxide is prescribed in the specifications, either the train-absorption method as described in Sections 62 – 64 or the evolution-volumetric method as described in Sections 65 – 68 shall be used.

Train-Absorption Method

62. Apparatus Assembly

62.1 Place a 250-mL Erlenmeyer flask on a gauze over a burner. Fit the flask with a two-hole rubber stopper, one opening to carry a 25-cm (10-in.) reflux condenser and the other a thistle tube equipped with a three-way stopcock. Draw out the end of the thistle tube to a small point, and place it in the stopper so that the point is very close to the bottom of the flask. Attach a small funnel to the straightaway end of the stopcock for the introduction of acid into the flask. Attach the

[12] The molar ratio can be calculated using the factor 1.317.

other opening of the stopcock (which is to receive air) to a purifying tube containing soda-asbestos (Ascarite) or any other suitable carbon dioxide (CO_2) absorbent. Attach to the top of the reflux condenser a train consisting of the following: (*a*) a drying tube containing a dehydrating agent such as concentrated sulfuric acid (H_2SO_4, sp gr 1.84) or anhydrous magnesium perchlorate ($Mg(ClO_4)_2$), (*b*) a weighed tube containing Ascarite and magnesium perchlorate, and a second weighed tube containing H_2SO_4 (sp gr 1.84). Attach to this train a protective U-tube containing anhydrous calcium chloride ($CaCl_2$), and connect the U-tube to an aspirator.

63. Reagent

63.1 *Hydrochloric Acid (1 + 1)*—Mix equal volumes of concentrated hydrochloric acid (HCl, sp gr 1.19) and water.

64. Procedure

64.1 Set up the apparatus, leaving out the weighed train, and aspirate with a slow stream of the dry carbon dioxide (CO_2)-free air until the apparatus is free of CO_2. Insert the train and continue to aspirate for 30 min. Check the weight of the train to determine whether the air is passing through too fast, or whether the system is free of CO_2. The system must be free of leaks. Weigh a sufficient portion of the sample to yield approximately 0.2 g of CO_2 into the Erlenmeyer flask, cover with 20 mL of freshly boiled water, and close the apparatus with the train in place. Add 20 mL of HCl (1 + 1) very slowly through the funnel; do not apply heat to the flask. The rate of adding acid should be carefully controlled so that the gas does not pass through the train too rapidly. As soon as the acid is added, start aspiration gently. When the absorption begins to slacken, start heating gently and continue until the contents of the flask have boiled 15 to 20 min. Stop heating, and continue aspirating until the flask has cooled. Remove the train and weigh. The increase in weight represents CO_2. The amount of this increase multiplied by 2.41 equals sodium carbonate (Na_2CO_3). If potassium carbonate (K_2CO_3) only is present, the increase in weight multiplied by 3.14 equals K_2CO_3.

Evolution-Volumetric Method[13]

65. Apparatus

65.1 The apparatus shall be assembled as shown in Fig. 3 and shall consist of the following:

65.1.1 *Evolution or Sample Flask*, *A*—A 1-L, round-bottom, ring-neck flask of heat-resistant glass,[14] provided with a 2-hole rubber stopper.

65.1.2 *Dropping Funnel*,*B*—A dropping funnel provided with a stopcock and having a stem long enough to reach well down into the lowest bulb of the Allihn condenser.

65.1.3 *Erlenmeyer Flask*,*C*—A heat-resistant glass[14] flask having a capacity of 300 mL and fitted with a 1-hole rubber stopper.

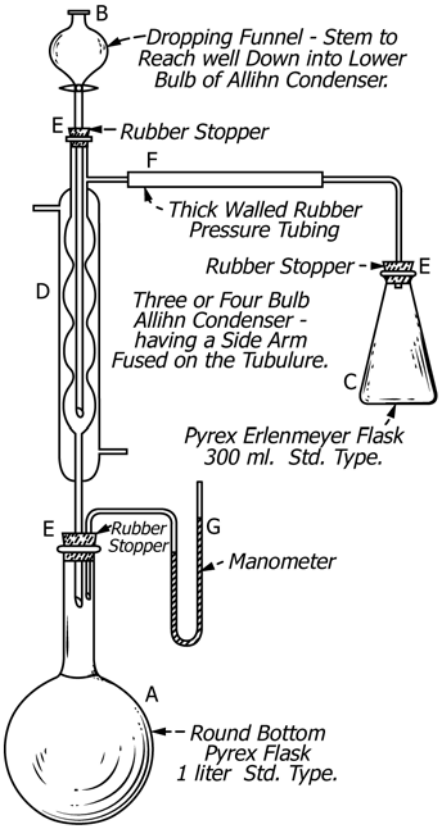


FIG. 3 Evolution Apparatus for Determination of Carbonates in Soaps

65.1.4 *Condenser*,*D*—A 3 or 4-bulb Allihn condenser having a jacket approximately 20 cm in length and with a side arm fused on the tubulure.

65.1.5 *Manometer*,*G*—A mercury manometer for use in maintaining the prescribed pressure in the test apparatus.

66. Reagents

66.1 *Alkaline Absorbent Solution*—Mix equal volumes of 1 *N* sodium hydroxide (NaOH, carbonate-free) and 1 *N* barium chloride ($BaCl_2 \cdot 2H_2O$), allow to settle overnight and filter before using.

66.2 *Hydrochloric Acid* (0.5 *N*)—Prepare and standardize a 0.5 *N* hydrochloric acid (HCl) solution.

66.3 *Hydrochloric Acid (1 + 2)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 2 volumes of water.

66.4 *Magnesium Chloride Solution (200 g/L)*—Dissolve 200 g of magnesium chloride ($MgCl_2$) in water and dilute to 1 L.

66.5 *Methyl Orange Indicator Solution (1 g/L)*—See 30.2.

66.6 *Phenolphthalein Indicator Solution (10 g/L)*—See 30.3.

66.7 *Trichlorbenzene (1-2-4 Isomer)*—1-2-4 trichlorbenzene, boiling point about 213°C, specific gravity about 1.47.

[13] This procedure is described by Hitchcock, L. B., and Devine, R. E.," Evolution Volumetric Method for Carbon Dioxide," *Oil and Soap*, Vol XVIII, No. 4, April 1941, p. 80.

[14] Borosilicate glass has been found satisfactory for this purpose.

67. Procedure

67.1 Weigh a sufficient portion of the sample to yield approximately 0.2 g of carbon dioxide (CO_2) into the evolution flask. Add about 400 mL of unboiled water to which has been added 2 mL of the alkaline absorbent solution to prevent loss of CO_2. Heat the flask over a steam bath until the soap is dissolved and cool the dissolved sample until the flask is slightly warm to the hand. Add 30 mL of the $MgCl_2$ solution to the thoroughly cooled dissolved sample. A few glass beads may be added to the flask to prevent bumping when the solution is boiled. Place 25 mL of the alkaline absorbent solution in the Erlenmeyer flask, and connect the apparatus as shown in Fig. 3, including cooling water for the condenser. Evacuate the air through the dropping funnel with a suitable aspirator pump, reducing the pressure to 65 to 80 mm as indicated on the manometer. Care should be taken to maintain a proper reduced pressure throughout the test.

67.2 Add HCl (1 + 2) containing a few drops of methyl orange indicator through the dropping funnel until an acid reaction is obtained in the solution in the evolution flask, avoiding a large excess of acid. Add the trichlorbenzene through the dropping funnel in the proportion of approximately 1 mL to every 2 g of the sample. Precautions should be taken to prevent air entering the system at any time during the test. Place a burner with a *small flame* immediately in contact with the bottom of the evolution flask, and heat continuously for 30 min. Remove the flame and fill the evolution flask and the condenser with CO_2-free water at approximately 50°C to just below the side arm on the condenser. Agitate the Erlenmeyer flask at frequent intervals from the time that the HCl is added until the evolution flask and condenser have been filled with water. Disconnect the Erlenmeyer flask guarding against entrance of air by tightly stoppering the flask unless the solution is titrated immediately. Titrate the absorbent solution in the Erlenmeyer flask drop by drop with 0.5 *N* HCl until neutral to phenolphthalein indicator.

67.3 *Blank*—Make a blank determination without the soap, using the same quantities of reagents and distilled water. The blank establishes the values of the alkaline absorbent solution in terms of 0.5 *N* HCl and automatically corrects for any CO_2 present in the reagents.

68. Calculation

68.1 Calculate the percentage of CO_2 in the sample as follows:

$$CO_2,\ \% = [(B - S) \times 0.022 \times N \times 100]/W \qquad (13)$$

where:

B = millilitres of HCl required for titration of the blank,
S = millilitres of HCl required for titration of the sample,
N = normality of the HCl, and
W = grams of sample used.

The percentage of CO_2 in the sample multiplied by 2.41 equals the percentage of sodium carbonate (Na_2CO_3). If potassium carbonate only is present, the percentage of CO_2 multiplied by 3.14 equals the percentage of K_2CO_3.

PHOSPHATES

69. Application

69.1 This method is applicable to any species of alkali metal phosphates free of interfering ions. The method may be used for the analysis of soap and synthetic detergent builders if the sample is properly prepared (see 74.2).

70. Summary of Test Method

70.1 All of the phosphate present is converted, by acid hydrolysis, to the ortho form and titrated between pH 4.3 and 8.8 with sodium hydroxide solution.

71. Interferences

71.1 Heavy metals such as iron, aluminum, calcium, magnesium, etc., that will precipitate either as insoluble phosphates or hydroxides before the upper end point is reached, will interfere. Interference also occurs if borates, sulfites, carbonates, or other buffering materials are present. The last two and much of the borate will be expelled during the acid hydrolysis boil. Ammonia or other weak bases also will interfere. The most common interference is from silicic acid. Experiment and experience in analysis of spray-dried synthetics, have shown that unless the ratio of the percentage of silicon dioxide (SiO_2) to the percentage of phosphorus pentoxide (P_2O_5) approaches or exceeds 0.2, the interference by silicates will be so slight that it may be neglected. Larger amounts must be dehydrated but need not be removed by filtration during preparation of the sample.

72. Apparatus

72.1 *Electrometric Titration Apparatus* equipped with glass and calomel electrodes. Any standard pH meter, capable of performing titrations accurate to ± 0.1 pH and accurately standardized at pH 4.0 and 8.0 is suitable.

72.2 *Gas Burners,* preferably of the chimney or Argand type.

72.3 *Muffle Furnace* with suitable pyrometer and controls for maintaining temperatures up to 550°C.

72.4 *Evaporating Dish* or large crucible, of porcelain or silica.

72.5 *Motor Stirrer,* air or electric.

72.6 *Beaker,* 400-mL.

73. Reagents

73.1 *Hydrochloric Acid (sp gr 1.19)*—Concentrated (HCl).

73.2 *Mixed Indicator* (*optional*)—Prepare the following solutions:

73.2.1 *Methyl Orange Solution (0.5 g/L)*—Dissolve 0.05 g of methyl orange in water and dilute to 100 mL.

73.2.2 *Phenolphthalein, Alcohol Solution* (5.0 g/L)—Dissolve 0.50 g of phenolphthalein in alcohol (50 %) and dilute to 100 mL with alcohol.

73.2.3 *Thymol Blue Solution (0.4 g/L)*—Dissolve 0.04 g of thymol blue in water and dilute to 100 mL.

73.2.4 *Methylene Blue Solution (1.0 g/L)*—Dissolve 0.10 g of methylene blue in water and dilute to 100 mL.

73.2.5 *Alcohol (90 %)*—Alcohol (90 %) prepared from alcohol conforming to Formula No. 3A or 30 of the U.S. Bureau of Internal Revenue. Mix the solutions in the following proportions:

Methyl orange solution	32 mL
Phenolphthalein solution	32 mL
Thymol blue solution	8 mL
Methylene blue solution	4 mL
Alcohol	24 mL

The individual components are stable indefinitely. The mixed indicator should be prepared at least weekly. In practice, 3 mL of this mixed indicator are used in a final volume of approximately 250 mL of solution to be titrated. The lower end point is taken as the first change from gray to a definite green; the upper end point is the change from pink to a bright purple.

73.3 *Sodium Hydroxide, Standard Solution* (0.5 or 1.0 N)—Prepare a 0.5 or 1.0 *N* carbonate-free solution of sodium hydroxide (NaOH) and standardize accurately.

73.4 *Sodium Hydroxide Solution (50 %)*—Dissolve sodium hydroxide (NaOH) in an equal weight of water. When using, decant the solution from the settled carbonate. A more dilute solution may be used. NaOH solutions must be protected from carbon dioxide (CO_2) contamination.

74. Preparation of Sample Solution

74.1 If a qualitative test has shown the presence of phosphates and their determination is desired, the matter insoluble in alcohol or the ash from the incineration of an original sample may be used. An original sample should always be used when the highest accuracy is desired.

74.2 Commercial sodium or potassium phosphates need no special preparation except solution in water. Weigh a portion of the well-mixed sample to the nearest 0.001 g, transfer directly to a 400-mL beaker, and dissolve in about 100 mL of water. Neutralize to litmus paper with HCl and add 10 mL excess. The optimum size of sample is given by the formula:

$$\text{Grams of sample} = (N \times 280)/P \quad (14)$$

where:

N = normality of the NaOH solution to be used in the titration, and
P = percentage of P_2O_5 expected in the sample.

74.3 Soap products may be analyzed by using the filtrate from the silicon dioxide (SiO_2) determination. Use care not to exceed the sample weight prescribed in 74.2. Alternatively the sample may be prepared as described in 74.4.

74.4 Built synthetic products may be analyzed by using the alcohol-insoluble portion, but the following procedure is more rapid and quite as accurate. Weigh a sample, of size chosen by the formula in 74.2 (but not to exceed 10 g) to the nearest 0.001 g. Place the sample in a porcelain or silica evaporating dish, or large crucible, and ignite gently over a low gas burner until most of the volatile combustible matter is burned off. Transfer to a muffle, operated at not over 550°C, for 10 to 15 min. The ignited residue need not be free of carbon and usually is of a grayish color. Cool and add cautiously 10 mL of HCl. Evaporate to dryness, take up with 50 mL water and 10 mL of HCl, and transfer to a 400-mL beaker.

75. Procedure

75.1 Each solution in a 400-mL beaker, prepared as described in 74.2, should have a volume of about 100 mL and contain an excess of at least 10 mL of HCl. Cover with a watch glass and boil gently for a minimum of 30 min. Up to 60 min may be necessary for phosphates of the glass type. All phosphates must be in the ortho form. Cool to room temperature (20 to 30°C).

75.2 Dilute to 200 mL, place on an electrometric titration stand (Note 13), and neutralize to a pH of 4.3. Most of the neutralization may be made with NaOH solution (50 %), but final adjustment should be made with the standard NaOH solution (0.5 or 1.0 *N*) to be used in the titration. Cool again, if necessary, to maintain the temperature below 30°C. Titrate carefully to the upper end point (pH 8.8) recording the titration between end points (*T*).

NOTE 15—The mixed indicator may be used for this titration but with some small sacrifice of accuracy. If the samples have been prepared by the ignition method, they must be filtered and the paper washed thoroughly, after the acid hydrolysis, as particles of carbon obscure the visual end point. The color changes can be checked by comparison with pH meter readings to acquire familiarity with the exact shade required. For greatest accuracy, titration with a pH meter is recommended.

76. Calculation

76.1 Calculate the percentage of total P_2O_5 as follows:

$$\text{Total } P_2O_5, \% = (TN \times 7.098)/W \quad (15)$$

where:

T = millilitres of NaOH solution required for titration of the sample,
N = normality of the NaOH solution, and
W = grams of sample in the sample solution.

TETRASODIUM PYROPHOSPHATE

77. Reagents

77.1 *Ethyl Alcohol, Neutral* (95 %)—Denatured ethyl alcohol, 95 %, neutral to phenolphthalein, conforming to either Formula No. 3 A or No. 30 of the U.S. Bureau of Internal Revenue.

77.2 *Hydrochloric Acid* (0.5 *N*)—Prepare and standardize a 0.5 *N* hydrochloric acid (HCl) solution.

77.3 *Sodium Hydroxide Solution* (0.5 *N*)—Prepare and standardize a 0.5 *N* sodium hydroxide (NaOH) solution against sodium pyrophosphate ($Na_4P_2O_7$) prepared by recrystallizing the technical product three times from water, and igniting at 400°C to constant weight.

77.4 *Sulfuric Acid* (0.1 *N*)—Prepare and standardize a 0.1 *N* sulfuric acid (H_2SO_4) solution.

77.5 *Zinc Sulfate Solution (125 g/L)*—Dissolve 125 g of zinc sulfate ($ZnSO_4 \cdot 7H_2O$) in water and dilute to 1 L, filter, and adjust the pH to exactly 3.8 with a glass electrode using 0.1 *N* sulfuric acid (H_2SO_4).

78. Procedure

78.1 Accurately weigh a sample containing an equivalent of approximately 1 g of $Na_4P_2O_7$, and digest with 200 mL of hot, freshly boiled, neutral alcohol. Filter through a filter paper or Gooch crucible with suction, and wash with hot alcohol until free from soap. Change receivers, and wash the alcohol-insoluble portion remaining on the filter paper with hot water until washings are neutral to phenolphthalein.

78.2 Transfer the filtrate to a suitable vessel, cool, and add sufficient water so that the resulting solution will just cover the electrodes of a glass electrode titration assembly. Adjust the pH of the solution to exactly 3.8 with 0.5 *N* HCl. Add 50 mL of $ZnSO_4·7H_2O$, and allow 5 min for the reaction to become complete as shown by the pH becoming constant. Titrate the liberated acid with 0.5 *N* NaOH until a pH of 3.8 is again reached. This titration is a measure of the pyrophosphate content.

79. Calculation

79.1 Calculate the percentage of tetrasodium pyrophosphate in the soap as follows:

$$Na_4P_2O_7,\ \% = (A/B) \times F \times 100 \qquad (16)$$

where:

A = millilitres of NaOH required for titration of the acid,
F = grams of $Na_4P_2O_7$ equivalent to 1 mL of the NaOH solution used for the titration as calculated by standardization against $Na_4P_2O_7$, and
B = grams of sample used.

SULFATES

80. Reagents

80.1 *Barium Chloride Solution* (100 g/L)—Dissolve 100 g of barium chloride ($Ba·Cl_2·2H_2O$) in water and dilute to 1 L.

80.2 *Hydrochloric Acid (sp gr 1.19)*—Concentrated (HCl).

81. Procedure

81.1 For most determinations the matter insoluble in alcohol obtained in Section 20 may suffice. If a determination of the highest accuracy is desired, ignite 10 ± 0.10 g of the sample and use the ash from the ignition. Digest with 100 mL of water, cover with a watch glass, and carefully neutralize to methyl orange with HCl. When neutralized, add 5 mL excess of HCl, filter, and wash the residue thoroughly. (Evaporation to dryness is unnecessary unless gelatinous silica should have separated or polyphosphates are present. Evaporation should never be performed on a bath heated by gas.)

81.2 Make up the filtrate to 250 mL in a beaker and boil. To the boiling solution add 15 to 20 mL of $BaCl_2$ solution slowly drop by drop from a pipet. Continue boiling until the precipitate is well formed, or digest on a steam bath overnight. Set aside overnight or for a few hours, filter through a prepared Gooch crucible, ignite gently, and weigh as barium sulfate ($BaSO_4$). Calculate to sodium sulfate (Na_2SO_4), or alkaline sulfate known to be present.

GLYCERIN, SUGARS, AND STARCH

Glycerin in the Absence of Sugars

82. Reagents

82.1 *Periodic Acid Solution*—Dissolve 5.4 g of periodic acid (H_5IO_6) in 100 mL of water, add 1900 mL of glacial acetic acid ($CH_3·COOH$), and mix thoroughly. Store the solution in a dark, glass-stoppered bottle or store in the dark in a clear, glass-stoppered bottle.

82.2 *Potassium Iodide Solution (150 g/L)*—Dissolve 15 g of potassium iodide (KI) in water and dilute to 100 mL.

82.3 *Sodium Thiosulfate, Standard Solution* (0.1 *N*)—Prepare and standardize a 0.1 *N* solution of sodium thiosulfate ($Na_2S_2O_3$).

82.4 *Starch Indicator Solution*—Dissolve 10 g of soluble cold starch in 1 L of water.

83. Procedure

83.1 Weigh approximately 10 g of the sample to the nearest 0.01 g. If starch is present, it will be necessary to remove it as matter insoluble in alcohol as described in Section 20. Add 91 mL of chloroform measured from a buret to within ± 0.2 mL to a 1-L volumetric flask. Then add 25 mL of glacial acetic acid from a graduate.

NOTE 16—If soap contains more than 10 % moisture, adjust the amount of chloroform added so that the total volume of fatty acid and chloroform will equal 100 ± 1 mL.

83.2 Transfer the sample quantitatively to the volumetric flask and add approximately 500 mL of water. Stopper and shake until sample is dissolved (see Note 17). If the soap does not react readily, warm contents of the flask and shake (see Note 18). If warmed, cool to room temperature before proceeding.

NOTE 17—Cork stoppers must never be used where periodic acid can come in contact with them.

NOTE 18—If the aqueous phase is alkaline, due to large amounts of builder in the soap, add concentrated sulfuric acid (H_2SO_4, sp gr 1.84) in 0.5-mL increments until the solution is definitely acid to litmus.

83.3 Add water to the mark, stopper, and mix thoroughly by inverting. Set aside until the aqueous and chloroform layers separate.

83.4 Pipet 50 mL of periodic acid solution into a series of 400-mL beakers. Prepare two blanks by adding 100 mL of water to each.

83.5 Pipet 100 mL of the aqueous solution into a 400-mL beaker containing 50 mL of periodic acid solution and shake gently to effect thorough mixing (see Note 19). Cover with a watch glass and allow to stand 30 min (see Note 20).

NOTE 19—If the aqueous solution contains suspended matter, filter before pipeting the portion for test.

NOTE 20—Samples may be allowed to stand 1½ h at room temperature before titrating, but never longer. Do not allow to stand in bright or direct sunlight.

83.6 Add 20 mL of KI solution, mix by shaking gently, and allow to stand at least 1 min, but never more than 5 min before titrating. Do not allow to stand in bright or direct sunlight.

83.7 Dilute to approximately 200 mL with water and titrate with 0.1 *N* $Na_2S_2O_3$ solution. Use the variable speed electric stirrer to keep the solution thoroughly mixed. Continue the titration to the disappearance of the brown iodine color. Add 2 mL of starch indicator solution and continue the titration to the disappearance of blue iodo-starch color. Read the buret to the nearest 0.01 mL.

83.8 Determine the blanks exactly like the sample, by proceeding as in 83.6 and 83.7.

83.9 If the volume of $Na_2S_2O_3$ solution required for titration of the sample described in 83.6 and 83.7 is less than 0.8 times the volume of $Na_2S_2O_3$ required for the titration of the blank proceed as follows:

83.9.1 Repeat the test using smaller portions of the sample solutions (50, 25, 10, and 5 mL) in the procedure described in 83.5 – 83.7 until the volume of $Na_2S_2O_3$ solution required for titration of the sample is more than 0.8 times the volume of $Na_2S_2O_3$ required for the blank.

83.9.2 If 10 mL (or less) of the sample solution is necessary to bring the value within the limit required by 83.9.1, repeat the test, starting at the beginning with a smaller sample, referring to 83.1 to find the proper amount of sample to weigh.

NOTE 21—The volume of $Na_2S_2O_3$ solution required for the titration of the sample must be more than 0.8 times the volume of $Na_2S_2O_3$ solution required for titration of the blank to assure an adequate excess of periodic acid.

84. Calculation

84.1 Calculate the percentage of glycerin to the nearest 0.1 % as follows:

$$W_a = W_s V/900 \tag{17}$$

$$\text{Glycerin, \%} = [(B - S)N \times 2.302]/W_a$$

where:

W_a = grams of sample represented by the aliquot used in accordance with 83.5 or 83.9,
W_s = grams of sample used in accordance with 83.1 or 83.9,
V = volume in millilitres of the aliquot used in accordance with 83.5 or 83.9,
B = volume of $Na_2S_2O_3$ solution required for titration of the blank,
S = volume of $Na_2S_2O_3$ solution required for titration of the sample, and
N = normality of the $Na_2S_2O_3$ solution.

Glycerin in the Presence of Sugars

85. Procedure

85.1 Proceed as in the determination of glycerin in the absence of sugar (see Section 83), taking a sample so that the sum of the glycerin and sugar is not more than 3.0 g. (If starch is present, this must first be removed as described in Section 83.) The solution must be boiled in all cases at least 20 min to ensure complete inversion of sucrose as in Section 90. Determine the amount of potassium dichromate ($K_2Cr_2O_7$) solution required to oxidize both the sugar and glycerin. Determine also the sugar by the method described in the determination of sugar (see Sections 89 and 90).

86. Calculation

86.1 Calculate the percentage of glycerin as follows:

$$\text{Glycerin, \%} = [(0.01142A - 0.0100A)/B] \times 100 \tag{18}$$

where:

A = millilitres of $K_2Cr_2O_7$ required to oxidize both sugar and glycerin,
B = grams of sample used,
0.01142 = equivalent for sugar, and
0.0100 = equivalent for glycerin.

Starch

87. Reagents

87.1 *Hydrochloric Acid (2 + 1)*—Mix 2 volumes of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water.

87.2 *Sodium Hydroxide* (NaOH).

88. Procedure

88.1 Separate the matter insoluble in water as described in Section 22, using a sample of soap that will yield not more than 3 g of starch. Transfer the insoluble matter, without drying, to a 500-mL flask provided with a reflux condenser, add 20 mL of HCl and 200 mL of water, and boil for 2½ hr. Cool the solution, and nearly neutralize it with NaOH. Dilute the volume to 250 mL, filter, and determine the reducing sugars by the gravimetric method as described in the method for the determination of sugar (Section 89).

88.2 Calculate the amount of dextrose (*d*-glucose) equivalent to the cuprous oxide obtained and then the amount of starch, as follows:

$$D = 1.259C, \tag{19}$$

$$S = 93.0D/W$$

where:

D = grams of dextrose,
C = grams of cuprous oxide obtained,
S = weight % starch, and
W = grams soap sample from 88.1.

Sugars

89. Apparatus and Reagents

89.1 The apparatus and reagents shall be the same as those described in the standard Munson-Walker Method.[15]

90. Procedure

90.1 Dissolve 10 ± 0.01 g of the sample in 200 mL of hot water in a 600-mL beaker. Decompose with 25 mL of sulfuric acid (H_2SO_4, 1 + 4); then boil gently for 20 min to invert the sucrose completely. Cool the solution, remove the heat, and rinse the cake of fatty acids. Extract the acid liquid with 25 mL

[15] Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, Sugar, and Sugar Products, Section XXXIV, Paragraph 28, 9th Ed, 1960, p. 427.

of ether. Neutralize the acid liquid with NaOH solution, transfer to a 500-mL graduated flask, dilute to the mark, and mix thoroughly. Determine the invert sugar in 50 mL of this solution by the Munson-Walker Method. To calculate sugar (sucrose) multiply the amount of invert sugar found by 0.95. (If starch is present, first remove as described in Section 20, and then proceed as above.)

VOLATILE HYDROCARBONS

91. Summary of Test Method

91.1 This method requires a source of dry, oil-free steam which is passed through the sample treated with acid, sufficient to liberate the fatty acids from the soap. The steam is next passed through strong NaOH solution to scrub out any volatile fatty acids, while the volatile hydrocarbons are condensed with the steam in a suitable arrangement which allows the excess water to flow away, leaving the volatile hydrocarbons in the measuring buret. The method may be applied to samples containing substances immiscible with water and volatile with steam. (For solvents heavier than water the trap as shown in Fig. 1 for determining water by the distillation method (Method B) should be used. (See Sections 15 – 17).)

92. Apparatus

92.1 The apparatus and its arrangement are shown in Fig. 4. The following are the important items:

92.1.1 *Steam Trap*,*A*—A 1-L round-bottom ring-neck flask equipped with a siphon tube to the drain from the bottom of the flask and provided with a means of regulating the steam flow into the flask.

92.1.2 *Evolution or Sample Flask*, *B*—A 1-L round-bottom ring-neck flask. In case large samples are desirable the size of this flask may be increased.

92.1.3 *Caustic Scrubber Flask*,*D*—A steam-jacketed metal flask is preferred, but a 1-L Florence flask provided with a steam coil of 0.32-cm (0.125-in.) copper tubing around the upper half may be used. If the glass flask is used it should be provided with a safety bucket below it and should be renewed frequently since the strong caustic dissolves the glass rather rapidly. This flask should be connected to the condenser by a Kjeldahl connecting tube, *E*, or similar safety device. The inlet for the steam into the evolution and scrubber flasks should extend nearly to the bottom of the flasks and should be bent at right angles and parallel to the sides of the flask.

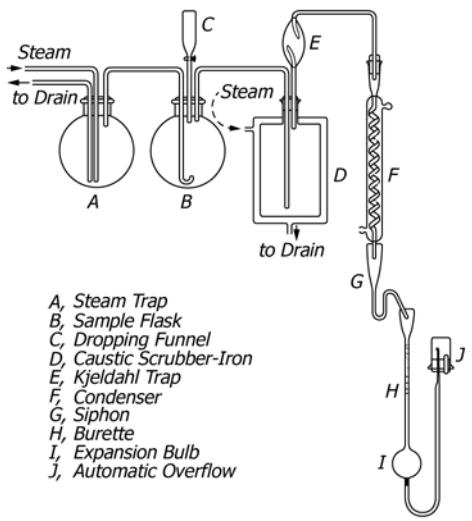


FIG. 4 Volatile Hydrocarbon Apparatus

92.1.4 *Condenser*,*F*—A 30.5-cm or longer spiral condenser of sufficient bore so the condensate will not readily close it.

92.1.5 *Measuring Buret*,*H*—A 10-mL buret calibrated to 0.1 mL and carrying a bulb, *I*, of approximately 100-mL capacity, at the lower end. If desired, an ordinary 10-mL Mohr type buret may be used having attached to it by rubber tubing a bulb of proper capacity that has been blown in the laboratory. An ordinary buret funnel may be placed in the top of the buret in place of the special flared-out top shown in Fig. 4. The stoppers used should be of a good grade of rubber and should have been thoroughly cleaned free from any surface sulfur and should be given a steam distillation in position for several hours before use on a sample. Insulating the flasks and tubing to reduce condensation aid distillation and its control.

93. Reagents

93.1 *Gum Arabic,* commercial grade.

93.2 *Sodium Hydroxide Solution (44 %)*—Dissolve 440 g of sodium hydroxide (NaOH) in 560 mL of water.

93.3 *Sodium Hydroxide,* solid, sticks.

93.4 *Sulfuric Acid (1 + 3)*—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 3 volumes of water.

94. Procedure

94.1 Place 150 mL of NaOH solution and several sticks of solid NaOH to provide against dilution in the scrubber flask. Rinse out the condenser and buret with acetone. Attach a rubber tubing to the lower end of the buret, fill the buret and tubing with water, and raise the outer end of the tubing so that the water level in the buret is near the top of the scale when the water is flowing to the drain from the automatic overflow, *J*. Be sure that the connections are tight and that the tubing contains no air bubbles. Place the condenser in position so that the lower end extends directly into the upper end of the buret just above the water level or connect to an adapter siphon, *G*, which discharges into the buret. The cooling water should be 15.5°C or colder. Ice water may be desirable for low-boiling hydrocarbons.

94.2 Weigh 100 ± 0.5 g of the sample (cut into cubes of about 1-cm edges) or 50 ± 0.3 g of the sample of soap powder and transfer to the evolution flask (see Note 22). Add about 10 g of gum arabic and 100 mL of water. Place the flask in position with 100 mL of H_2SO_4 in a dropping funnel, *C*, carried in the stopper. Connect with the steam and wash the flasks and the condenser, making sure that the stoppers are tightly fitting and held in place by wiring. Rubber connections in the lines between the evolution flask and condenser should be avoided.

NOTE 22—For some samples the volatile hydrocarbon content may be so low that a larger sample than 50 or 100 g is desirable. The size of the evolution flask may need to be increased if larger samples are used. The

amount of water in the evolution flask and acid used should also be correspondingly increased.

94.3 Add the acid to the sample slowly to avoid excessive frothing. While adding the acid, turn on the steam cautiously, so adjusting the pressure by a bleeder valve that just enough steam flows to prevent any liquid from backing into the steam trap flask.

94.4 When all the acid has been added, turn on enough steam to cause brisk distillation, taking care that no liquid is carried over from the evolution and wash flasks and that the condenser water does not become warm.

94.5 Continue the distillation until there is no increase in the volume of the upper layer for 45 min or no small droplets can be noted in the condensate.

94.6 When distillation is completed, shut off and drain the condenser water, and allow the steam to heat up the condenser to drive out the last traces of volatile hydrocarbon. Shut off the steam as soon as vapor begins to issue from the lower end of the condenser. Immediately open the stopcock of the dropping funnel to prevent NaOH being drawn into the evolution flask.

94.7 Stopper the buret and allow its contents to come to room temperature or bring them to a definite temperature by immersing the buret for 1 to 2 h in a water bath held at 25°C.

94.8 Read the volume of the upper layer to the nearest 0.01 mL. The volume multiplied by the specific gravity equals the weight of the volatile hydrocarbon. The specific gravity should be determined at the temperature at which the volume is read. A small Sprengel tube made of 3-mm glass tubing is convenient for this purpose.

95. Calculation

95.1 Calculate the percentage of volatile hydrocarbons as follows:

$$V = [(M \times S)/W] \times 100 \quad (20)$$

where:

V = percentage of volatile hydrocarbons,
M = millilitres of volatile hydrocarbons,
S = specific gravity of hydrocarbons, and
W = grams of sample used.

COPPER
(Trace Amounts)

96. Summary of Test Method

96.1 Copper forms a colored compound with sodium diethyldithiocarbamate in a neutral solution. Photometric measurement is made at approximately 440 nm.

97. Interferences

97.1 None of the usual constituents of soaps and soap products interfere in this method.

98. Apparatus

98.1 *Photometer*—A spectrophotometer or filter photometer suitable for making measurements at approximately 440 nm.

98.2 *Absorption Cells,* 1-cm.

98.3 *Separatory Funnels,* glass-stoppered, 125-mL.

98.4 *Funnels,* 25 mm in diameter.

98.5 *Mixing Cylinders,* glass-stoppered, 10-mL.

98.6 *Volumetric Flasks,* glass-stoppered, 500-mL.

98.7 *Pipets,* volumetric, 5-mL.

98.8 *Buret,* 10-mL.

99. Reagents and Materials

99.1 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH). Redistill directly from a chemically resistant glass[13] vessel or pass the ammonia gas into water with external cooling.

99.2 *Carbon Tetrachloride* (CCl_4).

99.3 *Citric Acid Solution (300 g/L)*—Dissolve 30 g of citric acid in 70 to 80 mL of water and dilute to 100 mL with water.

99.4 *Copper, Standard Solution* (1 mL = 400 µg Cu)—Weigh 0.2 ± 0.0001 g of clean electrolytic copper, in the form of sheet or light turnings, into a 50-mL beaker. Add 10 mL of HNO_3 (1 + 1) and cover the beaker with a watch glass. After cessation of reaction, add about 20 mL of water and transfer the solution to a 500-mL volumetric flask. Wash the beaker five times with 20-mL portions of water, adding the washings to the volumetric flask. Dilute to the mark with water at room temperature and mix the solution by inverting the flask several times.

99.5 *Copper, Standard Solution* (1 mL = 8 µg Cu)—Prepare a working standard solution by pipetting 10 mL of the stock solution into a 500-mL volumetric flask and diluting to the mark with water at room temperature. Invert the flask several times to mix the solution.

99.6 *Cotton,* absorbent.

99.7 *Ethyl Alcohol (3 + 1)*—Mix 750 mL of ethyl alcohol with 250 mL of water.

99.8 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl). Redistill the acid directly from a chemically resistant glass[14] vessel or pass the HCl gas into water with external cooling.

99.9 *Nitric Acid* (1 + 1)—Mix equal volumes of concentrated nitric acid (HNO_3, sp gr 1.42) and water.

99.10 *Phenol Red Indicator Solution*—Dissolve 0.10 g of powdered phenol red[16] in 20 mL of ethyl alcohol and 80 mL of water.

99.11 *Sodium Diethyldithiocarbamate Solution (0.2 %)*—Dissolve 1 g of sodium diethyldithiocarbamate[16] in 500 mL of water. Extract the solution once with 200 mL of CCl_4 and discard the CCl_4 extract. This solution should be made up fresh weekly and stored in a refrigerator.

[16] These reagents may be obtained from the Eastman Kodak Co., Rochester, NY.

99.12 *Stopcock Grease*—Do not use stopcock grease from metal tubes.[17]

100. Preparation of Calibration Curve

100.1 Place 50 mL of ethyl alcohol (3 + 1) in each of the four 125-mL separatory funnels and add to each funnel, respectively, 1, 3, 6, and 10 mL of copper solution (1 mL = 8 µg Cu).

100.2 Add 2 mL of citric acid solution to each funnel and extract the contents with two successive 25-mL volumes of CCl_4. Shake for about 30 s each time and discard the extracts.

100.3 Add 2 drops of phenol red indicator solution to the extracted solutions and add NH_4OH dropwise until the end point (red) is reached. Add 2 mL of sodium diethyldithiocarbamate solution.

100.4 Shake the mixture with 3.0 mL of CCl_4 for at least 90 s. Drain the lower layer through a wisp of absorbent cotton, contained in a 25-mm funnel, into a 10-mL glass-stoppered mixing cylinder. The cotton shall be rolled to give a compact thin plug about 1 in. long and inserted snugly into the stem of the funnel so that only a small quantity projects into the conical portion. Shake the contents of the separatory funnel with two more 3-mL portions of CCl_4, again collecting the extracts in the mixing cylinder. Wash the cotton with CCl_4, removing the funnel at the instant that dilution to the 10-mL mark occurs.

100.5 Thoroughly mix the contents of the mixing cylinder. If the solution is perfectly clear, add directly to a 1-cm absorption cell; otherwise filter into the cell as described in 100.4, using cotton. Cover the cell to retard evaporation and immediately read the absorbance versus CCl_4 at 440 nm.

100.6 *Blank*—Prepare a blank by repeating the procedure described in 100.1 – 100.5 in every detail except to omit the addition of the copper solution. If the absorbance versus CCl_4 is more than 0.030 the distilled water should be redistilled.

100.7 Subtract the photometric reading for the blank versus CCl_4 from the reading for the solution versus CCl_4 and plot the corrected photometric reading for the solution as abscissa against the micrograms of copper as ordinate on linear graph paper.

101. Procedure

101.1 Transfer 2.00 ± 0.10 g of the sample, weighed to the nearest 0.01 g, to a 100-mL beaker.

101.2 Add 40 mL of ethyl alcohol (3 + 1) and 1 mL of HCl. Heat with stirring to dissolve the sample. Pour while hot into a 125-mL separatory funnel and wash the beaker with a small volume (10 to 15 mL) of alcohol (3 + 1). Cool under tap water and add 25 mL of CCl_4. Add 2 mL of citric acid solution and shake the stoppered funnel for 30 s. Discard the lower layer. Extract with a second 25-mL portion of CCl_4 and again discard the extract.

101.3 Add 2 drops of phenol red indicator solution to the extracted solutions and add NH_4OH dropwise until the end point (red) is reached. Add 5 mL of sodium diethyldithiocarbamate solution.

101.4 Shake the mixture with 3.0 mL of CCl_4 for at least 90 s. Drain the lower layer through a wisp of absorbent cotton, contained in a 25-mm funnel, into a 10-mL glass-stoppered mixing cylinder. The cotton shall be rolled to give a compact thin plug about 1 in. long and inserted snugly into the stem of the funnel so that only a small quantity projects into the conical portion. Shake the contents of the separatory funnel with two more 3-mL portions of CCl_4, again collecting the extracts in the mixing cylinder. Wash the cotton with CCl_4, removing the funnel at the instant that dilution to the 10-mL mark occurs.

101.5 Thoroughly mix the contents of the mixing cylinder. If the solution is perfectly clear, add directly to a 1-cm absorption cell; otherwise filter into the cell as described in 101.4, using cotton. Cover the cell to retard evaporation and immediately read the absorbance versus CCl_4 at 440 nm.

101.6 *Blank*—Prepare a blank by repeating the procedure described in 101.1 to 101.5 in every detail except to omit the addition of the sample.

102. Calculation

102.1 Calculate the copper content of the sample, in parts per million, as follows:

$$\text{Copper, ppm} = (S - B)/2 \quad (21)$$

where:

S = micrograms of copper equivalent to the photometric reading for the sample obtained from the standard curve, and

B = micrograms of copper equivalent to the photometric reading for the reagent blank obtained from the standard curve.

103. Precision and Bias

103.1 Because of the nature and the wide variety of materials being tested, this test method is not amenable to the generation of precision and bias data. However, the method continues to be used and referenced.

[17] Heavy Duty Celvascene packed in glass jars has been found satisfactory for this purpose. It may be obtained from the Distillation Products Industries, Division of Eastman Kodak Co., Rochester, NY.