tween fair and high solubility, whereas the potassium soaps go abruptly into solution, at almost the same temperature and concentration of each soap.

The only soaps that are even moderately soluble at room temperature are potassium laurate, myristate, and oleate, the potassium salt of acids from coconut oil, and the sodium oleate. The other sodium and potassium soaps of the saturated fatty acids require elevated temperatures for solution.

Phase diagrams for the five commonest potassium soaps are developed and recorded.

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Rapid Volumetric Method for the Determination of Silica in Soap

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THE gravimetric method for the determination of silica in soaps involves a time-consuming evaporation and dehydration with concentrated sulfuric acid. There is a great chance for error due to spattering and insufficient dehydration. Losses due to the difficulty in handling the gelatinous silica are common. The volumetric method described below eliminates these disadvantages and is both rapid and accurate.

In 1929 Siegel (1) introduced a method for the volumetric determination of alkali-fluorides and silicic acid based on the reaction:

$$SiO_2 + 6NaF + 4HCl \rightarrow Na_2SiF_6 + 4NaCl + 2H_2O$$

Korol and Koluzhskaya (2) found that the determination of SiO_2 in water glass by this method proceeded very slowly and resulted in an indifferent endpoint. The addition of an excess of HCl and back titration with NaOH resulted in ambiguous results due to the fact that Na_2SiF_6 itself is titratable. These workers avoided this difficulty by employing potassium chloride to convert the sodium salt into the less soluble K_2SiF_6 and by titrating in the presence of alcohol.

The method of Korol and Koluzhskaya is capable of good results in the analysis of sodium silicate solutions but, when applied to the determination of SiO_2 in soap, immediate difficulty is encountered. In attempting to apply the method to the determination of SiO_2 in soap, it was found that the presence of phosphates and carbonates necessitated several modifications of their method. As described in this paper, these modifications consist in bringing the hot solution of the ashed sample to exact neutrality by adding an excess of N/2 HCl and back-titrating to a phenolphthalein endpoint with N/2 KOH. The required amount of potassium chloride is then added, followed by an excess of N/2 HCl and the required amount of NaF. After allowing sufficient time for the reaction to proceed to completion, the excess HCl is titrated with N/2 KOH. Boiling of the solution before adjustment of the initial endpoint is necessary to remove CO_2 from the solution.

Procedure

Reagents Required. The following reagents are required for use in the procedure:

N/2 Hydrochloric Acid.

N/2 Potassium Hydroxide.

Phenolphthalein Indicator solution prepared by dissolving 1 gram of phenolphthalein in 120 ml. of alcohol, adding 100 ml. of water, thoroughly mixing and neutralizing with dilute alcoholic KOH to a faint pink color.

Potassium Chloride (KCl).

Sodium Fluoride (NaF).

Neutral alcohol (95% ethyl alcohol, U.S.S.D. Formula 3a) prepared by neutralizing cold alcohol to a phenolphthalein endpoint with dilute alcoholic KOH.

Method

Accurately weigh 2 to 3 grams of the sample into a platinum dish. Carefully ignite over a Meker burner to a white ash. Dissolve the ash in approximately 100 ml. of distilled water (temperature 90-100°C.) and transfer to a 500-ml. Erlenmeyer flask. If difficultly oxidizable char is encountered, dissolve the ash as completely as possible in hot water, filter the solution, return the paper and char to the platinum dish, and again ignite. Dissolve the residue in a small volume of hot water and add to the filtrate already obtained.

Add several drops of phenolphthalein indicator solution and titrate to an approximate phenolphthalein endpoint with N/2 hydrochloric acid. Add an excess of about 5 ml. of the N/2 hydrochloric acid. Bring the solution to a boil to expel CO_2. Rinse down the walls of the flask with distilled water and titrate the contents of the flask with N/2 potassium hydroxide to an exact phenolphthalein endpoint. Cool the titrated solution under a stream of cold tap water.

Transfer the cooled solution to a 1000-ml. Erlenmeyer flask whose interior has previously been coated with paraffin. Use a commercial grade of white paraffin with melting point of 55-60°C. Add 20.0 grams of potassium chloride and exactly 40 ml. of N/2 hydrochloric acid from a burette. Add 5.0 grams of sodium fluoride and allow the mixture to stand for 10 to 15 minutes. Add a volume of cold neutral alcohol equal to the total volume of the solution already present in the flask. Allow to stand for an additional 5 minutes. Back titrate the excess N/2 hydrochloric acid with N/2 potassium hydroxide solution employing phenolphthalein indicator. The endpoint is taken when the color persists for one minute:

Calculation:

$$\%\ SiO_2 = \frac{(B - T) \times N \times F}{W}$$

B = ml. of N/2 KOH equivalent to 40 ml. of N/2 HCl.

T = ml. of KOH required for back titration.

N = Normality factor of N/2 KOH.

F = Equivalent weight of $SiO_2 \times 100$.

W = Weight of sample.

Results

A number of sprayed soaps were analyzed for their silica content by both the usual gravimetric method (3, 4) and the volumetric method described above. The results obtained are shown in Table I.

To determine the precision of the volumetric method several determinations were made on Sample

F (cf. Table I). The results obtained are shown in Table II.

TABLE I

Comparison of the Results Obtained in the Analysis of Soap for Silica Content by the Gravimetric and Volumetric Methods

Sample	% SiO_2	
	Gravimetric	Volumetric
A	4.80	4.76; 4.84
B	9.86	9.94
C	6.58	6.71
D	10.71	10.58
E	11.93	12.03
F	10.08	10.07
G	7.46	7.37
H	14.48	14.48

TABLE II

Volumetric Estimation of SiO_2 vs. Gravimetric Determination Using Sample F (Table I)

Determination No.	% SiO_2 Volumetric Method	% SiO_2 Gravimetric Method	Error
1	10.14	10.08	+0.06%
2	10.10	....	+0.02%
3	10.25	....	+0.17%
4	10.08	....	0.00%
5	10.12	....	+0.04%
6	10.07	....	−0.01%

Discussion

The values given in Table I indicate that the method gives results agreeing satisfactorily with those obtained by applying the more lengthy but exact gravimetric method. The utility of the volumetric method is due to the rapidity with which a determination may be run.

It has been found that if the paraffin is applied to the flask in a thin coating, it is quite adherent. Such coated flasks may be used for several determinations before the wax cracks away from the glass. A thin coating of wax is desirable, also, to enable better examination of the visual endpoint. It is unfortunate that owing to the nature of the reagents employed it is impractical to follow the course of this reaction electrometrically.

Acknowledgment

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Report of the American Representative on the Fat and Oil Commission of the International Union of Chemistry

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The following matters were considered by the commission and action taken as noted:

Samples. For large-size units, such as copra and olives, a minimum is 1 kilo; for all seeds except very small ones, 500 grams; for such as linseed, sesame, etc., 100 grams.

Moisture. For large samples the units are to be crushed but for very small seeds they may be used whole. A sample of 5 ± 0.5 gram weighed to 1 mg. is to be dried in a dish, preferably of aluminum, 7 cm. in diameter and 3-4 cm. high at 103 ± 2°. Weighing is done after 3 hours then reweighed to constant weight, or until deviations between 2 weighings are no more than 5 mg.

Fatty Matter. The extraction shall be with petroleum ether distilling at 40-60°C., having a bromine index below 1. Use of pentane or normal hexane is permissible. The sample shall be 10 ± 1 gram accurate to 1 mg. The proposal of the Dutch commission to dry for 45 minutes at 103-5° to inactivate enzymes was opposed by the British and French Commissions and set aside for further consideration. Wet seeds are to be dried at about 10% relative humidity. The first extraction is carried out with finely ground material for 4 hours, the second for 2 hours. The solvent is removed by distillation and final traces of solvent are removed by warming to 100° for not more than 20 minutes, at the same time passing a current of air.

Free Alkali in Soap. The barium chloride method was in general considered unsatisfactory. Absolute alcohol shall be used with a 10-gram sample in amount such that the water in the soap will not dilute it below 95%. Dissolved gas in the alcohol shall be eliminated by refluxing for 10 minutes. The alcohol shall be neutralized to phenolphthalein at 70° with 0.1 *N* alcoholic potassium hydroxide. Then dissolve the soap by refluxing and titrate at 70°C. with 0.1 *N* alcoholic sulfuric acid, up to 0.1% alkali or 0.2 *N* for high concentrations.

Free Alkali Carbonate. For small amounts determine the carbon dioxide. Alternatively, after titration of free alkali, add an amount of carbon-dioxide-free water equal to the volume of alcohol and titrate to bicarbonate with 0.1 *N* sulfuric acid. Where the precipitate in determination of free alkali is appreciable, filter and subject to mineral analysis.

Rosin in Soap. The method of Vizern and Guillot was adopted in preference to the MacNickol method.

The Halphen test was preferred to the Liebermann-Storch for detection of small amounts of rosin.

Soluble and Insoluble Volatile Acids. The Reichert-Meissl value and Polenske number are to be expressed as mg. of potassium hydroxide per gram of sample. Distillation is to take 19-21 minutes. Cooling for 15 minutes at 15° is retained.

Discussion of details of the digitonine method for sterols, thiocyamate index, and peroxide index or Lea index was indecisive.

It is proposed to publish the methods of the Commission in 1947 and to reconvene in Paris in July, 1948.