an increase in the apparent F.F.A., possibly due to the dissolving of the acid from the surface of the adsorbent. These conclusions apply to a dry oil. Where adsorption is conducted on a moist oil, an alkaline carbon gives appreciable reduction of F.F.A. and this is attributed to the presence of moisture promoting a reaction of the F.F.A. with the alkali (in a high pH carbon) to form soap, which is readily adsorbed by carbon.

Only one experiment was conducted on the influence of pH of the adsorbent on the Kreis test (4), and this indicates that carbons with a pH of 6.1 or higher have a beneficial effect on the Kreis test. This should be checked by further study.

Peroxide bodies present in an oil are adsorbed by active clays and carbons, and this work confirmed previous studies (5) that lowering the pH of an adsorbent results in increased removal of peroxide bodies. Although lowering the pH of an adsorbent produced an oil with a lower initial Peroxide Value, this is not necessarily reflected in greater stability. In fact, greater removal of initial peroxides is often associated with poorer stability—the Peroxide Value subsequently increasing at a more rapid rate. Whether this change is due to greater removal of stabilizing substances by adsorbents with a low pH or whether it is due to a chemical reaction occurring in the oil when in contact with low pH adsorbents is something we do not yet know.

The author wishes to express appreciation to Messrs. R. A. Hagberg, A. A. Aikey, and H. F. Laughlin of this laboratory for their cooperation in this work.

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Report of Soap Analysis Committee, AOCS; ASTM Committee D-12, 1944

DURING the current year the Soap Analysis Committee has been engaged in cooperative studies on two projects as follows:

1. Methods of analysis of special soaps containing synthetic detergents.
2. Two proposed methods for the determination of free caustic alkali and carbonate in potash paste soaps.

Notwithstanding the urgency of other matters and the shortage of manpower in most laboratories, we are pleased to report that 15 laboratories were able to cooperate in the program.

1. Methods of Analysis of Special Soaps Containing Synthetic Detergents

It should be explained that this study was initiated because of the large quantities of these soaps now being produced for the Army and Navy departments. Briefly, these products, in bar form, consist of homogeneous blends of one or more of the various synthetic detergents (usually sulfated types) with soap. Moisture contents of most of the brands being produced will fall in the range of 5 to 30%, active synthetic contents from 10 to 25%, anhydrous soap contents from 25 to 40%, the balance being largely inorganic salts including sodium sulfate, sodium chloride, sodium silicates and sodium carbonates. A small amount of unsaponifiable matter is sometimes present due to so-called unreacted oily material present in some of the synthetic detergents in common use.

At first glance it would appear that the analysis of such products would be readily approached on the same analytical basis as that of the ordinary soaps, but the presence of the active components of the synthetic detergents and the appreciable amounts of inorganic salts has made it necessary to modify the usual procedures considerably. Consequently, the committee is of the opinion that it is desirable to publish a rather complete set of modified analytical methods to cover these special types of soap.

The methods employed in these studies were based on the Army and Navy procedures included in the specifications for these types of soaps, incorporating such modifications suggested by the experience of the various cooperating laboratories as appeared to be advisable. Three samples of these special soaps, selected from commercial production of three companies manufacturing these products, were used in these studies by the 15 collaborating laboratories. The results of the collaborators on these three samples are shown in Tables I, II, and III. Considering that most laboratories participating in this work did not have much experience with some of these methods, it is considered that the results, for the most part, are in good agreement.

A meeting of the main committee was held in Chicago on October 24, 1944, for the purpose of reviewing and discussing the results of the cooperative work. It was the consensus that the data indicated, with some further slight modifications of the methods, a satisfactory analysis of these types of detergents can be obtained. Below is a summary of the action taken by the committee on the individual determinations.

Moisture. Two methods were used in the studies, the standard oven moisture at 105°C. and the standard distillation method. The committee voted to offer the oven method as the tentative standard because it gave more consistent results than those obtained by the distillation procedure. In the oven method the average deviation from the mean was 0.45% as against 0.89% for the distillation method.

Free Alkali or Free Acid. The standard procedure for ordinary soaps was used. Although the percentages shown in the tables are about equally divided, both acid and alkaline, the results are all considered close to the neutral point. It should be pointed out that, although the figures in column 2b. (free acid as oleic) appear to be high, the alkali equivalent of the free acid figures shown is only about one-seventh of these values. For example, in Table I the average for free acid as oleic is shown as 0.28%. On an alkali equivalent basis this figure calculates 0.04% which compares reasonably well with the corresponding free alkali average of 0.02%. The committee voted to adopt the standard procedure used for ordinary soaps in determining free alkali or free acid as a tentative method, with the qualification that the alcoholic solution should be heated to incipient boiling under an air cooled reflux condenser prior to titration, which should be carried out immediately.

Anhydrous Salt-Free Soda Soap. The method involves a direct determination of the fatty acid content combined as soap and corrects for any free fatty matter present in the sample. As would be expected in a determination of a relatively high component and involving a correction factor which in itself was not easily determined, the results were somewhat variable, showing 1.46% deviation from the mean. Notwithstanding this rather wide latitude of results, the committee voted to adopt the proposed method as tentative with certain refinements as follows:

a) Instead of separatory funnels use extraction cylinders or Stokes flasks, equipped with siphons.
b) To avoid emulsions, remove the bulk of fatty acids without shaking and the balance, with thorough shaking, using a total of six extractions.
c) After neutralizing to methyl orange end point with 0.5N H_2SO_4, use 5 ml. of 1:1 sulfuric acid as excess for acidulation instead of 5 ml. of 0.5N sulfuric acid. It is believed that the strength of the acid should be increased to effect complete acidulation of soap in the presence of the synthetics.
d) A note will be appended to the procedure permitting the addition of salt to inhibit emulsion difficulties.

Alcohol Soluble Matter. This is a very important determination and, while not usually reported in the final analysis, is necessary since it represents the sum of (1) anhydrous soda soap, (2) active synthetic, (3) sodium chloride, and (4) free fatty matter. Each of these constituents is determined separately, except the active synthetic which is obtained by difference. Results showed 0.69% deviation from the mean.

The committee recommended tentative adoption of this procedure as outlined with the requirement that a 2 g. sample be weighed directly instead of using an aliquot of a standard solution.

Matter Insoluble in Water. Procedure employed was the same as the standard method used for soap. The results were considered good, showing a deviation from the mean of 0.06%. The committee adopted the procedure outlined as tentative.

Total Alkalinity of Matter Insoluble in Alcohol. The procedure was the same as that employed for soap. Results were considered satisfactory, showing a deviation from the mean of 0.05%. This method likewise was adopted as tentative, with a recommendation to convert this value to sodium carbonate even though it may not be present as such. Although this value enters into the calculation of inorganic salts, the amount present is usually very small, and hence would have little, if any, effect on the magnitude of the final result of inorganic salts.

Sodium Silicate. The standard procedure for ordinary soaps was used. The results were good, showing an average deviation from the mean of 0.14%. This method was also adopted as a tentative standard.

Fatty Matter. Two methods were proposed, one involving four petroleum ether extractions of the alcohol-water solution of alcohol soluble matter, and the second, seven petroleum ether extractions of a similar alcohol-water solution of the anhydrous soap, that is, after removal of the synthetic detergent. Results between laboratories showed 0.24 and 0.32% average deviation from the mean for the two methods respectively. Method II gave somewhat higher results than Method I.

The committee voted the adoption of Method I, which involves the extraction of the alcohol-water solution of the alcohol soluble content, as a tentative procedure with the following modifications:

a) Instead of separatory funnels, use extraction cylinders or Stokes flasks, equipped with siphons.
b) Extract seven times (instead of four times used in the cooperative study) with 50 ml. portions of petroleum ether at a maximum temperature of 25°C.
c) A note will be included to permit the use of 10 g. of anhydrous sodium sulphate to prevent emulsion difficulties.

Chloride in Alcohol Soluble Matter. Two methods were studied, namely (1) Volhard, and (2) Mohr titration methods. The former showed 0.25% and the latter 0.09% deviation from the mean. Both methods require some further revision of technique, but in general gave concordant results. Notwithstanding the expression of some laboratories favoring the Volhard method, the committee recommended the adoption of the Mohr method tentatively with a provision specifying the volume of indicator to be used and the determination of a suitable blank.

Rosin. The standard McNicoll method was used. The results showed an average deviation from the mean of 0.28%. This method was adopted as tentative.

Active Synthetic. This component is determined by difference, that is, total alcohol soluble, less the sum of anhydrous soap, sodium chloride and free fatty matter. Since its accuracy depends upon the accuracy of each of these latter determinations, it was anticipated that the results would not be too consistent. Average deviation from the mean for the three samples was 1.49%. It was the opinion of the committee, as the experience and technique of the operators are improved and the suggested modifications to the other individual methods involved are put into effect, that the results will become less variable. On this premise, the committee voted the adoption of the method as tentative.

Calculation of Neutral Inorganic Salts. Here again the value is obtained by difference, that is, 100% minus the sum of moisture, alcohol soluble, water insoluble and alkaline salts. In this calculation, the sodium chloride which is present in the alcohol soluble must be added back to the difference obtained as just outlined since the alcohol soluble matter contains substantially all of the sodium chloride content. As with the determination of active synthetic, the results of all laboratories reporting varied appreciably. The average deviation from the mean on the three samples was 1.04%. This procedure was voted also as tentative by the committee.

TABLE I

1944 AOCS-ASTM Cooperative Studies—Soap Containing Synthetic Detergents—Sample No. 44-1 (Synthetic detergent = 2/3 Nacconol HG and 1/3 duPont Paste MP 189 SX)

	1. Moisture		2a. Free Alkali as NaOH	2b. Free Acid as Oleic	3. Anhyd. Salt Free Soda Soap	4. Alcohol Sol. Matter	5. Mat. Ins. in Water	6. Total Alk. of Mat. Ins. in Alcohol	7. Sodium Silicate	8. Fatty Matter		9. Chloride in Alcohol Sol. Matter		10. Rosin	11. Syn. Det. (By Diff.)	12. Cal. of Neutral Inorganic Salts
	Method A (Oven)	Method B (Distillation)								Method I	Method II	Method I	Method II			
			Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O
	Pct.	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
Lab. No. 1	24.82	24.00	0.02	......	29.09	57.36	0.20	0.39	0.33*	1.25	2.13	2.40	3.50	0	23.52	20.55
Lab. No. 2	25.29	25.31	......	0.60	31.43	58.24	0.11	0.16	0.05	0.89	1.12	2.97	3.23	0.19	22.66	19.61
Lab. No. 3	....	23.6	......	0.29	26.73	57.17	0.10	0.32	......	0.78	......	3.49	......	......	26.18	20.89
Lab. No. 4	26.04	25.50	0.01	......	34.12	55.27*	0.22	0.21	0.16	2.56*	3.26*	2.93	3.16	0	15.66*	22.10
Lab. No. 5	....	27.04	......	0.06	32.29	58.50	0.10	0.17	......	0.54	......	1.96	......	......	23.72	18.19
Lab. No. 6	25.77	26.34	......	0.24	30.48	56.21	0.22	0.14	0.03	2.58*	3.94*	2.96	4.20*	0	20.09	23.02
Lab. No. 7	25.90	26.30	0.03	......	31.73	57.12	TR*	0.33	0.20	0.86	0.88	2.27	3.23	1.00	21.29	20.78
Lab. No. 8	25.72	25.51	......	0.20	31.68	58.55	0.05	0.16	0	1.65	1.43	1.90	3.40	......	23.29	18.21
Lab. No. 9	26.09	25.95	0.02	......	30.3	58.0	0.09	0.26	0.01	0.70	1.08	3.19	3.24	0	23.7	20.0
Lab. No. 10																
Analyst No. 1	24.40	22.0	0.01	......	30.33	57.52	0.05	0.19	0.07	0.77	0.93	......	3.47	0.27	22.87	20.71
Analyst No. 2	25.59	25.50	0.01	......	31.75	57.51	0.11	0.26	0.08	0.59	1.07	2.86	3.22	0	22.05	20.15
Analyst No. 3	25.75	25.92	0.02	......	30.55	57.18	0.05	0.21	0.04	0.93	0.83	3.16	3.27	0.57	22.43	20.78
Analyst No. 4	25.50	....	0.01	......	31.52	57.06	0.07	....	......	0.96	1.52	......	3.49	......	21.09	....
Analyst No. 5	25.40	....	0.02	......	31.87	57.84	......	....	......	......	......	......	3.48	......	20.67	....
Lab. No. 11	25.6	....	......	0.36	28.6	58.4	0.1	0.3	0.02	0.88	1.1	3.0	3.4	......	25.5	19.4
Lab. No. 12	25.53	23.54	0.02	......	26.29	55.49*	0.11	0.11	0.03	0.56	1.16	3.15	3.26	0	25.78	22.43
					25.70										25.24	22.29
Lab. No. 13	24.95	24.65	0.01	......	31.99	55.02*	0.15	0.27	0.09	0.62	0.38	2.71	3.30	......	19.52	22.57
Lab. No. 14	25.31	25.75	......	0.43	31.91	59.03	0.07	0.24	0.04	0.66	0.98	2.81	3.05	0.17	23.09	18.52
Lab. No. 15	24.36	23.45	......	0.06	29.38	59.10	0.20	0.24	0.02	0.77	1.29	1.42	3.41	......	25.43	19.08
High	26.09	27.04	0.03	0.60	34.12	59.10	0.22	0.39	0.20	1.65	2.13	3.49	3.50	1.00	26.18	23.02
Low	24.36	22.00	0.01	0.06	25.70	56.21	0.05	0.11	0	0.54	0.38	1.42	3.05	0	19.52	18.19
Average	25.41	25.02	0.02	0.28	30.39	57.75	0.12	0.23	0.06	0.84	1.14	2.70	3.32	0.20	23.06	20.52
% Deviation from mean†	0.40	1.11	0.005	0.14	1.67	0.66	0.05	0.06	0.04	0.19	0.26	0.44	0.12	0.22	1.56	1.22

* Not included in average.

† Deviation from the mean represents the sum of the variance of individual values from the arithmetical average, divided by the number of values included in the average.

TABLE II

1944 AOCS-ASTM Cooperative Studies—Soap Containing Synthetic Detergents—Sample No. 44-2 (Synthetic detergent = 100% Nacconol HG)

	1. Moisture		2a. Free Alkali as NaOH	2b. Free Acid as Oleic	3. Anhyd. Salt Free Soda Soap	4. Alcohol Sol. Matter	5. Mat. Ins. in Water	6. Total Alk. of Mat. Ins. in Alcohol	7. Sodium Silicate	8. Fatty Matter		9. Chloride in Alcohol Sol. Matter		10. Rosin	11. Syn. Det. (By Diff.)	12. Cal. of Neutral Inorganic Salts
	Method A (Oven)	Method B (Distillation)								Method I	Method II	Method I	Method II			
			Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O
	Pct.	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
Lab. No. 1	4.83	5.20	0.03	......	38.84	60.95	0.61	0.31	0.31	1.05	0.96	0.35	0.75	0.92	20.31	13.88
Lab. No. 2	5.07	4.99	0.01	......	39.92	60.98	0.68	0.23	0.61	0.71	0.84	0.42	0.57	0.62	19.78	13.62
Lab. No. 3	......	5.7	......	0.16	27.24*	61.29	0.50	0.27	......	0.65	......	0.75	......	......	32.65*	13.69
Lab. No. 4	4.21	4.11	0.02	......	42.90	59.47	0.61	0.21	1.33	1.73	6.69*	0.41	0.74	1.62	14.43*	15.12
Lab. No. 5	......	4.21	......	0.04	40.81	60.32	0.55	0.17	......	0.62	......	0.26	......	......	18.65	14.22
Lab. No. 6	5.53	5.76	......	0.04	39.78	59.54	0.39	0.20	0.98	2.42*	1.87	0.57	0.56	1.29	16.79	15.44
Lab. No. 7	5.16	5.29	0.04	......	41.03	60.31	0.38	0.28	0.37	0.62	0.78	0.55	0.53	0.84	18.04	14.57
Lab. No. 8	5.44	5.63	0.01	......	40.28	61.31	0.58	0.02*	0.94	0.62	0.70	0.34	0.61	......	19.97	13.43
Lab. No. 9	3.91	5.49	0.01	......	39.7	57.4	0.45	0.24	0.78	0.55	0.59	0.47	0.51	1.34	16.7	17.9
Lab. No. 10	2.61*	4.0	0.02	......	36.34	60.79	0.49	0.18	0.19	0.70	1.02	......	2.85*	0.76	20.74	16.39
Lab. No. 11	3.7	......	......	0.21	35.4	61.7	0.5	0.4	1.0	0.68	0.94	0.5	0.6	......	24.9	13.1
Lab. No. 12	5.27	5.64	0.02	......	39.88	61.04	0.52	0.14	0.71	0.31	0.85	0.65	0.49	1.04	20.25	13.03
					39.34										20.33	13.59
Lab. No. 13	4.40	4.20	......	......	38.71	60.74	0.47	0.18	0.84	0.47	0.38	0.39	0.66	......	21.07	14.14
Lab. No. 14	5.20	5.13	0.03	......	41.23	61.33	0.43	0.26	0.82	0.50	1.18	0.47	0.45	0.73	18.47	12.76
Lab. No. 15	4.27	4.85	0.06	......	39.87	61.48	0.60	0.26	0.16	0.85	1.03	0.50	0.62	......	20.23	13.33
High	5.53	5.76	0.06	0.21	42.90	61.7	0.68	0.4	1.33	1.73	1.87	0.75	0.75	1.62	24.9	17.9
Low	3.7	4.0	0.01	0.04	35.4	57.4	0.38	0.14	0.16	0.31	0.38	0.34	0.45	0.62	16.7	12.76
Average	4.75	5.01	0.03	0.12	39.60	60.57	0.52	0.24	0.70	0.72	0.93	0.47	0.60	1.02	19.73	14.26
% Deviation from mean	0.54	0.54	0.013	0.07	1.25	0.78	0.07	0.05	0.28	0.21	0.24	0.09	0.07	0.27	1.44	1.01

* Not included in average.

TABLE III

1944 AOCS-ASTM Cooperative Studies—Soap Containing Synthetic Detergents—Sample No. 44-3 (Synthetic detergent = 50% Nacconol HG and 50% Detergent No. 92 Paste)

	1. Moisture		2a. Free Alkali as NaOH	2b. Free Acid as Oleic	3. Anhyd. Salt Free Soda Soap	4. Alcohol Sol. Matter	5. Mat. Ins. in Water	6. Total Alk. of Mat. Ins. in Alcohol	7. Sodium Silicate	8. Fatty Matter		9. Chloride in Alcohol Sol. Matter		10. Rosin	11. Syn. Det. (By Diff.)	12. Cal. of Neutral Inorganic Salts
	Method A (Oven)	Method B (Distillation)								Method I	Method II	Method I	Method II			
			Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O	Calc. to 25% H_2O
	Pct.	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
Lab. No. 1	23.44	23.00	0.02	......	32.75	59.17	0.12	0.24	0.23	1.93	2.27	1.91	2.56	3.04	22.08	18.03
Lab. No. 2	24.36	24.26	0.01	......	33.35	58.51	0.07	0.09	0.01	1.51	2.04	2.23	2.42	2.17	21.07	17.69
Lab. No. 3	....	22.9	......	0.22	27.16*	57.57	0.04	0.23	......	1.19	......	2.35	......	......	26.87*	19.53
Lab. No. 4	23.41	21.13	0.01	......	34.94	57.86	0.12	0.15	0.06	3.16*	4.53*	2.07	2.40	2.20	17.69*	19.92
Lab. No. 5	....	24.86	......	0.11	35.00	59.57	0	0.16	......	0.92	......	1.93	......	......	21.71	17.20
Lab. No. 6	24.30	25.02	......	0.07	34.43	56.10*	0.10	0.05	0.02	3.80*	5.95*	2.54	2.30	2.31	15.44*	21.16
Lab. No. 7	23.67	23.70	......	0.07	34.77	58.40	0.01	0.17	0.13	1.03	1.72	1.60	2.41	2.18	19.84	18.83
Lab. No. 8	24.36	....	......	0.14	35.96	59.91	0	0.13	0	1.30	2.05	1.87	2.60	......	20.03	16.82
Lab. No. 9	24.66	23.95	......	0.12	34.6	59.4	0.05	0.16	0.01	0.87	1.12	2.36	2.36	2.48	21.5	17.8
Lab. No. 10	23.43	22.5	......	0.07	30.91	59.10	0	0.12	0.10	1.20	0.94	......	2.56	3.40	24.55	18.34
Lab. No. 11	24.1	....	......	0.29	30.4	60.1	0	0.2	0.4	1.3	1.3	2.4	2.5	......	25.9	17.2
Lab. No. 12	24.17	22.47	0.01	......	34.53	58.34	0.09	0.05	0	0.64	2.19	2.37	2.35	7.02*	20.56	18.95
					32.99										21.05	18.76
Lab. No. 13	23.60	23.40	......	......	34.26	58.51	0.15	0.12	......	0.64	0.67	2.23	2.52	......	21.24	18.48
Lab. No. 14	24.30	24.50	0.02	......	36.20	59.58	0.05	0.17	0.03	0.39	2.05	2.18	2.28	2.60	19.05	17.35
Lab. No. 15	23.35	21.25	......	0.03	31.24	59.27	0.22	0.21	0.03	1.52	1.64	1.94	2.56	......	23.95	17.91
High	24.66	25.02	0.02	0.29	36.20	60.1	0.22	0.24	0.4	1.93	2.27	2.54	2.60	3.40	25.9	21.16
Low	23.35	21.13	0.01	0.03	30.4	57.57	0	0.05	0	0.39	0.67	1.60	2.28	2.17	19.05	16.82
Average	23.94	23.30	0.01	0.14	33.76	58.95	0.07	0.15	0.09	1.11	1.63	2.14	2.45	2.55	21.73	18.37
% Deviation from mean	0.42	1.01	0.004	0.07	1.45	0.64	0.05	0.05	0.09	0.33	0.46	0.22	0.09	0.35	1.46	0.88

* Not included in average.

TABLE IV

Determination of Free Alkali and Potassium Carbonate in Potash Paste Soaps

	Method I KOH (a)	Method I KOH (b)	Method I KOH (c)
	Pct.	*Pct.*	*Pct.*
% KOH added	0.30	0.50	0.10
% KOH found			
Lab. No. 1			
Lab. No. 2	0.45	0.84	0.08
	0.45	0.76	0.08
Lab. No. 4			
Lab. No. 6	0.29	0.56	0.07
	0.29	0.77	0.08
		0.68	
Lab. No. 7	0.77	2.54	0.12
Lab. No. 9	0.65[1]	2.30[1]	0.10
Lab. No. 10	0.60	2.44	0.09
	0.56	2.40	0.09
Lab. No. 12			
Lab. No. 13	0.69	2.50	0.13
High	0.77	2.54	0.13
Low	0.29	0.56	0.07
Average	0.53	1.58	0.09
% Deviation from mean	0.14	0.86	0.014

	Method I K_2CO_3 (a)	Method I K_2CO_3 (b)	Method I K_2CO_3 (c)
	Pct.	*Pct.*	*Pct.*
% K_2CO_3 added	1.30	5.20	0.10
% K_2CO_3 found			
Lab. No. 1			
Lab. No. 2	1.05	4.73	0.11
	1.01	5.65	0.14
Lab. No. 4			
Lab. No. 6	1.29	5.25	0.13
Lab. No. 7	1.05	3.05	0.53
Lab. No. 9	*	*	0.63
Lab. No. 10	0.84	2.52	0.04
	0.79	2.72	0.00
Lab. No. 12			
Lab. No. 13	1.6	3.2	0.75
High	1.6	5.65	0.75
Low	0.79	2.52	0.00
Average	1.09	3.87	0.29
% Deviation from mean	0.20	1.14	0.26

	Method II KOH (a)	Method II KOH (b)	Method II KOH (c)
	Pct.	*Pct.*	*Pct.*
% KOH added	0.30	0.50	0.10
% KOH found			
Lab. No. 1	0.34	0.53	0.14
Lab. No. 2	0.44	0.51	0.11
	0.34	0.52	0.11
			0.10
Lab. No. 4	0.33	0.70	0.15
Lab. No. 6			
Lab. No. 7	0.28	0.39	0.00
Lab. No. 9			
Lab. No. 10			
Lab. No. 12	0.35	0.49	0.11
Lab. No. 13			
High	0.44	0.70	0.15
Low	0.28	0.39	0.00
Average	0.35	0.52	0.10
% Deviation from mean	0.03	0.06	0.03

	Method II K_2CO_3 (a)	Method II K_2CO_3 (b)	Method II K_2CO_3 (c)
	Pct.	*Pct.*	*Pct.*
% K_2CO_3 added	1.30	5.20	0.10
% K_2CO_3 found			
Lab. No. 1	1.32	5.28	0.13
Lab. No. 2	1.32	5.15	0.08
	......	......	......
Lab. No. 4	1.24	5.29	0.09
Lab. No. 6			
Lab. No. 7	1.47	5.50	0.31
Lab. No. 9			
Lab. No. 10			
Lab. No. 12	1.23	5.15	0.09
Lab. No. 13	1.27	5.10	0.10
High	1.47	5.50	0.31
Low	1.23	5.10	0.08
Average	1.31	5.24	0.13
% Deviation from mean	0.06	0.11	0.06

[1] Results—high probably because of hydrolysis of soap when titrated to phenolphthalein end point with aqueous HCl.

* K_2CO_3 could not be determined because of previous hydrolysis which had taken place and excess acid required to titrate to phenolphthalein end point.

2. Determination of Free Caustic Alkali and Potassium Carbonate in Potash Paste Soaps

Under the heading of Project No. 2, that is, determination of free KOH and K_2CO_3 in potash paste soaps, it is believed that this year's studies have indicated substantial progress. Two methods were studied, one of which was considered entirely unsatisfactory and hence the detailed procedure will not be included in this report. The second method, while perhaps needing some refinements, has shown unusually good comparisons between reporting laboratories. Results obtained by the various collaborators are shown in Table IV.

The procedure followed was briefly as follows:

> A sample of potash paste soap, approximately 50% anhydrous soap content was distributed to the committee, with instructions to prepare aqueous solutions of the soap and to add to each of six such samples—(three for the total alkalinity and three for the CO_2 determinations)—varying amounts of KOH and K_2CO_3 solutions of known compositions to give exactly 0.3%, 0.5%, and 0.1% free KOH and 1.30%, 5.20%, and 0.10% of K_2CO_3 respectively, all percentages noted being based on the original sample. All of these amounts were in addition to the free KOH and free K_2CO_3 present in the original soap. The analyses were then made on these prepared solutions as well as on a similar aqueous solution of the original soap to which none of the alkalies had been added. After correcting for this blank, the values obtained could thus be compared with the known amounts added as a check on the accuracy of the proposed method.

Briefly, the proposed method may be outlined as follows:

> An aqueous solution of the samples prepared as just described is titrated to methyl orange neutrality with standard acid, and a small amount of standard acid is added in excess. This acid neutralizes the total alkalinity due to soap plus free KOH and free K_2CO_3. The titration is then reversed with standard alkali and the solution brought to a phenolphthalein neutrality which means, of course, that the solution is definitely on the acid side of the true neutral point since the titration is conducted in an aqueous medium. At this stage the solution is evaporated almost to dryness, taken up in absolute alcohol and titrated to phenolphthalein neutrality. The difference in standard acid and standard alkalies used thus represents the alkalinity due to the sum of free KOH and K_2CO_3. The K_2CO_3 may then be determined by suitable means such as the standard Evolution-Volumetric or Train absorption methods and the free KOH determined by difference.

Included as part of this report is the new proposed procedure for the determination of KOH and K_2CO_3 in potash paste soaps, which was adopted as tentative.

Summary. As a result of the current year's studies, the committee has recommended the tentative adoption of 1. a complete set of methods for soaps containing synthetic detergents, and 2. a new procedure for the determination of free KOH and K_2CO_3 in potash paste soaps. The revised tentative methods are included as part of this report.

METHODS OF ANALYSIS FOR SOAPS CONTAINING SYNTHETIC DETERGENTS (TENTATIVE)

1. Moisture-Matter Volatile at 105°C. (oven method)

Apparatus

A porcelain or glass dish about 6 to 8 cm. in diameter and about 2 to 4 cm. in depth.

Procedure

Weigh 5 g. (±0.01 g.) of the sample in the dish and dry to constant weight in an air oven at a temperature of 105°C. (±2°C.). Constant weight is attained when successive heating for one hour periods shows a loss (or gain) of not more than 0.1 per cent.

2. Free Alkali or Free Acid

Reagents

Ethyl Alcohol (95%)—Freshly boiled ethyl alcohol, 95 per cent or higher and neutral to phenolphthalein; either Formula No. 3-A or No. 30 of the U. S. Internal Revenue Bureau.

Phenolphthalein Indicator—1% solution in neutral, redistilled alcohol.

Procedure

Digest 5 to 10 g. (±0.01 g.) of the sample in 200 ml. of freshly boiled neutral alcohol in a 300 ml. Erlenmeyer flask, equipped with an air-cooled reflux condenser, on a steam bath until the soap is dissolved. Remove the condenser, add 0.5 ml. of the phenolphthalein indicator, titrate immediately with standard acid or alkali solution, and calculate to NaOH if alkaline or to oleic acid, if acid.

3. Anhydrous Salt-free Soda Soap

Apparatus

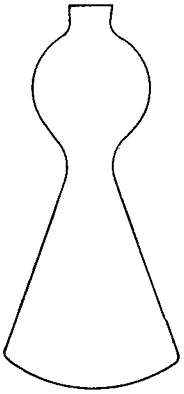

FIG. 1

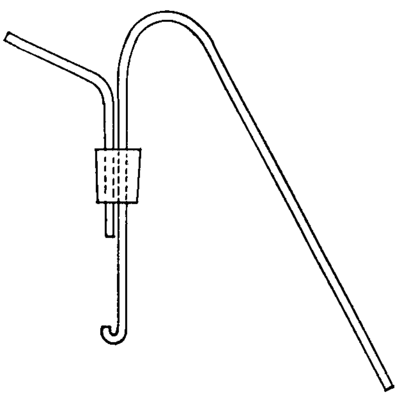

FIG. 2

Extraction Cylinder—The extraction cylinder shall be a 250-ml. graduated glass-stoppered cylinder about 39 mm. (1½ in.) in diameter and about 35.5 cm. (14 in.) in length, or

Stokes Flask—The Stokes flask shall be a 100-ml. round bottom flask (bottom of which is blown out) sealed onto a 150-ml. Erlenmeyer flask. A diagram of the Stokes flask is illustrated in Figure 1.

Siphons—The siphons shall consist of a two-hole rubber stopper fitted with slender glass tubing, as shown in Figure 2.

Reagents

a) *Ethyl Alcohol (95 per cent).* Freshly boiled ethyl alcohol, 95% or higher and neutral to phenolphthalein; either formula No. 3-A or No. 30 of the U. S. Internal Revenue Bureau.
b) *Methyl Orange Indicator* 0.1 per cent solution in distilled water.
c) *Sulphuric Acid (0.5N)* H_2SO_4.
d) *Sulphuric Acid (1:1)*—Slowly add 1 part of H_2SO_4 (sp.gr. 1.84) to 1 part of distilled water.
e) *Sodium Hydroxide Solution* (0.1N) NaOH.
f) *Phenolphthalein Indicator*—1% solution in neutral, redistilled alcohol.
g) *CP Sodium Chloride* anhydrous NaCl.
h) *CP Sodium Sulphate* anhydrous Na_2SO_4.
i) *Petroleum Ether* — For specifications see Chemical Analysis of Soaps in ASTM (D460-42) or AOCS LEFAX.

Procedure

Weigh 2 g. (±0.001 g.) of the sample into a tared 250-ml. beaker. Add 25 ml. of water and 25 ml. of 95 per cent neutral alcohol, and warm on the steam bath until solution is complete. Cool, add 5 drops of methyl orange indicator, and titrate with 0.5N sulphuric acid to a pink color. Add. 5 ml. of 1:1 sulphuric acid in excess. Transfer the contents of the beaker to a 250-ml. extraction cylinder or a Stokes flask, equipped with siphons. Wash the beaker alternately with equal parts of hot distilled water and hot 95% alcohol, adding washings to the extraction cylinder or Stokes flask, the total volume for extraction not to exceed 160 ml. in the extraction cylinder or the constricted portion of the Stokes flask. Wash the beaker with a small amount of petroleum ether to remove any traces of fatty acids and fatty matter and add to the extraction cylinder or Stokes flask. Add 50 ml. of petroleum ether and allow to stand for ½ hour without shaking. Remove the bulk of the fatty acids by drawing off the petroleum ether layer as closely as possible, by means of a slender glass siphon, into a separatory funnel of 500-ml. capacity. Repeat the extractions five more times with petroleum ether, using 50-ml. portions, shaking the cylinder thoroughly each time.[1] Combine the petroleum ether extracts and wash with small portions of distilled water until the water washings are no longer acid to methyl orange indicator. Dry the combined, washed, petroleum ether extracts with anhydrous sodium sulphate, and filter through paper into the original tared 250-ml. beaker. Wash the separatory funnel with two small portions of petroleum ether, filtering and adding washings to the beaker. Evaporate the petroleum ether on the steam bath until the odor of petroleum ether is no longer perceptible. Then place beaker in an oven at 100° to 105°C. (212° to 221°F.) for five minutes to insure complete removal of the solvent. Cool and weigh as fatty acids plus fatty matter. Dissolve the fatty acids and fatty matter in 50 ml. of neutral alcohol with warming; add phenolphthalein indicator and titrate with 0.1N NaOH to pink end point. (A blank test should be made on the NaOH solution for neutral salts and the proper corrections made if necessary.)

Calculation of results

$$\frac{(\text{ml. NaOH} \times \text{N NaOH} \times 0.022) + (\text{Weight of extract})}{\text{Weight of Sample}} \times 100 = \text{per cent soap plus fatty matter.}$$

Per cent anhydrous salt-free soda soap = per cent soda soap plus fatty matter (as determined above under paragraph 3) minus per cent fatty matter (as determined under paragraph 8).

4. Alcohol Soluble Matter

Reagents

a) *Ethyl Alcohol (absolute)*—Freshly boiled, 200 proof ethyl alcohol, and neutral to phenolphthalein; either Formula No. 3-A or No. 30 of the U. S. Internal Revenue Bureau.

b) *Ethyl Alcohol (95%)*—Freshly boiled, ethyl alcohol, 95 per cent or higher and neutral to phenolphthalein; either Formula No. 3-A or No. 30 of the U. S. Internal Revenue Bureau.

Procedure

Weigh 2 g. (±0.001 g.) of the sample into a 250-ml. beaker, add 100 ml. of 95 per cent ethyl alcohol, cover the beaker, and heat on the steam bath with frequent stirring and maceration of the sample until completely disintegrated. Let settle and filter the supernatant liquid through a tared Gooch crucible with suction into a tared 300-ml. Erlenmeyer flask, retaining as much of the residue as possible in the beaker. Repeat this extraction three times with 25-ml. portions of hot 95% ethyl alcohol, each time retaining as much of the residue as possible in the beaker. Finally, evaporate any remaining alcohol, and dissolve the residue in the smallest possible quantity of hot, distilled water (5 ml. is sufficient). Reprecipitate the alcohol insoluble matter by slowly adding, with vigorous stirring, 50 ml. of absolute ethyl alcohol. (Note: Solution and reprecipitation of alcohol insoluble matter is necessary for complete separation from alcohol-soluble matter.) Heat the solution to boiling on the steam bath, filter, and transfer the precipitate quantitatively to the Gooch crucible, washing several times with 95 per cent ethyl alcohol. Evaporate the combined filtrate and washings in the Erlenmeyer flask on the steam bath and then dry to constant weight at 105°C.(±2°C.). Calculate total alcohol soluble matter. Reserve the flask and contents for the determination of free fatty matter. The Gooch crucible and contents are reserved without drying for the determination of matter insoluble in water and *total alkalinity of matter insoluble in alcohol* (alkaline salts).

5. Matter Insoluble in Water

Wash the alcohol insoluble matter retained in the Gooch crucible (paragraph 4) thoroughly with hot distilled water until the washings are no longer alkaline to phenolphthalein. Reserve the filtrate for determination of *alkalinity of matter insoluble in alcohol* (paragraph 6). Dry the crucible and residue to constant weight at 105°C. (±2°C.) and calculate the per cent matter insoluble in water.

6. Total Alkalinity of Matter Insoluble in Alcohol (Alkaline Salts)

Reagents

a) *Methyl Orange Indicator* 0.1% solution in distilled water.

Procedure

Titrate the water solution obtained under matter insoluble in water (paragraph 5) with standard acid, using methyl orange indicator. Calculate the alkalinity to sodium carbonate (Na_2CO_3).

7. Sodium Silicate

The method described in Procedure 42 of ASTM Chemical Analysis of Soaps (D460-42) or in paragraph X of AOCS Methods for Sampling and Analysis of Commercial Soaps shall be used for the determination of sodium silicate.

8. Fatty Matter

Apparatus

Extraction Cylinder—Stokes Flask and Siphons. For description refer to paragraph 3, "Anhydrous Salt-Free Soda Soap."

Reagents

a) *Ethyl Alcohol (95 per cent)*—Freshly boiled ethyl alcohol, 95% or higher and neutral to phenolphthalein; either Formula No. 3-A or No. 30 of the U. S. Internal Revenue Bureau.

b) *Petroleum Ether* — For specifications see Chemical Analysis of Soaps in ASTM (D460-42) or AOCS LEFAX.

c) *Sodium Hydroxide* 0.2N NaOH.

d) *Phenolphthalein Indicator* 1% solution in neutral, redistilled alcohol.

e) *CP Sodium Sulphate,* anhydrous Na_2SO_4.

Procedure

Dissolve the alcohol soluble matter obtained in paragraph 4 in a mixture of 25 ml. of water and 25 ml. of ethyl alcohol, warming if necessary. Transfer the solution to a 250-ml. extraction cylinder or a Stokes flask equipped with siphons. Wash the Erlenmeyer flask alternately with equal parts of hot distilled water and hot 95% alcohol, adding washings to the extraction cylinder or Stokes flask, the total volume for extraction not to exceed 160 ml. in the extraction cylinder or the constricted portion of the Stokes flask. Wash the Erlenmeyer flask with a small amount of petroleum ether to remove any traces of fatty matter and add to the extraction cylinder or Stokes flask. Cool the cylinder or flask under tap water to a temperature not to exceed 25°C. Add 50 ml. of petroleum ether and shake. Draw off petroleum ether layer as closely as possible, by means of a slender glass siphon, into a separatory funnel of 500-ml. capacity. Repeat the extractions six more times with petroleum ether, using 50 ml. portions, shaking the cylinder thoroughly each time.[1] Combine the petroleum ether extracts and wash four times with 10 ml. portions of 0.2N NaOH, adding the washings to the alcoholic solution which is reserved for the determination of chlorides in paragraph 9. Finally, wash the petroleum ether extract with small portions of water until the water

---

[1] Emulsions which may appear at this point may be broken by the addition of 10 g. of salt.

[1] Ten g. of anhydrous sodium sulfate may be added to break emulsion which may appear at this point.

washings are no longer alkaline to phenolphthalein. Transfer the washed petroleum ether extract to a tared 300-ml. Erlenmeyer flask, washing the separatory funnel with two small portions of petroleum ether. Evaporate the petroleum ether on the steam bath, and dry the residue in an oven at 100° to 105° C. (212° to 221° F.) to constant weight. Calculate the per cent fatty matter.

9. Chlorides in Alcohol Soluble Matter

Reagents

a) *Silver Nitrate Solution* 0.1N $AgNO_3$.
b) *Magnesium Nitrate Solution (20 per cent)*—Dissolve 200 g. of chloride-free magnesium nitrate $Mg(NO_3)_2 6H_2O$ in 1 liter of distilled water.
c) *Potassium Chromate Indicator*—Dissolve 5 g. of chloride-free potassium chromate K_2CrO_4 in distilled water and add solution of 0.1N silver nitrate until a slight red precipitate is produced, filter the solution, and dilute the filtrate to 100 ml.
d) *Calcium Carbonate* C. P. Chloride free $CaCO_3$.

Procedure

Treat the alcoholic solution remaining after the determination of fatty matter (paragraph 8) with 15 ml. of 20 per cent magnesium nitrate solution, heat on the steam bath until the precipitate is coagulated, filter, and wash with distilled water into a 500-ml. beaker. Add 1 ml. of potassium chromate indicator for every 100 ml. of solution. Titrate the solution containing the sample, with standard silver nitrate solution, until the red color formed by each drop begins to disappear more slowly upon stirring, showing that most of the chloride has been precipitated.

Prepare a blank by adding to another 500-ml. beaker the same volume of distilled water, magnesium nitrate solution, and potassium chromate indicator present in the beaker containing the sample. Add enough $CaCO_3$ to the blank so that the turbidity in both solutions appears to be the same when they are swirled. Using this for comparison, continue the titration of the solution containing the sample until a faint but distinct change of color occurs. At the end point the color should not be dark, just distinctly different (reddish-yellow) from that of the blank containing no silver chromate. Add to the blank enough standard silver nitrate solution so that the colors of the two solutions exactly match. This is the "blank" titration required to produce the end point and should be deducted from the standard silver nitrate solution used in the titration. One milliliter of the 0.1N silver nitrate solution ($AgNO_3$) is equivalent to 0.00585 g. of sodium chloride (NaCl).

10. Rosin

Prepare fatty acids for the rosin determination as per the extraction in paragraph 3 above under Anhydrous Salt-Free Soda Soap. Then the method described in paragraphs 29, 30, 31b of ASTM Chemical Analysis of Soaps (D460-42) or in paragraph VI of AOCS Methods for Sampling and Analysis of Commercial Soaps shall be used for the determination of rosin.

11. Synthetic Detergent (by difference)

Calculate the per cent anhydrous, salt-free, synthetic detergent as follows:

Per cent synthetic detergent = per cent alcohol soluble matter—(per cent soda soap + per cent fatty matter + per cent sodium chloride in alcohol soluble matter).

12. Calculation of Neutral, Inorganic Salts

Neutral, Inorganic Salts = [100% + % Sodium Chloride] —[% Moisture + % alcohol soluble + % matter insoluble in water + % total alkalinity of matter insoluble in alcohol (alkaline salts)].

METHODS FOR THE DETERMINATION OF FREE ALKALI AND POTASSIUM CARBONATE IN POTASH PASTE SOAPS (TENTATIVE)

Reagents

a) *Ethyl Alcohol (absolute)*—Freshly boiled 200 proof ethyl alcohol, and neutral to phenolphthalein; either Formula No. 3-A or No. 30 of the U. S. Internal Revenue Bureau.
b) *Phenolphthalein Indicator*—1% solution in neutral, redistilled alcohol.
c) *Methyl Orange Indicator*—0.1% solution in distilled water.
d) *Sulphuric Acid* N/2 H_2SO_4.
e) *Sodium Hydroxide* N/2 NaOH.

Procedure

1. Weigh 10 g. (±0.01 g.) of the sample into a 250-ml. beaker and dissolve in 100 ml. of freshly boiled distilled water.
2. Add a measured mount of N/2 H_2SO_4 sufficient to acidulate the solution to methyl orange indicator and bring to incipient boiling until fatty acids separate out in a clear layer. Excessive boiling should be avoided to preclude the possibility of volatilization of any low molecular weight fatty acids which may be present.
3. Add 0.5 ml. of phenolphthalein indicator, and while stirring the contents of the beaker, titrate with N/2 NaOH until solution is almost neutral but still slightly on the acid side to phenolphthalein.
4. Evaporate to dryness on a steam bath and dissolve in 200 ml. of freshly boiled neutral absolute ethyl alcohol. Titrate to neutrality with N/2 NaOH to phenolphthalein.
5. The difference between the N/2 H_2SO_4 used in paragraph 2 and the sum of the N/2 NaOH required in paragraphs 3 and 4 equals the ml. of acid equivalent to KOH plus K_2CO_3.
6. On a separate sample, determine CO_2 by the standard Evolution-Volumetric method or standard Train absorption method. Calculate the CO_2 thus determined to % K_2CO_3.
7. Calculate the ml. N/2 acid equivalent to the K_2CO_3 determined in paragraph 6. Deduct this figure from the total acid equivalent of the sum of KOH and K_2CO_3 as determined in paragraph 5 to obtain the equivalent of free KOH. Calculate to per cent of free KOH.

The personnel of the committee for the current year is as follows:

H. C. Bennett
Eugene W. Blank
J. N. Borglin
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Charles J. Gundel
C. P. Long
J. W. McBain
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Burr H. Ritter
B. N. Rockwood
F. W. Smither
Foster D. Snell
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B. S. Van Zile

M. L. Sheely, *chairman.*