Standard Methods for the Sampling and Analysis of Commercial Soaps and Soap Products

M. L. Sheely, *Chairman*, Soap Analysis Committee.

THE following methods for the sampling and analysis of commercial soaps and soap products were recommended for adoption by the *Soap Analysis Committee* of the American Oil Chemists' Society and were officially adopted by this society on October 13, 1933,[1] with the provision that all methods will be considered tentative only. From time to time, as coöperative work may justify, the individual methods will be taken up for revision and official adoption. For the most part these methods are identical to the standard methods adopted by the American Chemical Society[2] with a few exceptions, notably the methods for moisture, rosin, unsaponified and unsaponifiable. A few minor corrections have also been made to other methods.

The present membership of the Soap Analysis Committee of the American Oil Chemists' Society is as follows:

*A. K. Church, Lever Bros. Co., Cambridge, Mass.
C. P. Long, Procter & Gamble Co., Ivorydale, Ohio.
R. C. Newton, Swift & Co., Chicago, Illinois.
L. F. Hoyt, Larkin Co., Inc., Buffalo, N. Y.
R. B. Trusler, The Davies-Young Soap Co., Dayton, Ohio.
M. A. Beck, Van Camp Oil Products Co., Louisville, Ky.
W. A. Peterson, Kirkman & Son, Inc., Brooklyn, N. Y.
H. P. Trevithick, New York Produce Exchange, New York, N. Y.
J. M. Burmaster, The Southern Cotton Oil Co., New Orleans, La.
H. C. Bennett, Los Angeles Soap Co., Los Angeles, Calif.
H. E. Cutts, Stillwell & Gladding, Inc., New York, N. Y.
Wm. Roth, The Andrew-Jergens Co., Cincinnati, Ohio.
F. W. Smither, Bureau of Standards, Washington, D. C.
M. L. Sheely, *Chairman*, Armour Soap Works, Chicago, Ill.

The membership of the American Chemical Society Committee at the time of this adoption[2] was as follows:

Percy H. Walker, Bureau of Standards, Washington, D. C.
C. P. Long, The Globe Soap Co., Cincinnati, Ohio.
J. R. Powell, Armour Soap Works, Chicago, Illinois.
R. E. Divine, Armour Soap Works, Chicago, Illinois.
Archibald Campbell, *Chairman*, The Globe Soap Co., Cincinnati, Ohio.

**Deceased.*

A—Sampling

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.

I. CAKE SOAPS, FLAKE AND POWDERED SOAP PRODUCTS, WHEN PACKED IN CANS OR CARTONS.—One cake (can or carton) shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 lbs. 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 5,000 lbs. The total sample shall in all cases consist of not less than three cakes (cans or cartons) taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs.

Wrap the individual cakes (cans or cartons) tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector shall accurately weigh each wrapped cake (can or carton), record its weight and the date of weighing on the wrapper, place the wrapped cakes (cans or cartons) in an airtight container which should be nearly filled, and seal, mark, and send to the laboratory for test. Samples should be kept cool until tested.

II. FLAKE AND POWDERED SOAP PRODUCTS WHEN IN BULK.—A grab sample of not less than ½ lb. shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 100 lbs. In case of smaller containers, a grab sample of not less than ½ lb. shall be taken at random from each lot of containers totaling not more than 10,000 lbs. The total samples shall in all cases consist of not less than three grab portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs. The inspector shall rapidly mix the sample, place in an airtight container, which shall be filled, and seal, mark, accurately weigh, record its weight and date of weighing on the package, and send to the laboratory for test. Samples should be kept cool until tested.

III. LIQUID SOAP.—A sample of not less than ½ pt. shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 10 gal. each. In case of smaller containers, a sample of not less than ½ pt. shall be taken at random from each lot of containers totaling not more than 1,000 gal. The total sample shall in all cases consist of not less than three portions of ½ 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 samples drawn, place in clean, dry cans or bottles, which shall be completely filled and securely stoppered with clean corks or caps; seal, mark, and send to the laboratory for test.

IV. PASTE SOAP PRODUCTS.—(1) *When packed in cans or cartons of 5 lbs. or less.* One can or carton shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 lbs. In case of smaller containers, a can or carton shall be taken at random from each lot of containers totaling not more than 5,000 lbs. The total sample shall in all cases consist of not less than 3 cans or cartons taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs. Wrap, seal, mark, and send to laboratory for test.

(2) *When packed in bulk.* Take a trial sample at random of not less than ½ lb. from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 lbs. In case of smaller containers a trial sample shall be taken at random from each lot of containers totaling not more than 5,000 lbs. The total sample shall in all cases consist of not less than 3 half-pound portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 10 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 10 lbs. The inspector shall promptly place the combined sample in a clean, dry,

air- and watertight container, which shall be filled, and seal, mark, and send to the laboratory for test.

B—Preparation of Samples

I. CAKE SOAP.—In case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. When the sample is large, each cake may be quartered and one-quarter of each cake run through the chopper. With samples that cannot be handled as above, select a cake of average weight, quarter it by cutting at right angles in the center and shave equally from all freshly cut surfaces sufficient soap for analysis. Mix and weigh out all portions for analysis promptly. Preserve the remainder in an airtight container in a cool place.

II. POWDERED AND CHIP SOAPS.—Rapidly disintegrate and mix the sample; if desired, quarter down to about 1 lb. and weigh out all portions for analysis at once. Unused portions of the sample for analysis shall be preserved in an airtight container in a cool place.

III. LIQUID SOAP.—No preparation of the sample, other than thorough mixing, is necessary unless it is received during very cold weather, when it should be allowed to stand at least 1 hr. after it has warmed up to room temperature (20° to 30° C.) before it is noted whether it forms a satisfactory lather.

IV. PASTE SOAP PRODUCTS.—Mix thoroughly by kneading and quarter down to about 1 lb. Weigh out all portions for analysis promptly and preserve remainder in an airtight container in a cool place.

C—Methods of Analysis

When a determination shows nonconformity with the specifications, a duplicate shall be run.

I. MOISTURE.—The oven method given below is generally applicable to all soaps. Experience has shown, however, that certain exceptions to this method must be made if accurate results are desired. These exceptions include: (a) For soaps containing appreciable amounts of sodium silicate the distillation method is preferred. (b) Soaps of linseed and other oxidizing oils absorb oxygen and if the oven method is used may gain in 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 soaps.

(1) *Matter Volatile at* 105° *C.* (Oven Method). Weigh 5 g. (± 0.01 g.) of the sample in a porcelain or glass dish about 6 to 7 cm. in diameter and 4 cm. deep, dry to constant weight in an air oven at a temperature of 105° C. (± 2° C.).

(2) *Distillation Method.*[3] For soaps containing from 5 to 25% of moisture and volatile matter use a 20 g. (± 0.04 g.) sample. For soaps containing more than 25% moisture and volatile matter use a 10 g. (± 0.02 g.) sample. The weighed sample is carefully transferred to a 500 cc. Erlenmeyer flask. Add approximately 10 g. of anhydrous, fused sodium acetate to prevent violent frothing, and then follow with 100 cc. of xylol which has previously been saturated with water by shaking the xylol with a small quantity of water and distilling. Use the xylol distillate for the determination. Attach the Erlenmeyer flask to a 5 or 6 cc. Bidwell-Sterling distillation receiver, which is connected to a reflux condenser (19″ Liebig condenser). Calibrate the capacity of the Bidwell-Sterling receiver at 25° C. Prior to starting the determination, fill the Bidwell-Sterling receiver with saturated xylol by pouring in through the reflux condenser. For diagram of apparatus, see *Soap,* Volume 7, No. 11, November, 1931, page 35.

So that the refluxing will be under better control, wrap the flask and the tube leading to the receiver with asbestos cloth. Apply heat to the flask by means of a gas burner or an electric heater and distil slowly. The rate at the start should be approximately 100 drops per minute. When the greater part of the water has apparently distilled over, increase the distillation rate to 200 drops per minute until no more water is collected. Purge the reflux condenser during the distillation with 5 cc. portions of xylol to wash down any moisture adhering to the walls of the condenser. The water in the receiver may be made to separate from the xylol by using a spiral copper wire. Move the wire up and down in the condenser occasionally, thus causing the water to settle to the bottom of the receiver. Reflux for at least two hours, after which time the heat is turned off. Adjust the water distilled over into the receiver to 25° C. Read the volume of water and calculate the percentage of moisture in the soap, as follows:

$$\frac{\text{Volume in c.c. at } 25^\circ \text{ C.} \times 0.997}{\text{weight of sample}} \times 100 = \%\text{ moisture in soap}$$

II. TOTAL MATTER INSOLUBLE IN ALCOHOL. FREE ALKALI OR FREE ACID.—(1) *Matter insoluble in alcohol.* Digest hot a 2 to 10-g. (± 0.01 g.) sample with 200 cc. of freshly boiled ethyl alcohol neutral to phenolphthalein (94 per cent or higher). Filter through a counterpoised filter paper neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper, or in the crucible, with hot neutral alcohol until free from soap. Dry the filter paper, or crucible, and residue at 100° to 105° C. for 3 hrs., cool, and weigh the total matter insoluble in alcohol. (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 C-XI; phosphates, C-XII; sulfates, C-XIII; silicates, C-XX; borax, C-IX; starch, C-XIV(4).)

(2) *Free alkali or free acid.* Titrate the filtrate from the above, using phenolphthalein as indicator, with standard acid or alkali solution, and calculate the alkalinity to sodium hydroxide (or potassium hydroxide) or acidity to oleic acid.

(3) *Matter insoluble in water.* Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue, extract it with water at 60° C., and wash the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing.) Dry the filter and residue at 100° to 105° C. for 3 hrs., cool, and weigh matter insoluble in water. The nature of this matter may be determined by further examination.

(4) *Total alkalinity of matter insoluble in alcohol.* (*Alkaline salts.*) Titrate the filtrate from the determination of matter insoluble in water 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 parties interested.

III. COMBINED ALKALI. TOTAL ANHYDROUS SOAP.—Dissolve 5 to 10 g. (± 0.01 g.) of the sample, depending upon the anhydrous soap content, in 100 cc. of water in a 250-cc. Erlenmeyer flask. When solution is complete, add dilute sulfuric acid in slight excess, insert a small funnel in the neck of the flask, and heat the flask at 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 two 20-cc. portions of ethyl ether. Dissolve the fatty acids in the ether used for washing the aqueous liquid and shake with 10-cc. portions of water until they are no longer acid to methyl orange. Unite the water portions used for washing and shake with 20 cc. of ether. Wash this ether until the wash water is neutral to methyl orange. Save the acid water for chloride determination. Unite the ether solutions (if necessary, filter, washing the paper with ether) in a suitable weighed vessel, add 100 cc. of neutral alcohol free from carbon dioxide, add phenolphthalein and titrate to exact neutrality with standard sodium hydroxide solution. Evaporate off the alcohol, dry to constant weight as in the determination of matter volatile at 105° C. and calculate the percentage of soda soap. This soap naturally includes any mineral oil and neutral fat, which, if determined separately, must be deducted from the result to obtain the true soap. Calculate the combined sodium oxide (Na_2O) and deduct from the weight of soda soap to give the anhydrides. If the original soap was potash soap, proper calculation must be made to reduce to potassium oxide (K_2O), or the titration made directly with standard potassium hydroxide solution. 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 sodium or potassium hydroxide solution for neutral salts and the proper corrections made if necessary.) With 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 can be used after neutralizing any free acid or alkali. Evaporate off the alcohol on a steam bath, take up in water and proceed as above.

With soap products containing a high percentage of matter insoluble in alcohol where approximate results will suffice, such as may be the case with cleansers, soap powders, scouring compounds, pastes, etc., and where agreed upon by the parties interested, the alcoholic solution, obtained after filtering off and washing the matter insoluble in alcohol, may be evaporated directly in a weighed vessel, dried at 105° C. to constant weight, and the result reported as soap.

IV. Chloride.—Neutralize with chlorine-free alkali the acid water obtained in paragraph C-III. Titrate with standard silver nitrate solution, using potassium chromate as indicator, and calculate the result to sodium chloride or potassium chloride as the character of the soap indicates.

In case the total anhydrous soap is not to be determined it will be more convenient to use the following method.[4] Dissolve 5 g. (± 0.1 g.) of the sample in 300 cc. of water, boiling if necessary to effect solution. Add an excess of neutral, chlorine-free magnesium nitrate solution (about 25 cc. of a 20 per cent $Mg(NO_3)_2 \cdot 6H_2O$ solution). Without cooling or filtering, titrate with standard silver nitrate solution, using potassium chromate as indicator.

V. Unsaponified and Unsaponifiable Matter.[5]—*Extraction Cylinder:* The cylinder shall be a 250 cc. glass stoppered cylinder about 35 mm. (1⅜″) in diameter and about 30 cm. (12″) high.

Petroleum Ether: Redistilled petroleum ether, boiling under 75° C. shall be used. A blank must be made by evaporating 250 cc. with about 0.25 g. of stearin or 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.

Determination: Weigh 5 g. (± 0.2 g.) of the prepared sample into a 250 cc. Erlenmeyer flask or beaker which contains approximately 0.1 g. bicarbonate of soda, and dissolve in 100 cc. of 50% redistilled ethyl alcohol. Warm and shake to effect solution, keeping the temperature under 60° C., and filter off any undissolved residue on a Gooch crucible with an asbestos pad or in a funnel using an asbestos pad deposited on a perforated porcelain disc. Wash three times with hot 50% alcohol and then with 5 cc. of hot 95% alcohol. Wash with a small amount of petroleum ether to remove any traces of unsaponified and unsaponifiable. Transfer the entire alcohol-water and ether filtrate to the extraction cylinder and make up to the 160 cc. mark with 50% redistilled ethyl alcohol. Add 50 cc. of petroleum ether, shake vigorously for one minute and allow to settle until both layers are clear. The volume of the upper layer should be about 40 cc. Draw off petroleum ether layer as closely as possible by means of a slender glass siphon, into a separatory funnel of 500 cc. capacity. Repeat the extraction at least six times using 50 cc. of petroleum ether each time. Wash the combined ether extracts in a separatory funnel first with a mixture of 15 cc. of N/10 sodium hydroxide solution and 15 cc. of 95% alcohol, and then three times with 25 cc. portions of 10% alcohol, shaking vigorously each time. Transfer the petroleum ether extract to a beaker and evaporate off the petroleum ether on a steam bath in an air current.

Test the residue for solubility with 50 cc. of petroleum ether at room temperature. Filter and wash free from the insoluble residue, if any; evaporate and dry in the same manner on the steam bath in a current of air, and finally in an air oven at 101° C. for 30 minutes. Weigh and return to the oven, re-weighing at 15 minute intervals until constant weight is reached. Take up the residue in 50 cc. of warm ethyl alcohol, neutralized to phenolphthalein, titrate to the same color as original neutral alcohol with N/25 sodium hydroxide solution and calculate to oleic acid. Deduct this figure from the gross weight previously found and report as "Unsaponified and Unsaponifiable Matter." (Note.—Any blank from the petroleum ether must be deducted from the weight before calculating the unsaponified and unsaponifiable matter.)

Unsaponifiable Matter: Weigh 5 g. (± 0.2 g.) of the prepared sample into a 200 cc. Erlenmeyer flask. Add 30 cc. of redistilled 95% ethyl alcohol and 5 cc. of 50% aqueous potassium hydroxide and boil the mixture for one hour under a reflux condenser. Transfer to the extraction cylinder and wash to the 40 cc. mark with redistilled 95% ethyl alcohol. Complete the transfer, first with warm then with cold water till the total volume is 80 cc., and finally with a small quantity of petroleum ether. Cool the cylinder and contents to room temperature and add 50 cc. of petroleum ether; and then proceed with the extraction as outlined above under "Unsaponified and Unsaponifiable Matter," except the alkaline wash may be omitted; weigh the residue and correct for fatty acids in the usual manner. Report the result as "Unsaponifiable Matter."

From the total Unsaponified and Unsaponifiable Matter figure as found above, deduct the Unsaponifiable figure and report as "Unsaponified Matter."

(Note 1.—The Committee wishes to emphasize the necessity of thorough and vigorous shaking 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.)

(Note 2.—The above method will not remove all the unsaponifiable matter in soaps to which lanolin has been added. Many more extractions are required when substances of this nature are present.)

VI. Rosin.—*Wolff's Method, Modified.*[1] Dissolve 5 g. (± 0.01 g.) of the sample in 100 to 200 cc. of hot water, add a slight excess of dilute sulfuric acid, heat until the fatty acids collect in a clear layer, cool to room temperature, extract with a small portion of ethyl ether, draw off the water layer and wash the ether solution with water until free from mineral acid. Transfer to a 200 cc. Erlenmeyer flask, evaporate off the ether and dry 1 hr. at 105° C., cool and dissolve in 20 cc. of absolute alcohol.

First Esterfication: Add 10 cc. of a solution of one volume of concentrated sulfuric acid (sp. gr. 1.84) and 4 volumes of absolute alcohol, and boil on the steam bath for 4 min. under a reflux condenser. Remove from steam bath, add to the liquid about 5 times its volume of 7 to 10 per cent sodium chloride solution, and extract with ethyl ether. Shake out the aqueous portion 2 or 3 times with ether. Unite the ether solutions and wash with sodium chloride solution until the washings are neutral to methyl orange. Add 30 cc. neutral alcohol, and titrate the rosin acids with standard sodium hydroxide solution, using phenolphthalein as indicator.

Second Esterification: Evaporate the alcohol and ether on the steam bath and dissolve the soap with water, split with dilute sulfuric acid and extract the rosin acid with a small portion ethyl ether. Dry the ether extract with anhydrous sodium sulphate, filter into a 200 cc. Erlenmeyer flask and evaporate. Cool and dissolve in 20 cc. of absolute alcohol. Then proceed as above under "First Esterification." Calculate titration to rosin or rosin soap, as desired (1 cc. normal alkali = 0.346 g. rosin or 0.377 g. rosin soda soap). If the true fatty acid soap is desired, subtract the rosin soap from the total anhydrous soap obtained under C-III.

VII. TITER TEST.—(1) *Preparation of total fatty matter (fatty and rosin acids and unsaponified matter).* Dissolve about 50 g. of soap in 500 cc. of hot water, add 100 cc. of 30 per cent sulfuric acid, heat until the fatty matter collects in a clear layer, siphon off the acid layer and wash the fatty matter free from sulfuric acid with hot water. Decant the fatty matter into a dry beaker, filter, using a hot-water funnel, or placing both funnel and receiving beaker in a water-jacketed oven, and dry for 20 min. at the temperature of boiling water.

When other determinations are to be made on the total fatty matter, and volatile and readily oxidizable fatty acids are present, the following method should be used: Dissolve about 50 g. of the soap in 300 cc. of hot water, transfer to a separatory funnel, add 150 cc. of approximately 2 *N* sulfuric acid, cool somewhat, add 120 cc. of ether, shake, draw off the acid layer, and wash the ether layer free from acid with a strong salt (NaCl) solution. Then draw off the aqueous layer as completely as possible, transfer the ether layer to a flask (it is not necessary to transfer quantitatively), add 20 to 30 g. of anhydrous sodium sulfate, stopper the flask, shake, and let stand at a temperature below 25° C. until the ethereal liquid becomes perfectly clear, showing that all water has been taken up by the sodium sulfate. Filter through a dry paper into another Erlenmeyer flask, and completely evaporate off the ether by passing through the flask a current of dry air and heating the flask to a temperature not above 50° C.

(2) *Determination.*[6] (*a*) *Thermometer.* The thermometer shall be a standard titer thermometer graduated at zero and in tenth degrees from 10° to 65° C., and certified by the U. S. Bureau of Standards.

(*b*) *Procedure.* Transfer the fatty acids prepared as under VII(1), when cooled somewhat, to a titer tube 25 mm. by 100 mm. placed in a 16-oz. salt-mouth bottle of clear glass 70 mm. by 150 mm., fitted with a cork that is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly (about 100 r.p.m.) until the mercury remains stationary for 30 sec. Allow the thermometer to hang quietly with the bulb in the center of the tube and report the highest point to which the mercury rises as the titer of the fatty acids. The titer should be made in a room at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

VIII. ACID NUMBER OF FATTY ACIDS.—(1) *Preparation of fatty acids.* Follow procedure given under C-VII.

(2) *Determination.* In a 250-cc. Erlenmeyer flask dissolve 2 g. of the fatty acids, accurately weighed, in 20 to 30 cc. of neutral 95 per cent ethyl alcohol. Titrate with standard alkali, using phenolphthalein as indicator. Calculate the acid number (mg. of KOH per g. of fatty acids).

IX. BORAX DETERMINATION.[7]—Weigh 10 g. (± 0.02 g.) of the soap [or 5 g. (± 0.01 g.) if more than 5 per cent of borax is present] into a platinum dish and add 2.15 g. of fusion mixture consisting of 200 g. sodium carbonate, 15 g. silica in fine powder. To this mixture add 15 cc. of alcohol, mix with the aid of a glass rod and, after washing the rod with a little alcohol, evaporate the mass to dryness on the water bath. Ignite until the combustible material is destroyed, cover the dish with a piece of platinum foil and fuse. Completely disintegrate the fusion by boiling with water and transfer the solution to a 250-cc. round-bottom flask. Acidify with 20 cc. of dilute hydrochloric acid (1:1), heat nearly to boiling, and add a moderate excess of dry precipitated calcium carbonate. Connect 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 liquid below 100 cc.

Return the filtrate to the flask, add a pinch of calcium carbonate and again boil under a reflux condenser. Remove the flame and connect the top of the condenser with a water pump. Apply the suction until the boiling has nearly ceased. Cool to ordinary temperature, add 50 cc. of neutral glycerol and titrate the solution with 0.1 *N* sodium hydroxide, free from carbonate, using phenolphthalein as indicator. After the end-point is reached add 10 cc. more of glycerol and again titrate. Repeat this process until the addition of glycerol causes no further action on the end-point. The number of cubic centimeters required multiplied by 0.00955 will give the equivalent of borax ($Na_2B_4O_7 \cdot 10H_2O$) present in the solution.

X. DETERMINATION OF SILICA PRESENT AS ALKALINE SILICATES.—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 hydrochloric acid, finally adding the equivalent of from 5 to 10 cc. strong hydrochloric acid 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.

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 C-II(4) containing not more than 0.2 g. silica and add 5 to 10 cc. strong hydrochloric acid.

Evaporate the acidified solution (washing off and removing the cover glass if used) to dryness on steam bath or hot plate at a temperature not exceeding 200° C. Cool, moisten with concentrated hydrochloric acid, let stand 5 to 10 min., breaking up all lumps with a stirring rod. Add about 25 cc. of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

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, but finally heating to constant weight over the blast lamp; cool in a desiccator before weighing. If extreme accuracy is desired, moisten the contents of the crucible with water, add 10 cc. hydrofluoric acid and 4 drops of strong sulfuric acid, 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).[8]

To calculate sodium silicate ($Na_2Si_4O_9$) multiply weight of SiO_2 by 1.26.

XI. DETERMINATION OF CARBON DIOXIDE (CARBONATES).—For most determinations the dry matter insoluble in alcohol as obtained in C-II(1) will be suitable for this determination. In some cases it might be desired to run the test directly on an original sample of the soap. This should always be done when the highest accuracy is required. Any reliable absorption method for determining carbon dioxide may be used.[9]

The following is a method which has proved satisfactory:

A 250-cc. Erlenmeyer flask is placed on a gauze over a burner. The flask is equipped with a 2-hole rubber stopper, through one opening of which is a 10-in. reflux condenser and through the other a thistle tube equipped at the outer end with a 3-way stopcock. The lower end of the thistle tube is drawn to a small point, which is placed very close to the bottom of the flask. To the straightaway end of the stopcock is attached a small funnel for the introduction of acid to the flask. The other opening of the stopcock is attached to receive air from a purifying train consisting of a wash bottle containing concentrated sulfuric acid and a second at the outer end of the train containing a 50 per cent solution of potassium hydroxide. The top of the reflux condenser is attached first to a drying wash bottle containing concentrated sulfuric acid, and then to a weighed absorbing train consisting of a suitable potash bulb charged with 50 per cent potassium hydroxide, and a second containing concentrated sulfuric acid. This train is attached to a protective U-tube containing calcium chloride. The U-tube is attached to an aspirator.

Procedure: Set up the apparatus, leaving out the weighed train, and aspirate with a slow stream of the dry carbon-dioxide-free air until the apparatus is freed from carbon dioxide. Insert the train and continue the aspiration for ½ hr. Check the weight of the train to determine if the air is passing through too fast, or if the system is free from carbon dioxide. The system must be free from leaks. Weigh out 1 or 2 g. of the sample into the Erlenmeyer flask, cover with 20 cc. freshly boiled distilled water, close the apparatus with the train in place. Add 20 cc. dilute hydrochloric acid (1:1) through the funnel very slowly, with no heat being applied 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 stop the gas flow, 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 down. Remove the train and weigh. Calculate increase of weight as carbon dioxide. Carbon dioxide multiplied by 2.41 equals sodium carbonate.

XII. DETERMINATION OF PHOSPHATES.[10]—If a qualitative test has shown the presence of phosphates and their determination is desired, the matter insoluble in alcohol C-II(1) or the ash from the incineration of an original sample can be used. An original sample should always be used when the highest accuracy is desired.

(1) *Reagents. (a) Molybdate solution.* Dissolve 100 g. of molybdic acid in dilute ammonium hydroxide [144 cc. of ammonium hydroxide (sp. gr. 0.90) and 271 cc. of water]; pour this solution slowly and with constant stirring into dilute nitric acid [489 cc. of nitric acid (sp. gr. 1.42) and 1,148 cc. of water]. Keep the final mixture in a warm place for several days or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered vessels.

(b) Ammonium nitrate solution. Dissolve 100 g. of commercial ammonium nitrate, phosphate-free, in water, and dilute to 1 liter.

(c) Magnesia mixture. Dissolve 55 g. of crystallized magnesium chloride ($MgCl_2 . 6H_2O$) in water, add 140 g. of ammonium chloride, 130.5 cc. of ammonium hydroxide (sp. gr. 0.90), and dilute to 1 liter.

(d) Dilute ammonium hydroxide for washing. Dilute 100 cc. of ammonium hydroxide (sp. gr. 0.90) to 1 liter.

(2) *Determination.* Weigh out a 2-g. (± 0.01 g.) sample of the alcohol-insoluble or ash, and proceed as in C-X for removal of silica, saving the filtrate. Make up to 250 cc., concentrating if necessary. Pipet an aliquot of the solution corresponding to 0.50 g. or 1 g. into a 250 cc. beaker; add ammonium hydroxide in slight excess; and barely dissolve the precipitate formed with a few drops of nitric acid stirring vigorously. Add about 15 g. of crystalline ammonium nitrate or a solution containing that quantity. To the hot solution add 70 cc. of the molybdate solution for every decigram of phosphoric acid (P_2O_5) present. Digest at about 65° C. for 1 hour and determine whether or not the phosphoric acid has been completely precipitated by the addition of more molybdate solution to the clear supernatant liquid. Filter, and wash with cold water or preferably with the ammonium nitrate solution. Dissolve the precipitate on the filter with ammonium hydroxide (1:1) and hot water and wash into a beaker to a volume of not more than 100 cc. Neutralize with hydrochloric acid, using litmus paper or bromthymol blue as an indicator; cool; and from a buret add slowly (about 1 drop per second), stirring vigorously, 15 cc. of the magnesia mixture for each decigram of phosphoric acid (P_2O_5) present. After 15 minutes, add 12 cc. of ammonium hydroxide. Let stand until the supernatant liquid is clear (usually 2 hours), filter, wash the precipitate with the dilute ammonium hydroxide until the washings are practically free from chlorides, dry, burn first at a low heat and ignite to constant weight, preferably in an electric furnace, at 950-1,000° C.; cool in a desiccator, and weigh as $Mg_2P_2O_7$. Calculate and report the result as percentage of P_2O_5 or alkaline phosphate known to be present.

XIII. DETERMINATION OF SULFATES.—For most determinations the matter insoluble in alcohol obtained under C-II may suffice. If a determination of the highest accuracy is desired, ignite a 10-g. (± 0.10 g.) sample of the soap and use the ash from the ignition. Digest with 100 cc. of water, cover with a watch glass, and neutralize carefully with hydrochloric acid. When neutralized, add 5 cc. excess of hydrochloric acid, filter, and wash the residue thoroughly. (Evaporation to dryness is unnecessary unless gelatinous silica should have separated, and should never be performed on a bath heated by gas.)[11] Make up the filtrate to 250 cc. in a beaker, and boil. To the boiling solution add 15 to 20 cc. 10 per cent barium chloride solution slowly drop by drop from a pipet. Continue boiling until the precipitate is well formed, or digest on a steam bath over night. Set aside over night or for a few hours, filter through a prepared Gooch crucible, ignite gently, and weigh as barium sulfate. Calculate to sodium sulfate, or the alkaline sulfate known to be present.

XIV. DETERMINATION OF GLYCEROL, SUGAR, AND STARCH.—(1) *Determination of glycerol in the absence of sugar.*

SOLUTIONS REQUIRED

Potassium Dichromate, 74.552 g. per liter
Sodium Thiosulfate, 0.1 *N*
Potassium Iodide, 10 per cent

Dissolve an accurately weighed sample of the soap equivalent to not more than 3.0 g. of glycerol in 200 cc. of hot water in a 600-cc. beaker. (If starch is present, it will be necessary to remove the matter insoluble in water as described under this determination [C-II(1) and (3)]. Combine the alcohol and water solutions, evaporate off the alcohol, and proceed.) Decompose with 25 cc. sulfuric acid (1:4). If alcohol is present, volatilize it by boiling for 20 to 30 min. Cool, remove, and rinse the cake of fatty acids, transfer the acid water and rinsings to a 500-cc. graduated flask, add about 0.25 g. silver sulfate to precipitate traces of chlorides and soluble fatty acids. Make up to volume and mix contents thoroughly.

Transfer a filtered, accurately measured 50-cc. aliquot of the above to a 400-cc. beaker, to this add 75 cc. accurately measured potassium dichromate solution, followed by 25 cc. of sulfuric acid (sp. gr. 1.84). Cover with a watch glass, and oxidize by heating to 90° to 100° C. for 3 hrs. Conduct a blank in like manner but using 100 cc. of water, 25 cc. of sulfuric acid (sp. gr. 1.84), and 25 cc. accurately measured potassium dichromate.

Cool and make up the solution to 1,000 cc. in graduated flasks. The excess of potassium dichromate is determined by taking 50 cc. aliquot of the above, adding 50 cc. of water, 20 cc. of 10 per cent potassium iodide solution, and titrating the liberated iodine with 0.1 *N* thiosulfate, using starch solution as indicator.

Calculate the percentage of glycerol (1 cc. of the potassium dichromate solution equals 0.0100 g. of glycerol).

(2) *Determination of sugar.* Dissolve 10 g. (± 0.01 g.) of the soap in 200 cc. of hot water in a 600-cc. beaker. Decompose with 25 cc. of sulfuric acid (1:4), boil gently for 20 min. to invert the sugar completely. Cool, remove, and rinse the cake of fatty acids. Extract the acid liquid with 25 cc. of ether. Transfer the acid liquid to a 500-cc. graduated flask, make up to volume and mix thoroughly. Determine invert sugar in 50 cc. of this solution by the Munson-Walker Method.[12] To calculate sugar (sucrose) multiply the amount of invert sugar found by 0.95. (Note.—If starch is present, this must first be removed as described under XIV(1) and then proceed as above.)

(3) *Determination of glycerol in the presence of sugars.*[13] Proceed as above under (1), taking a sample so that the sum of the glycerol and sugar is not more than 3.0 g. [Note.—If starch is present, this must first be removed as described in XIV(1).] The solution must be boiled in all cases at least 20 min. to insure complete inversion of sugar. Determine the amount of potassium dichromate solution required to oxidize both the sugar and glycerol. Determine also the sugar by the method given in (2).

Calculate the percentage of glycerol after deducting the amount of potassium dichromate required by the sugar.

1 cc. potassium dichromate equals 0.0100 g. glycerol.
1 cc. potassium dichromate equals 0.01142 g. invert sugar.

(4) *Determination of starch.*[14] Separate the matter insoluble in water as under C-II(3), using a sample of soap that will give not more than 3 g. of starch. Transfer the insoluble matter, without drying, to a beaker and heat for 2½ hrs. with 200 cc. of water and 20 cc. of hydrochloric acid (sp. gr. 1.125) in a flask provided with a reflux condenser. Cool, and nearly neutralize with sodium hydroxide. Complete the volume to 250 cc., filter, and determine the reducing sugars by the gravimetric method as given under method for the determination of sugar.

Calculate the amount of dextrose (*d*-glucose) equivalent to the cuprous oxide obtained. This multiplied by 0.90 equals the amount of starch.

XV. VOLATILE HYDROCARBON.—Weigh approximately (depending on the amount of volatile hydrocarbons present) 250 g. (± 1.0 g.) of the sample into a flask of about 5-liter capacity, which is so placed on a gauze that it can be heated. Add 2 to 3 liters of distilled water. Place a 2-holed rubber stopper in the flask, through one hole of which is inserted a copper or brass tube extending into the flask and terminating in a small circular ring of the tubing, bent so that the ring is in a horizontal position. Numerous small holes are drilled in the upper side of this ring and the end of the tube is sealed. This ring should be near the bottom of the flask.

Through the other hole of the stopper is inserted a glass tube provided with a trap of suitable form, the upper end of which is bent so as to be connected with a plain Liebig condenser. The end of the condenser tube is bent so as to extend into a buret graduated to 0.1 cc.

Introduce steam (free from oil) into the flask through the brass tube and collect the distillate in the buret. When the buret becomes full, draw off the water by opening the stopcock. The foam which forms in the flask may be controlled by momentarily shutting off the steam and by regulating heat applied to the flask. (Note.—200 to 300 g. calcium chloride may be added to the flask containing the soap solution, to prevent foaming.)

Read from time to time the amount of hydrocarbon distillate which collects on the top of the water in the buret, and when there is no further increase in this distillate the operation is finished. Allow the buret to stand over night, tightly stoppered, and then, after reading the amount of distillate, draw off the water as carefully as possible. Determine the specific gravity of the distillate, and calculate the weight and percentage in the original sample.

Bibliography

(1) *Fall Meeting, American Oil Chemists' Society, October 12, 13, 1933, Oil and Soap,* 10, 230, (1933); 10,208, (1933).
(2) *Industrial and Engineering Chemistry,* 14, 1159, (1922).
(3) *Oil and Soap,* 9, 253, (1932).
(4) *Industrial and Engineering Chemistry,* 13, 813, (1921).
(5) *Soap,* 7, 29, (1931).
(6) *Industrial and Engineering Chemistry,* 11, 1163, (1919); *"Methods of Analysis of Assoc. Official Agr. Chem.,"* (1930), 317.
(7) *Industrial and Engineering Chemistry,* 5, 645, (1913).
(8) *Hillebrand, U. S. Geol. Survey, Bull.* 700, 102.
(9) *"Methods of Analysis of Assoc. Official Agr. Chem.,"* (1930), 115; Bur. Chem. Bull. 107, 169.
(10) *"Methods of Analysis of Assoc. Official Agr. Chem.,"* (1930), 14.
(11) *Hillebrand, U. S. Geol. Survey, Bull.* 700, 232.
(12) *J. Am. Chem. Soc.,* 28,663, (1906); *Bur. Chem. Bull.* 107; *"Methods of Analysis of Assoc. Official Agr. Chem.,"* (1930), 379.
(13) *Industrial and Engineering Chemistry,* 14, 54, (1922); Correction 14, 340, (1922).
(14) *"Methods of Analysis of Assoc. Official Agr. Chem.,"* (1930), 282; *Bur. Chem., Bull.* 107, 53.