Semi-Micro Analysis of Soap. I. Semi-Micro Determination of the Usual Constituents*

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OF LATE YEARS a number of papers have been published dealing with restricted aspects of the semi-micro analysis of fats and oils and indirectly of soap. Thus procedures have been described for the semi-micro determination of the acid and saponification value of fats and oils (1, 2) and for the semi-micro determination of the Thiocyanogen value (3). Gorbach (4) has discussed the micro determination of total fat, unsaponifiable, phosphatide, phosphorus, sterols and fat constants (acid number, saponification number, acetyl value, thiocyanogen number and peroxide value) while Chargaff (5) has described micro methods (really semi-micro) for the determination of iodine number and saponification number. Micro methods are, of course, in many cases readily adaptable to a semi-micro basis.

This paper presents for the first time a procedure for the complete semi-micro analysis of a soap. The question may rightly be raised as to the utility of employing semi-micro methods in the analysis of a soap. Apart from the speed and ease with which analyses can be completed it is frequently found that the successful solving of a research problem depends upon the ability to analyze completely a small sample or to run a series of successive determinations on a limited amount of material. In addition to problems arising from research it should be mentioned that quality complaints by consumers are frequently accompanied by soap residues of less than several grams aggregate weight. For these and several cognate reasons it is felt that semi-micro methods for the analysis of soap merit serious consideration.

The scheme of analysis employed in this study is shown in Figure 1. Reference to this schematic diagram while reading the text will facilitate following the descriptive outline of the various procedures.

It is a fortuitous circumstance that very little special apparatus is required for the semi-micro analysis of a soap beyond the usual micro glassware stocked by most laboratory supply houses. The apparatus required is described under each determination. A semi-micro balance sensitive to ± 0.05 mg. facilitates the work but is not absolutely necessary as Benedetti-Pichler (6) has shown that many ordinary analytical balances of American manufacture possess a sensitivity of ± 0.05 mg. In weighing the sample the method of swings should be employed (7).

A special apparatus setup is required for the determination of free fatty acids (or free caustic alkali) and unsaponified material. This is however readily constructed from ordinary laboratory ware and involves a minimum of glass working.

Experience with the procedures described in this paper will enable the analytical chemist to apply his acquired skill to the determination of such constituents as are less frequently encountered in the analysis of soap. Benedetti-Pichler (8) has summarized the factors which need to be considered in converting a macro procedure to a micro procedure. The same factors apply, though in a lesser degree when modifying a macro procedure to a semi-micro procedure. In general it suffices to multiply all masses of reagents and capacities of apparatus by the ratio obtained by dividing the mass of sample on the semi-micro scale by the mass of sample on the macro scale.

Sampling

At the outset of this work it was expected that considerable difficulty would be encountered in obtaining a homogeneous and representative sample for analysis. In particular it was felt that sprayed soap products would prove to be non-uniform in composition in amounts as small as 20 to 30 milligrams. It was found, on the contrary, that sprayed (granulated) soap products require only the usual quartering procedure (on a small scale) to insure uniformity of the analytical sample (9, 19).

Solid samples are prepared for analysis by quartering, if the sample is sufficiently large, and the entire quarter diced with a sharp knife or razor blade. The operation should be carried out as rapidly as possible on a non-porous and non-absorbent surface. If the sample is too small to admit of quartering, proceed as directed with the entire available sample.

Semi-micro samples can sometimes be obtained by employing a cork borer of small diameter to obtain 20- to 30-milligram portions. As each sample is obtained, it is immediately transferred to a stoppered weighing bottle which has been previously tared.

In many cases it is possible to weigh out all the necessary samples for analysis at one time. Such a procedure obviates difficulties due to the loss of moisture.

Liquid soap requires no preparation other than thorough mixing.

Mechanically mixed samples which are so imperfectly mixed as to show separate particles of the various constituents can be weighed in bulk, transferred to a 25-ml. volumetric flask, dissolved in a small volume of water and the solution made up to the mark with H_2O at room temperature. Separate aliquots of a solution so prepared can be employed for the different determinations required.

Mechanically mixed samples can sometimes be successfully ground fine in a mortar, but there is always the danger of loss or gain of moisture or absorption of CO_2 and the operation should be carried out with due regard for such a contingency.

Uniformity of the analytical sample obtained as described above was demonstrated by running repeat determinations on various constituents. From these determinations the average deviation of the mean was calculated. The values obtained are shown in Table I. It was found that the values obtained for the average deviation of the mean vary from approximately the same to five times as great as experienced in the macro-analysis of similar type products (10).

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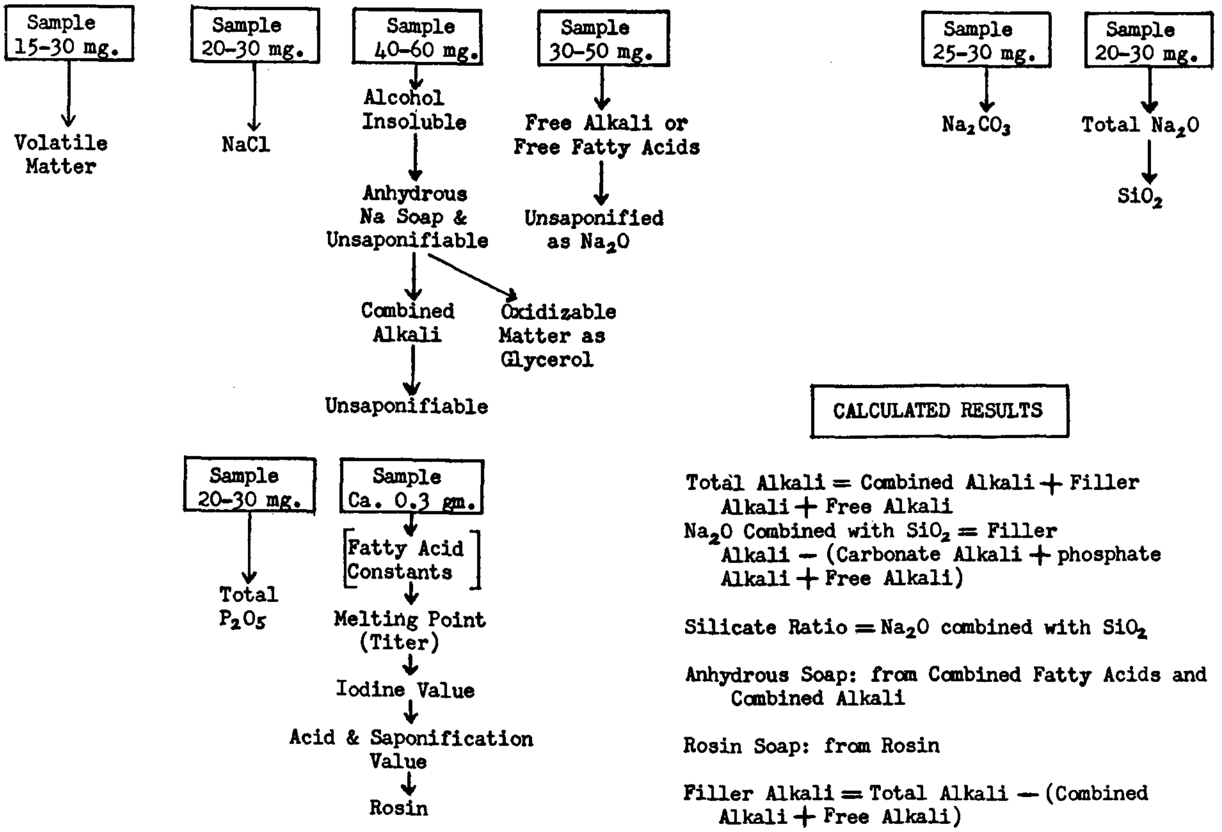
* By mistake Part II in this series of three articles was published in the September 1948 issue of the Journal, ahead of Part I.



Total Alkali = Combined Alkali + Filler Alkali + Free Alkali

Na_2O Combined with SiO_2 = Filler Alkali − (Carbonate Alkali + phosphate Alkali + Free Alkali)

Silicate Ratio = Na_2O combined with SiO_2

Anhydrous Soap: from Combined Fatty Acids and Combined Alkali

Rosin Soap: from Rosin

Filler Alkali = Total Alkali − (Combined Alkali + Free Alkali)

FIGURE 1.

SCHEMATIC DIAGRAM FOR THE SEMI-MICRO ANALYSIS OF SOAP

Reagents Required

In general the reagents required for any particular determination are given under the procedure for the determination. There are a few general reagents, however, which are used throughout and to avoid repetition are given here:

Phenolphthalein indicator solution: dissolve 0.5 gram phenolphthalein in 100 ml. of absolute ethyl alcohol.

Methyl orange indicator solution: dissolve 0.2 gram of methyl orange in 700-800 ml. of hot water, filter, and dilute to a liter with cold water.

Redistilled ammonium hydroxide: all ammonium hydroxide should be redistilled and stored in glass-stoppered pyrex bottles.

Determination of Moisture

Weigh 15 to 30 mg. of sample into a tared Coors porcelain boat (30 x 6 x 4 mm.) Transfer the boat and sample to a vacuum pistol dryer of the Abderhalden type. If the dryer is provided with a narrow metal shelf (approximately 20 x 125 mm.), as many as six samples may be run simultaneously. Acetylene tetrachloride (tetrachloroethane, B.P. 146.3) or a stable organic compound boiling at 140-150° C. should be employed as the heating medium. A suitable drying agent, such as anhydrous $CaSO_4$, is employed as the dessicant.

The sample is dried to constant weight in a vacuum of 8 cm. or less of mercury. If necessary, the sample may be weighed after undergoing drying for a minimum period of 3½ hours, but drying to constant weight results in more trustworthy values.

Air entering the drying apparatus during the re-establishment of normal atmospheric pressure should be dried by passage over the same drying agent employed in the apparatus. Allow the sample to cool in a long handled weighing bottle (piggie) and weigh. The loss in weight is calculated as per cent volatile matter.

Determination of Sodium Chloride

Accurately weigh between 20 and 30 mg. of sample and transfer to a 5-ml. beaker. Add 2 to 2.5 ml. of water and heat on the steam bath until the sample is completely dissolved. Add one drop of methyl orange indicator solution and 1:10 HNO_3 solution drop by drop until the fatty acids are liberated. Allow to stand on the steam bath until the fatty acids clear. Filter through a wet filter (No. 40 Whatman, 35 mm. in diameter) collecting the filtrate in a 25-ml. Erlenmeyer flask. Wash the paper and fatty acids with 3 to 4 ml. of hot water. To the filtrate add $CaCO_3$, a few milligrams at a time, with swirling, until the solution is neutral as shown by the yellow color of methyl orange. Allow the solution to cool to room temperature. Add one drop of potassium chromate solution and titrate with N/50 $AgNO_3$ solution. Run a blank simultaneously with the sample. Titrate both the blank and the sample to the same color of endpoint.

The potassium chromate solution is prepared by adding 62 grams of potassium chromate to 100 ml. of water. Add several drops of N/10 silver nitrate solution, shake thoroughly, and allow to settle for 1 to 2 hours. Filter and use the clear filtrate.

TABLE I

Precision of Results Obtained Employing Selected Semi-Micro Analytical Procedures for the Semi-Micro Analysis of a Commercial Sprayed Soap Product

Determination	Number of Determinations Made	Most Probable Value %	Extreme Values %	Mean Deviation	Average Deviation of the Mean(11) Semi-Micro Scale %	Average Deviation of the Mean(11)[1] Macro Scale %
Moisture	14	5.74	5.30- 6.09	0.19	±0.050	........[2]
Sodium Chloride	20	5.70	5.25- 6.38	0.25	±0.056	±0.018
Alcohol Insoluble	4	30.13	29.60-31.02	0.45	±0.22	±0.041
Anhydrous Soda Soap + U	4	60.17	59.85-60.40	0.24	±0.12	±0.073[3]
Silica (SiO_2)	8	8.72	8.04- 9.35	0.36	±0.13	±0.047
Total Alkali as Na_2O	8	16.35	15.96-16.66	0.20	±0.069	±0.060

[1] All deviations given are based on cooperative work by nine analysts with minimum individual experience in soap analysis of one year (10).

[2] No comparable value available.

[3] Value given is for anhydrous soda soap minus unsaponifiable.

Determination of Alcohol Insoluble

Accurately weigh between 40 and 60 mg. of sample into a 5-ml. beaker. Add 2 to 2.5 ml. of neutral absolute ethyl alcohol [redistilled over NaOH and protected from the air (protective tube filled with soda lime) to prevent absorption of CO_2] and place the beaker and contents on the steam bath. Cover with a small watch glass. Stir occasionally.

The alcohol is previously neutralized in bulk by adding a drop of phenolphthalein indicator solution, warming almost to boiling and adding N/50 NaOH to a faint pink color. The hot alcohol can conveniently be neutralized in a small separatory funnel which is closed with a $CaCl_2$ tube containing soda lime. The neutralized alcohol will stay pink for days under such storage conditions and is immediately available at any time by drawing off through the stopcock.

When the soap appears to be completely dissolved (15-20 minutes), filter off the alcohol insoluble material into a tared Gooch crucible (Coors porcelain, 15 x 15 mm., capacity 1.5 ml.). Wash the residue in the Gooch 5 to 6 times with neutral absolute alcohol employing a total volume of approximately 5 to 8 ml. Dry the residue in the Gooch in an air oven at 105°C. Allow to cool in a desiccator and weigh.

When using ethyl alcohol from a wash bottle the mouthpiece should be provided with a short absorption tube filled with soda lime to prevent absorption of CO_2 by the alcohol. A wash bottle properly designed for semi-micro work does not require the application of external pressure to perform its function (12).

Determination of Anhydrous Soda Soap and Unsaponifiable *

Collect the original alcohol solution and the washings from the determination of the alcohol insoluble material in a suction flask (25-ml. capacity). Transfer the alcohol solution and washings to an Erlenmeyer flask (10-ml. capacity). Evaporate carefully (steam or microburner) to a volume of approximately 3 to 4 ml. Add 4 ml. of water. Again evaporate to a volume of about 3 to 4 ml. Finally repeat the operation. Transfer the solution, with the aid of 2 to 3 ml. of hot H_2O to a glass stoppered mixing cylinder (10-ml. capacity).

Add one drop of methyl orange indicator solution and 1:10 sulfuric acid drop by drop until the fatty acids are liberated and the solution is acid. Cool under tap water.

Extract the solution six times, employing 2 ml. of ethyl ether for each extraction. On the first extraction swirl only, to avoid loss of liquid at the stopper. Siphon each extract into a 25-ml. suction flask. The apparatus should be arranged as shown in Figure 2. Completeness of the extraction can be determined by Edeler's method of placing a drop of the ether extract on a ground glass plate. If, upon evaporation of the ether, a grease stain appears, the extraction is incomplete and should be continued (13). Any residual fatty acids on the ground glass plate should be recovered.

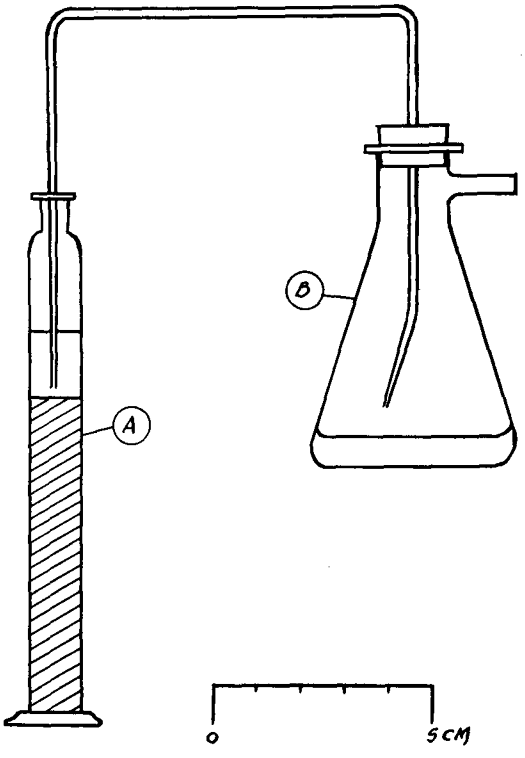


FIG. 2. Apparatus required for the semi-micro determination of anhydrous sodium soap + unsaponifiable.

Save the extracted solution for the determination of glycerol (vide).

Transfer the combined ether extracts (in several additions) to a tared 10-ml. Erlenmeyer flask. Evaporate the ether on the steam bath with a current of dry, filtered air to a volume of approximately 3 ml. Add 3 ml. of absolute ethyl alcohol (redistilled over NaOH and protected from the air to prevent absorption of CO_2).

Add one drop of phenolphthalein indicator solution and titrate to exact neutrality with N/20 NaOH.

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* The term unsaponifiable as employed in this paper refers to a mixture of unsaponifiable material and any unsaponified matter that may be present in admixture.

Continue to evaporate on the steam bath until the residue appears dry. Finally dry to constant weight in an air oven at 105°C., allow to cool in a desiccator and weigh against a tared flask.

Correct for neutral salts in the N/20 NaOH by titrating 5 ml. of the latter with N/20 HCl using phenolphthalein indicator solution (one drop). Evaporate the mixture to dryness on the steam bath. Dry to constant weight in an air oven at 105°C., allow to cool in a desiccator, and weigh against a tared flask.

Calculate the amount of NaCl which would be obtained by neutralizing 5 ml. of N/20 NaOH with N/20 HCl, assuming the N/20 NaOH to be 100% pure. Subtract this value (in grams) from the actual weight of NaCl obtained. Divide the value so obtained by 5 to obtain the neutral salt correction per ml. of N/20 NaOH. Correct the weight of sodium soap plus unsaponifiable by multiplying the number of ml. of N/20 NaOH required to titrate the total fatty acids plus unsaponifiable by the neutral salt correction per ml. of N/20 NaOH and subtracting the weight so obtained from the weight of anhydrous soda soap plus unsaponifiable.

Determination of Total Fatty Acids Plus Unsaponifiable (By Calculation)

To obtain the total fatty acids plus unsaponifiable the following formula may be employed:

$$\frac{\left(\begin{array}{c}\text{Weight of}\\\text{anhydrous}\\\text{sodium soap}\\+\text{U.}\end{array}\right)-\left[\left(\begin{array}{c}\text{ml. N/20 NaOH}\\\times 0.022\end{array}\right)+\left(\begin{array}{c}\text{ml. N/20 NaOH}\\\times\text{ neutral salt}\\\text{correction per}\\\text{ml. N/20 NaOH}\end{array}\right)\right]\times 100}{\text{Weight of sample}}$$

$$= \%\ \text{T.F.A. \& U.}$$

Determination of Unsaponifiable

To the anhydrous sodium soap plus unsaponifiable contained in the 10-ml. Erlenmeyer flask add 3 ml. of a 1:1 mixture of H_2O and absolute ethyl alcohol. Warm on the steam bath to complete solution. Transfer the solution with the aid of 2 to 3 ml. of hot 1:1 water-absolute ethyl alcohol, to a 10-ml. glass stoppered mixing cylinder.

Extract six times with 2-ml. volumes of petroleum ether. Siphon each extract into a 25-ml. suction flask. The apparatus employed in this procedure is the same as that employed for the extraction of total fatty acids plus unsaponifiable (see Figure 2).

Transfer the combined petroleum ether extracts (in several additions) to a 10-ml. Erlenmeyer flask. Evaporate on a steam bath in a current of filtered, dry air to constant weight. Allow to cool in a desiccator and weigh against a tared flask. Re-dry for an additional 15-minute period under the same conditions, cool and weigh. Repeat to constant weight. A blank should be run on the same volume of petroleum ether as employed in the determination.

To the residue add 5 ml. of neutral alcohol, warm on the steam bath, add one drop of phenolphthalein indicator and titrate with N/100 NaOH to a faint pink color. Calculate the titration to grams of oleic acid and subtract from the weight of unsaponifiable matter.

Determination of Glycerol

Reagents Required

N/5 $K_2Cr_2O_7$ dissolved in colorless, concentrated HNO_3.

Diphenyl Benzidine. 1% solution in concentrated H_2SO_4 (21).

0.005 N $K_4Fe(CN)_6$. This salt may be employed as a primary standard (22) or standardized against glycerol.

Procedure

The method employed for the determination is essentially that described by Raveux (14).

The extracted solution from the determination of anhydrous soda soap plus unsaponifiable freed of ethyl ether by twice evaporating to half volume should be transferred quantitatively to a 10-ml. volumetric flask and the solution brought to the mark with water at room temperature.

Accurately pipet 3 ml. of the solution and transfer to a 1 x 6 test tube or 25-ml. Kjeldahl flask. Add 2 ml. of N/5 $K_2Cr_2O_7$ dissolved in colorless nitric acid and 1 ml. of colorless, concentrated nitric acid.

Heat in a boiling water bath for 20 minutes. Remove from the bath and allow to cool to room temperature. Add about 30 ml. of H_2O and 0.3 ml. of diphenyl benzidine indicator solution. Titrate the excess $K_2Cr_2O_7$ solution with 0.005 N $K_4Fe(CN)_6$ solution until the red-violet color of the solution assumes a clear yellow green.

Two ml. of the N/5 $K_2Cr_2O_7$ solution require approximately 80 ml. of 0.005 N $K_4Fe(CN)_6$ solution. For this reason the 2 ml. of N/5 $K_2Cr_2O_7$ solution must be measured accurately. Use of an ordinary volumetric pipet will not prove satisfactory and it is recommended that the 2 ml. be measured by means of a Schollander micrometer buret (23) or weight buret.

The $K_4Fe(CN)_6$ solution deteriorates on standing and should be standardized daily or as often as used.

Determination of Free Alkali or Free Fatty Acid and Unsaponified Material

A special arrangement of apparatus is required for the determination of free alkali or free fatty acid and unsaponified material due to the avidity with which atmospheric CO_2 dissolves in alcohol.

The apparatus required for the determination is shown in Figure 3.

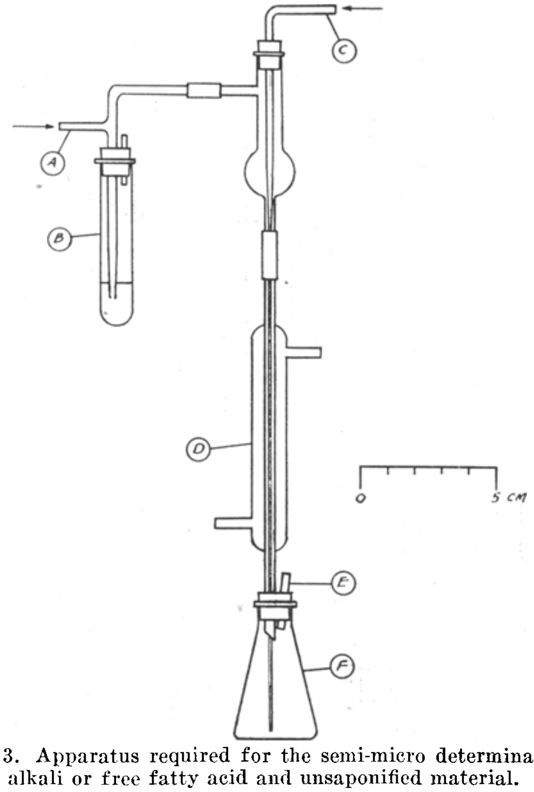

FIG. 3. Apparatus required for the semi-micro determination of free alkali or free fatty acid and unsaponified material.

Comparison of Analytical Results Obtained in the Analysis of Sprayed Soap Products by Macro and Semi-Micro Procedures

Constituent	Sprayed Soap No. 1				Sprayed Soap No. 2				Sprayed Soap No. 3				Sprayed Soap No. 4				Sprayed Soap No. 5			
	Macro		Semi-Micro		Macro		Semi-Micro		Macro		Semi-Micro		Macro		Semi-Micro		Macro		Semi-Micro	
	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis
Moisture		5.90		5.92		8.33		7.39		2.79		2.56		4.33		4.99		7.16		8.33
Total Fatty Acids	57.25	53.87	56.87	53.50	58.36	53.47	57.86	53.55	70.69	68.73	71.32	69.50	59.45	56.87	59.57	56.60	57.48	53.37	58.47	53.60
T. F. A. & U.	59.96	56.42	59.84	56.30	60.20	55.15	60.22	55.74	72.22	70.22	72.75	70.89	61.38	58.72	61.23	58.18	59.67	55.40	60.13	55.12
Free F. A. as % Na_2O	Nil	Nil	Nil	Nil	0.02	0.02	0.03	0.03	Nil	Nil	Nil	Nil								
Unsaponified as % Na_2O	0.05	0.05	0.04	0.04	0.06	0.06	0.05	0.05	0.09	0.09	0.08	0.08								
Unsaponifiable	2.71	2.55	2.98	2.80	1.83	1.68	2.37	2.19	1.53	1.49	1.43	1.39	1.93	1.85	1.66	1.58				
Rosin	5.32	5.01	5.42	5.10	4.20	3.85	4.44	4.11	Nil	Nil	Nil	Nil	9.25	8.85	9.56	9.08	4.31	4.00	5.14	4.71
Titer °C.[1]		36.6°		39.2°		34.9°		37.4°		38.8°		41.1°		38.5°		41.4°		35.2°		39.2°
Iodine Value		70.1		68.0		79.9		81.0		71.0		70.9								
Acid Value % KOH		19.47		19.71		19.92		19.58		19.19		19.82		19.65		19.84		19.83		19.88
Sap. Value % KOH		19.49		19.85		20.35		20.05		20.20		20.01								
Anhydrous Na Soap	61.82	58.17	61.22	57.60	63.07	57.78	62.25	57.62	76.46	74.34	76.88	74.92	64.17	61.39	64.22	61.02	62.12	57.67	63.13	57.87
Glycerol	0.22	0.21	0.21	0.20	0.11	0.10	0.12	0.11	0.17	0.17	0.19	0.19	0.21	0.20	0.21	0.20				
Total Alkali as % Na_2O (Corrected)	18.18	17.11	18.71	17.60	15.73	14.41	15.54	14.38	13.96	13.57	12.91	12.58					19.58	18.18	19.67	18.03
Free Caustic Alkali as % Na_2O	0.01	0.01	0.02	0.02	Nil	Nil	Nil	Nil	0.03	0.03	0.03	0.03					Nil	Nil	Nil	Nil
Combined Alkali as % Na_2O	6.44	6.06	6.20	5.83	6.63	6.07	6.34	5.87	7.58	7.37	7.82	7.62								
Alcohol Insoluble	30.27	28.48	31.41	29.55	30.85	28.26	32.36	29.95	13.08	12.72	12.87	12.54	28.05	26.84	29.55	28.08	29.23	27.14	30.33	27.80
Total Alkali of Filler as % Na_2O	11.73	11.04	12.51	11.77	9.10	8.34	9.19	8.51	5.50	5.35	5.06	4.93								
Na_2CO_3	13.40	12.61	13.55	12.75	2.91	2.67	2.88	2.67	2.55	2.48	2.54	2.48	12.21	11.68	11.95	11.35	13.51	12.54	14.16	12.98
SiO_2					14.53	13.31	15.08	13.96	2.50	2.43	2.87	2.80	8.54	8.17	8.07	7.67	5.27	4.89	5.02	4.60
Na_2O Combined with SiO_2					3.65	3.34	3.90	3.61	0.80	0.78	0.71	0.69								
$Na_2O : SiO_2$ Ratio					1:3.99		1:3.87		1:3.12		1:4.06									
NaCl	5.90	5.55	6.45	6.07	5.24	4.80	4.89	4.53	9.74	9.47	9.48	9.24	5.64	5.40	5.95	5.65	6.03	5.60	6.09	5.58
$Na_4P_2O_7$	4.90	4.61	5.13	4.83	8.06	7.38	7.75	7.17	6.88	6.69	6.16	6.00	4.64	4.44	4.75	4.51				
					99.40	99.39	99.24	99.25	100.63	100.64	100.26	100.27								

Constituent	Sprayed Soap No. 6				Sprayed Soap No. 7				Sprayed Soap No. 8				Sprayed Soap No. 9				Sprayed Soap No. 10			
	Macro		Semi-Micro		Macro		Semi-Micro		Macro		Semi-Micro		Macro		Semi-Micro		Macro		Semi-Micro	
	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis
Moisture		4.44		4.27		5.19		4.89		5.48		4.72		6.55		5.27		8.55		7.64
Total Fatty Acids	58.76	56.14	58.53	56.04	58.87	55.82	59.69	56.79	55.17	52.14	54.37	51.80								
T. F. A. & U.	60.88	58.16	61.26	58.66	61.32	58.14	62.29	59.26	56.57	53.46	56.35	53.68								
Free F. A. as % Na_2O	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil								
Unsaponified as % Na_2O	0.08	0.08	0.08	0.08	0.04	0.04	0.03	0.03	0.03	0.03	0.02	0.02								
Unsaponifiable	2.11	2.02	2.74	2.62	2.45	2.32	2.60	2.47	1.40	1.32	1.97	1.88								
Rosin	5.60	5.35	5.72	5.48	5.72	5.42	4.34	4.13	2.90	2.74	2.62	2.50	3.53	3.30	3.31	3.14				
Titer °C.[1]		37.4°		39.8°		36.4°		38.4°		37.2°		38.8°		37.7°		38.8°		36.2°		38.4°
Iodine Value		67.2		66.8		69.2		71.0		64.7		62.3								
Acid Value % KOH		19.33		19.47		19.93		19.60		20.24		20.25		20.02		20.19		19.86		20.39
Sap. Value % KOH		19.58		19.63		20.00		19.81		20.40		20.45								
Anhydrous Na Soap	63.38	60.55	63.06	60.38	63.67	60.37	64.25	61.13	59.63	56.36	58.70	55.92	58.79	54.94	57.71	54.67	62.31	56.98	63.42	58.58
Glycerol	0.38	0.36	0.42	0.40	0.31	0.29	0.28	0.27	0.19	0.18	0.18	0.17								
Total Alkali as % Na_2O (Corrected)	17.97	17.17	18.49	17.70	17.98	17.05	17.50	16.65	17.87	16.89	18.23	17.37								
Free Caustic Alkali as % Na_2O	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.01	0.01	0.01	0.01								
Combined Alkali as % Na_2O	6.50	6.21	6.30	6.03	6.77	6.42	6.46	6.15	6.33	5.98	6.09	5.80								
Alcohol Insoluble	28.76	27.48	31.35	30.02	28.12	26.66	26.12	24.85	33.50	31.66	29.70	28.29	32.97	30.81	28.82	27.30	31.57	28.87	29.24	27.01
Total Alkali of Filler as % Na_2O	11.45	10.94	12.17	11.65	11.18	10.60	11.01	10.47	11.53	10.90	12.13	11.56								
Na_2CO_3	12.23	11.68	12.04	11.53	13.00	12.33	12.88	12.25	7.85	7.42	7.72	7.35	2.09	1.95	2.16	2.05	3.91	3.58	3.79	3.50
SiO_2	9.11	8.70	8.87	8.49	8.69	8.24	8.68	8.26	11.25	10.63	11.11	10.58					15.35	14.04	15.62	14.43
Na_2O Combined with SiO_2	2.30	2.20	2.82	2.70	1.22	1.16	1.19	1.13	2.51	2.37	3.19	3.04								
$Na_2O : SiO_2$ Ratio	1:3.95		1:3.14		1:7.10		1:7.31		1:4.50		1:3.48									
NaCl	5.84	5.58	5.62	5.38	5.74	5.44	5.73	5.45	7.50	7.09	7.25	6.91	7.53	7.04	7.28	6.90	4.61	4.22	4.59	4.24
$Na_4P_2O_7$	4.26	4.07	4.93	4.72	5.02	4.76	4.89	4.65	9.50	8.98	9.50	9.05					6.40	5.85	6.34	5.86
	99.61	99.60	100.50	100.49	100.10	100.10	100.50	100.50	99.83	99.83	99.62	99.62								

[1] Values on the semi-micro basis are melting points.

The determination is initiated by weighing 30 to 50 mg. of sample into the 10-ml. Erlenmeyer flask (F). Attach the flask to the reflux condenser (D) and introduce CO_2 free air through the air line (A). The pressure column (B) maintains a slight excess of air in the system when outlet (E) is closed. Allow the air to flow for about a minute to displace all CO_2 from the flask and then, while continuing the air flow, add 2 to 3 ml. of neutralized alcohol from a separatory funnel to the sample in the flask. This is readily accomplished by inserting the drawn-out tip of a separatory funnel into the outlet (E) of the flask. The alcohol is previously neutralized while hot, transferred to the separatory funnel and permitted to cool to room temperature before use. In place of a stopper the separatory funnel should be provided with a soda-lime tube to prevent absorption of CO_2 by the alcohol while cooling to room temperature.

Dissolve the alcohol soluble constituents of the sample by warming the contents of the flask to refluxing over a micro burner. A rubber policeman is employed to close the opening (E) of the flask during the refluxing operation. The air line (A) need not be turned off during the operation as any excess pressure is released through (B).

When as much of the sample as will dissolve in alcohol is in solution, remove the micro burner and rubber policeman. Insert the tip of a micro buret through the flask opening (E) and titrate with either N/250 HCl or N/250 KOH depending upon whether the sample reacts acid or alkaline to phenolphthalein indicator. During the titration operation stirring is accomplished by a stream of CO_2 free air supplied from the line (C). Usually sufficient phenolphthalein indicator is present in the neutralized alcohol to permit obtaining a satisfactory endpoint. Calculate the titration to either free fatty acids as per cent Na_2O or free caustic alkali as per cent Na_2O, depending upon whether the solution is acid or alkaline to phenolphthalein indicator.

Filter the titrated solution through a Gooch crucible into a 25-ml. filter flask using a minimum volume of the neutralized alcohol to accomplish the operation. Transfer the filtered solution to a 25-ml. Erlenmeyer flask. Add N/250 KOH drop by drop to the phenolphthalein endpoint. Disregard the volume of N/250 KOH required. Add 1 ml. of N/50 alcoholic KOH to the contents of the flask and reflux on a hot plate for 10 minutes. The volume of N/50 alcoholic KOH must be measured accurately; preferably by use of a Schollander micrometer buret (23) or similar device. Back titrate with N/250 HCl. A blank should be run simultaneously with the sample. Calculate the difference in buret readings between the blank and sample to obtain unsaponified material as per cent Na_2O.

Values obtained by employing the above procedure and the usual macro method are compared in Table II. Additional examples are given in Tables III and IV.

Determination of Sodium Carbonate

The apparatus employed for the determination of the carbonate content of the sample is that described by Wyatt (15). It is recommended that the weighed sample (in a porcelain boat) be placed in the dry alkalimeter and air aspirated through the apparatus for 30 minutes. Weigh the CO_2 absorption tube. Replace the absorption tube and add the specified volume of 2 N HCl to decompose the carbonate. The remainder of the procedure is carried out as described by Wyatt (15).

TABLE II

Comparison of Values for Free Alkali or Free Fatty Acid and Unsaponified Material Obtained by the Semi-Micro and Macro Procedures

Sample	Free Fatty Acid % Na_2O		Free Caustic Alkali % Na_2O		Unsaponified Material % Na_2O	
	Macro	Semi-Micro	Macro	Semi-Micro	Macro	Semi-Micro
Sprayed-Soap A	......	......	0.02	0.01	0.08	0.08
Sprayed Soap B	......	......	0.01	0.02	0.03	0.04
Flake Soap C	......	......	0.01	0.02	0.04	0.03
Flake Soap D	0.02	0.03	......	......	0.02	0.02

Determination of Total Alkali

Accurately weigh between 20 and 30 mg. of sample into a small platinum dish (capacity 10 ml.). Thoroughly char the sample over a micro burner flame. Momentarily fuse the alkali salts. Allow the dish and contents to cool. Add 2 to 3 ml. of hot water and place on the steam bath until solution is complete. Transfer the solution to a 25-ml. Erlenmeyer flask with the aid of a small volume of hot water, add two drops of methyl orange indicator solution and titrate with N/50 HCl. Calculate the total alkali as Na_2O. Save the titrated solution for the determination of SiO_2.

The amount of alkali found must be corrected for untitrated Na_2O if phosphates are present. It is necessary to add one-third of the per cent Na_2O present in the form of $Na_3Po_4 \cdot H_2O$ or/and one-half of the per cent Na_2O present in the form of $Na_4P_2O_7$. Data for additional phosphates frequently encountered in soap ananlysis can be determined from the general rule that at methyl orange neutrality one Na for each P remains untitrated.

Determination of SiO_2

Transfer the titrated solution from the determination of total alkali to a small platinum dish (10-ml. capacity). Add five drops of concentrated H_2SO_4 and evaporate to copious white fumes. Cool. Add 1 ml. of water and five drops of concentrated H_2SO_4. Rotate the dish with tilting until all portions of the residue have been thoroughly wetted. Again evaporate over a burner *to copious white fumes.* Add 2-3 ml. of water, heat and filter through a No. 40 Whatman filter (35-mm. diameter). Wash the filter thoroughly with hot water. Transfer the paper and residue to a small platinum crucible (5-ml. capacity) and ignite over a burner or in a muffle. Allow to cool in a desiccator and weigh.

Determination of Total P_2O_5

Accurately weigh 20-30 mg. of the sample into a 5-ml. beaker. Add 2 ml. of H_2O. Heat on the steam bath to complete solution. Add one drop of methyl orange indicator solution and two drops of 1:1 HCl. Continue to warm on the steam bath until the fatty acids form a clear layer.

Filter through a No. 40 Whatman paper (35-mm. diameter) into a platinum dish (10-ml. capacity). Add 10 drops of concentrated H_2SO_4 and evaporate over a burner *to copious white fumes. Do not allow to go to dryness.* Cool. Add 1 ml. of water and five drops of concentrated H_2SO_4. Rotate the dish with tilting until all particles of the residue have been

TABLE IV

Comparison of Analytical Results Obtained in the Analysis of Bar Soaps by Macro and Semi-Micro Procedures

Constituent	Bar Soap No. 1				Bar Soap No. 2				Bar Soap No. 3			
	Macro		Semi-Micro		Macro		Semi-Micro		Macro		Semi-Micro	
	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis
Moisture		9.58		9.27		17.17		14.52		8.40		6.45
Total Fatty Acids	90.06	81.40	89.69	81.30	89.87	74.43	89.90	76.85	87.72	80.34	85.90	80.30
T. F. A. & U.	90.84	82.10	90.51	82.04	90.91	75.29	91.27	78.02	90.28	82.68	88.94	83.14
Free Fatty Acids as % Na_2O	0.04	0.04	0.04	0.04	0.05	0.04	0.04	0.03	0.01	0.01	0.01	0.01
Unsaponified as % Na_2O	0.05	0.05	0.04	0.04	0.02	0.02	0.01	0.01	0.05	0.05	0.04	0.04
Unsaponifiable	0.77	0.70	0.82	0.74	1.04	0.86	1.37	1.17	2.56	2.34	3.04	2.84
Rosin	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Titer °C.[1]		38.1°		40.6°		39.6°		43.2°		37.3°		39.4°
Iodine Value		43.0		45.1		45.3		44.6		42.6		44.5
Acid Value % KOH		21.36		21.36		21.14		21.22		21.58		21.65
Saponification Value % KOH		21.59		21.78		21.15		21.38		21.72		21.96
Anhydrous Na Soap	97.73	88.33	97.26	88.16	97.43	80.69	97.25	83.13	95.34	87.32	93.24	87.16
Glycerol	0.29	0.26	0.34	0.31	0.23	0.19	0.21	0.18	0.61	0.56	0.63	0.59
Total Alkali as % Na_2O (Corrected)	10.90	9.85	10.93	9.91	10.86	8.99	10.80	9.23	11.06	10.13	11.06	10.34
Free Caustic Alkali as % Na_2O	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Combined Alkali as % Na_2O	10.77	9.73	10.81	9.80	10.65	8.82	10.54	9.01	10.74	9.84	10.30	9.63
Alcohol Insoluble	0.98	0.89	0.98	0.89	0.50	0.41	0.67	0.57	1.23	1.13	1.98	1.85
Water Insoluble	0.17	TiO_2[2] 0.15	......[3]	......[3]	Nil	Nil	Nil	Nil	0.17	0.16[2]	......[3]	......[3]
Total Alkali of Filler as % Na_2O	0.13	0.12	0.12	0.11	0.21	0.17	0.26	0.22	0.32	0.29	0.76	0.71
Na_2CO_3	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
SiO_2	0.17	0.15	0.05	0.05	0.12	0.10	0.09	0.08	0.32	0.29	0.40	0.37
Na_2O Combined with SiO_2	0.13	0.12	0.12	0.11	0.21	0.17	0.26	0.22	0.32	0.29	0.76	0.71
$Na_2O:SiO_2$ Ratio	1:1.25		1:0.45		1:0.59		1:0.36		1:1.0		1:0.52	
NaCl	0.55	0.50	0.54	0.49	0.87	0.72	0.87	0.74	0.62	0.57	0.74	0.69
	99.64	99.64	99.13	99.13	99.90	99.90	100.05	100.04	99.77	99.77	98.81	98.81

Constituent	Bar Soap No. 4				Bar Soap No. 5			
	Macro		Semi-Micro		Macro		Semi-Micro	
	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis	Dry Basis	As Recd. Basis
Moisture		8.19		7.15		7.82		5.64
Total Fatty Acids	89.96	82.58	89.52	83.10	89.62	82.58	88.72	83.70
T. F. A. & U.	90.63	83.19	90.31	83.83	90.41	83.30	89.83	84.75
Free Fatty Acids as % Na_2O	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Unsaponified as % Na_2O	0.05	0.05	0.06	0.06	0.07	0.06	0.07	0.07
Unsaponifiable	0.66	0.61	0.79	0.73	0.78	0.72	1.11	1.05
Rosin	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Titer °C.[1]		39.0°		42.0°		40.0°		42.6°
Iodine Value		49.6		47.0		46.7		45.6
Acid Value % KOH		20.80		20.89		20.76		20.84
Saponification Value % KOH		20.95		20.92		20.90		20.93
Anhydrous Na Soap	97.35	89.36	96.71	89.77	96.97	89.35	95.98	90.55
Glycerol	0.50	0.46	0.43	0.40	0.38	0.35	0.43	0.41
Total Alkali as % Na_2O (Corrected)	10.67	9.79	10.92	10.14	10.59	9.76	10.90	10.28
Free Caustic Alkali as % Na_2O	0.01	0.01	Nil	Nil	Nil	Nil	Nil	Nil
Combined Alkali as % Na_2O	10.41	9.56	10.32	9.58	10.35	9.54	10.22	9.64
Alcohol Insoluble	0.92	0.84	1.14	1.06	1.28	1.18	1.72	1.62
Water Insoluble	0.07	0.06	......[3]	......[3]	Nil	Nil	Nil	Nil
Total Alkali of Filler as % Na_2O	0.24	0.22	0.60	0.56	0.23	0.22	0.68	0.64
Na_2CO_3	0.10	0.09	......[3]	......[3]	0.02	0.02	Nil	Nil
SiO_2	0.37	0.34	0.51	0.47	0.51	0.48	0.77	0.73
Na_2O Combined with SiO_2	0.19	0.17	0.60	0.56	0.22	0.21	0.68	0.64
$Na_2O:SiO_2$ Ratio	1:2.00				1:2.29		1:.1.14	
NaCl	0.62	0.57	0.65	0.60	0.61	0.58	0.69	0.65
	99.86	99.85	99.69	99.68	99.49	99.53	99.66	99.67

[1] Values on the semi-micro basis are melting points.
[2] Water insoluble material identified as TiO_2.
[3] Not determined.

thoroughly wetted. Evaporate over a burner *to copious white fumes*. Add 2-3 ml. of H_2O, heat and filter through a No. 40 Whatman filter (35-mm. diameter). Wash the filter thoroughly with hot water. The residue may, if desired, be ignited, cooled, and weighed as SiO_2.

Collect the filtrate in a 20-ml. beaker. Evaporate to a volume of 3-4 ml.

Add one drop of methyl orange indicator solution and add concentrated NH_4OH drop by drop until the solution is slightly alkaline. Warm on the steam bath for one-half hour.

Filter through a No. 40 Whatman filter (35-mm. diameter) and wash the precipitate thoroughly with hot water.

To the filtrate add concentrated HCl drop by drop to slight excess. Add 5 ml. of magnesia mixture solution [this solution is prepared according to the directions of the Bureau of Standards (16). Dissolve 50 grams of $MgCl_2 \cdot 6H_2O$ and 100 grams of ammonium chloride (NH_4Cl) in 500 ml. of water, add a slight excess of NH_4OH and allow to stand overnight. Filter off any precipitate that forms, make the solution slightly acid to litmus with concentrated HCl and dilute to a volume of 1,000 ml.] and mix well by stirring. Chill the solution and add 1:1 NH_4OH dropwise, slowly and with constant stirring until the first white crystals appear. Continue stirring for two minutes and then add an excess of 1 ml. 1:1 NH_4OH. Allow to stand overnight.

Filter through a No. 40 Whatman paper (70-mm. diameter). Wash the precipitate thoroughly with 1:10 NH_4OH and finally with 1 ml. of slightly ammoniacal 5% ammonium nitrate solution.

Transfer the paper and precipitate to a previously ignited and weighed porcelain crucible. Dry the crucible and contents in an oven and finally ignite in a muffle. Cool in a desiccator and weigh as $Mg_2P_2O_7$.

Determination of Fatty Acid Constants

Preparation of Fatty Acids. Place approximately 0.25 gram of soap in a 30-ml. beaker. Add about 10 ml. of hot water. Place on the steam bath until the sample is in solution. Add 2 to 3 drops of methyl orange indicator solution and sufficient 1:3 sulfuric acid, dropwise with constant stirring, to decompose the soap and liberate the fatty acids. Add a drop of 1:3 sulfuric acid in excess. Place on the steam bath until the fatty acids clear. Siphon off the acid water layer, add 10 ml. of hot water and 2 to 3 drops of methyl orange indicator solution and warm on the steam bath until the fatty acids again clear. Siphon off the water layer. Repeat this operation until the fatty acids are free of mineral acid. After the last siphoning add 2 to 3 ml. of ethyl ether. Separate the aqueous and ether phases in a small separatory funnel. Add ca. 0.25 gram of anhydrous Na_2SO_4 to the ether phase and allow to stand until the ether solution is clear. Filter through a No. 40 Whatman paper (3.5 cm. diameter) and evaporate the ether solution on the steam bath under a stream of dry, filtered air until all odor of ethyl ether has disappeared.

Determination of Melting Point of Fatty Acids

The melting point of the fatty acids is determined in the usual manner, employing a glass capillary tube to contain the sample and a liquid (water) bath as a heating medium. After the fatty acids have been placed in the capillary tube it should be allowed to remain in a refrigerator for at least 24 hours before determination of the melting point.

A large number of observations have shown that melting points obtained with a glass capillary average about 2.5 degrees greater than the titer point (20).

Determination of the Iodine Number

Accurately weigh 10 to 25 mg. of the prepared fatty acids into a 25-ml. glass-stoppered Erlenmeyer flask. Add 1 ml. of chloroform and tilt the flask to bring the chloroform into contact with the sample. Allow to stand a sufficient length of time for the sample to be completely dissolved.

Add 2 ml. of Wijs iodine solution from a pipet. Stopper the flask and place in the dark for exactly one-half hour. Add 5 ml. of 2% potassium iodide solution and titrate with N/50 $Na_2S_2O_3$ solution using starch solution as indicator. The starch solution is prepared as described by Benedetti-Pichler (18). Run a blank simultaneously.

Determination of the Acid Value

Accurately weigh 20 to 30 mg. of the prepared fatty acids into a 25-ml. Erlenmeyer flask. Add 5 ml. of neutral alcohol and 1 to 2 drops of phenolphthalein indicator solution. Warm on the steam bath to dissolve the sample. Titrate with N/20 NaOH to a pink endpoint and calculate the acid value as milligrams of KOH per gram of sample.

Determination of the Saponification Value

The method of Ketchum (2) is followed without modification.

Determination of Rosin

Accurately weigh 20-30 mg. of sample into a 25-ml. Erlenmeyer flask. Sinnhuber and Ruggles have described a convenient method for the weighing of semi-micro oil samples (17). Add 2 ml. of naphthalene-B-sulfonic acid solution (40 grams/liter anhydrous methyl alcohol) from a 5-ml. buret calibrated in 0.02 ml. Attach a reflux condenser and boil the contents of the flask for 20 minutes. At the same time run a blank. At the conclusion of the 20-minute boiling period cool the contents of both flasks. Add one drop of phenolphthalein indicator solution and titrate with N/50 alcoholic KOH to a permanent pink endpoint (30 seconds) using a chamber buret. The chamber should be calibrated to hold 15 ml. The balance of the buret should contain 10 ml. and be calibrated in 0.02 ml. Titrate the blank to the same endpoint.

Results

Table III presents a comparison of analytical results obtained in the analysis of sprayed soap products by macro and semi-micro procedures. Table IV presents a comparison of analytical results obtained in the analysis of bar soaps by macro and semi-micro procedures. In general the macro procedures were those of the Official A.O.C.S. Methods (9) or were closely similar.

It is the usual practice in this laboratory to determine the pyrophosphate content by titration after treatment with zinc sulfate. In addition the total P_2O_5 content is determined. The difference between the total P_2O_5 content and the P_2O_5 equivalent to the determined value of pyrophosphate is calculated to Na_2HPO_4.

In the examples shown in Table III this was not done inasmuch as the semi-micro analytical scheme includes a total P_2O_5 determination and does not differentiate between pyrophosphate and Na_2HPO_4. The values on the macro scale therefore represent total P_2O_5 calculated to pyrophosphate. Normally the values would be 0.2 to 0.4% less.

Considering the fact that sprayed products frequently show segregation of various constituents (particularly sodium chloride) the results obtained by the semi-micro procedure compare favorably with those obtained by employing macro procedures. Some discrepancy is due to the unfortunate fact that a time period of 2 to 4 months elapsed between the analyses on the macro scale and the subsequent analyses on a semi-micro scale. It is known that minor chemical changes occur in sprayed soaps upon storage. Simultaneously there is increased mechanical segregation of filler constituents due to dusting as a result of the sample losing moisture. Such changes are reflected in the total alkali and filler alkali relationships. Values for pyrophasphate and sodium chloride also tend to become erratic with elapse of time. The summation of analytical results for the five complete analyses given in Table III confirm these statements.

Table IV presents a comparison of analytical results obtained in the analysis of bar soaps by the standard macro procedure and by the semi-micro procedure. There is a reasonable agreement of the values in most cases.

It will be noticed that water insoluble material was not determined on a semi-micro scale. It was found that the TiO_2 present invariably passed into the filtrate unless an inordinately thick asbestos mat was provided in the Gooch crucible employed for the filtration. In the latter case the time required for the filtration rendered the determination impractical. No further attempts were made in regard to devising a procedure for this determination inasmuch as a semi-micro colorimetric method has been devised for the determination of TiO_2.

It will also be noted that the $Na_2O:SiO_2$ ratios on the macro and semi-micro basis do not agree very closely. It is perhaps misleading and undoubtedly meaningless to attempt to evaluate such a ratio when the amounts of material involved are of the order of 0.2% and less. The ratios given in Table III, where the magnitude of the quantities involved is greater, show a satisfactory agreement.

The values for moisture, obtained by the semi-micro method described in this paper (vacuum oven) have been compared with values obtained on a macro scale by xylol distillation. Both methods yield values that check within reasonable limits. On a macro scale the xylol distillation method yields values directly comparable with those obtained by use of a vacuum oven. It will be noted upon comparing the values obtained by macro-methods with those obtained by semi-micro methods (Tables III and IV) that there are a few instances where discrepancies exist. In such cases the semi-micro values represent the average of one or more determinations and probably are closer to the true value than the macro value.

Discussion

After acquiring experience with semi-micro methods, it will be found quite feasible to combine various of the procedures in one with a consequent saving of sample. Such shortcuts are left to the ingenuity of the analytical chemist.

It is possible to make a complete analysis of a sprayed soap product as outlined in Figure 1 on approximately 0.53 gram of sample. By saving the fatty acids from the various determinations, other than those listed under "Determination of Fatty Acid Constants," and employing the recovered fatty acids for the determination of the fatty acid constants, a complete analysis of a sprayed soap can be made on 0.25 gram or less of sample. Appreciably less will be required for the complete analysis of an unfilled soap. These estimates do not, of course, allow for analytical accidents or for checking purposes.

There are several precautions to be observed in semi-micro soap analysis. Separate policemen should be reserved for use in acid or alkali solution. They should be new and made of firm (uncracked) fresh rubber.

An adjustable stream of filtered, CO_2 free air should be available at all times for use in stirring solutions during titration.

The precise determination of free fatty acid or free caustic alkali and unsaponified material on a macro scale is difficult. Unless one is experienced with the procedure and can proceed rapidly with the determination atmospheric CO_2 is quite apt to lead to discordant results. On a semi-micro scale the determination is somewhat tedious but due to precautions taken to prevent free access of CO_2 the values can be considered to be more accurate, than those obtained on a macro scale.

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Summary

A procedure for the complete semi-micro analysis of soap has been developed. Semi-micro methods are valuable in research work and in legal cases where limited quantities of sample are available. In general, the analytical results obtained on a semi-micro basis and on a macro basis are comparable. Very little special apparatus is required for the semi-micro analysis of a soap, and most of the procedures employed present analogies with the usual methods of soap analysis.

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22. *Ibid.*, Vol. II, p. 286.
23. Schollander, Science *95*, 177 (1942).