A glycerol balance of the same kettle used for illustration in Table I is shown in Table II. The discrepancy between the incoming and outgoing glycerol is less than 1%, which falls within the experimental error of sampling, material weighing, and chemical analyses. Somewhat less spent lye was taken off the first change than is normal, but this deficiency was compensated for in the second change when a larger than normal lye was taken off.

The percentage of glycerol left in the neat soap, 0.35%, represents a loss of nearly 5% of the glycerol actually available from the fats and oils charged to the kettle. This is equivalent to a kettle recovery of about 95%.

Conclusions

1. Glycerol distribution in the curd and lye layers approaches a ratio, as the electrolyte strength increases, in which the glycerol concentration in the water of the lye layer is about 1.3 times the glycerol concentration in the water of the curd layer. A high distribution ratio is conducive to a more effective glycerine recovery.
2. Conditions for the most favorable glycerol distribution ratio are vigorous boiling on a hard grained curd for a sufficient length of time to assure thorough mixing.
3. The yield of glycerol from the kettle was 95% exclusive of that in the neat soap.

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The author expresses appreciation for the analytical work performed by J. P. Pettid.

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The Determination of Borax in Soap

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IT has been found in this laboratory that the method for the determination of borax contained in a Federal Specification (1) and also in the Official Methods of the American Oil Chemists' Society (2) is both very lengthy and of unsatisfactory accuracy. The procedure involves fusing the borax-soap with sand and soda ash, solution of the fused mass in dilute acid, repeated refluxing with calcium carbonate, filtration, and titration of the filtrate with standardized alkali in the presence of mannitol or neutral glycerol to the phenolphthalein endpoint.

Blank and Troy (3) have devised a method which is claimed to be superior to the above procedure. It depends on removal of the soap by acidification and extraction of the fatty acids released, followed by quantitative precipitation of any soluble silicates, carbonates, and ortho-phosphates present with excess strontium chloride solution. Strontium metaborate is soluble under these conditions and is converted to boric acid by acidification of the filtrate, which is then titrated in the usual way in the presence of mannitol or glycerol.

Consistently low results and poor reproducibility have been obtained with the Blank and Troy method in this laboratory. It is believed that these low results are due, at least in part, to mechanical loss of borax during the removal of soap fatty acids by several extractions with petroleum ether. It was found that the soap can be quickly and completely removed by precipitation with the same precipitating reagent, strontium chloride, used to precipitate silicates, carbonates, and phosphates. In this way soap and interfering alkalies are removed simultaneously. Another refinement in the Blank and Troy method was the substitution of methyl purple indicator (4) for methyl red in adjusting the acidity of the solution prior to the final titration. Methyl purple gives a sharper endpoint than methyl red and thus is especially desirable with low borax samples. It was also found desirable to obtain complete removal of dissolved carbon dioxide from the solution before the final titration.

TABLE I

Determination of Borax in Soap-Borax Mixtures by Federal Specification Method (1)

Sample No.	Soap-Borax Ratio [1]	Borax Added (Grams)	Borax Found (Grams)	% Recovery	Average % Recovery	Average Deviation
1A	......[2]	0.0000	0.0020	......	......	......
1B	......	0.0000	0.0022	......	......	......
1C	......	0.0000	0.0024	......	......	......
2A	19:1	0.2623	0.2207	84.1	87.8	5.0
2B	19:1	0.2536	0.2416	95.3	......	......
2C	19:1	0.2545	0.2138	84.0	......	......
3A	3:1	1.2857	1.1527	89.7	90.6	1.4
3B	3:1	1.2833	1.1886	92.6	......	......
3C	3:1	1.2871	1.1506	89.4	......	......
4A	1:3	3.8479	3.6223	94.1	93.6	0.5
4B	1:3	3.8292	3.5646	93.1	......	......
5A	......[3]	5.1309	4.8306	94.2	94.5	0.2
5B	......	5.1180	4.8418	94.6	......	......
5C	......	5.1077	4.8297	94.6	......	......

[1] Total sample weight in each analysis was approximately 5 grams.
[2] Samples marked 1 are all soap and contain no borax.
[3] Samples marked 5 are all borax and contain no soap.

Analyses of soap-borax mixtures of varying ratios of soap to borax were conducted using the federal specification procedure. the Blank and Troy method, and the method described below. Soap-borax mixtures containing either trisodium phosphate or sodium metasilicate were also analyzed by these methods to determine the effect of the presence of other alkaline salts.

Materials and Reagents

The following materials were used in this study: Borax, C. P. ($Na_2B_4O_7 \cdot 10H_2O$), was assayed by a mannitol titration method given in Scott (5) and found to contain the equivalent of 102.5% $Na_2B_4O_7 \cdot 10H_2O$; this value was verified by dehydrating a

TABLE II

Determination of Borax in Soap-Borax-Alkali Mixtures by Federal Specification Method (1)

Sample No.	Soap-Borax-Alkali Ratio[1]	Borax Added (Grams)	Borax Found (Grams)	% Recovery	Average % Recovery	Average Deviation
1A	3:9:1	3.4590	3.4300	99.2	100.9	1.2
1B	3:9:1	3.4530	3.5333	102.3	......	......
1C	3:9:1	3.4624	3.5090	101.3	......	......
2A	2:3:3	1.9240	2.7404	142.4	142.2	2.3
2B	2:3:3	1.9272	2.8038	145.4	......	......
2C	2:3:3	1.9246	2.6702	138.8	......	......
3A	3:9:1	3.4593	3.1811	91.9	90.7	0.8
3B	3:9:1	3.4524	3.0979	89.7	......	......
3C	3:9:1	3.4614	3.1343	90.6	......	......
4A	2:3:3	1.9216	1.7753	92.4	91.2	1.3
4B	2:3:3	1.9230	1.7675	91.9	......	......
4C	2:3:3	1.9234	1.7150	89.2	......	......

[1] Samples marked 1 and 2 contain trisodium phosphate; samples marked 3 and 4 contain sodium metasilicate, pentahydrate.

sample at 1800°F. and converting the percentage of anhydrous borax obtained to borax containing 10 water molecules of hydration (6).

Soap, high-titer, neutral (88-92% soap)
Sodium metasilicate, technical ($Na_2SiO_3 \cdot 5H_2O$)
Trisodium phosphate, C. P. ($Na_3PO_4 \cdot 12H_2O$)

The following reagents are required for use in this procedure:

Hydrochloric acid, 1:1
Mannitol, C. P.
Methyl purple indicator (obtainable from most laboratory supply companies)
Phenolphthalein indicator, 1% in 95% ethyl alcohol
Sodium hydroxide solution, 25% by weight, carbonate-free
Sodium hydroxide solution, standard, 0.05N or 0.1N
Strontium chloride ($SrCl_2 \cdot 6H_2O$), 33⅓% by weight, or strontium nitrate [$Sr(NO_3)_2$], 26.5% by weight

Procedure

Accurately weigh a 5-gram sample into a 400-ml. beaker, add approximately 200 ml. of distilled water and warm on the steam bath until the sample has dissolved. Cool the solution to room temperature, transfer quantitatively to a 250-ml. volumetric flask, and make up to volume. A drop or two of ethyl alcohol will destroy any foam in the flask and will facilitate making the solution up to mark. Pipette an aliquot, conforming to the following table, into a 250-ml. beaker:

Estimated borax, %	Aliquot, ml.
0-10	100
10-50	50
50-100	25

TABLE III

Determination of Borax in Soap-Borax Mixtures by Blank and Troy Method (3)

Sample No.	Soap-Borax Ratio	Borax Added (Grams)[1]	Borax Found (Grams)	% Recovery	Average % Recovery	Average Deviation
1A	......[2]	0.0000	0.0139	......	......	......
1B	......	0.0000	0.0157	......	......	......
2A	19:1	0.1025	0.0855	83.4	81.9	1.0
2B	19:1	0.1014	0.0828	81.7	......	......
2C	19:1	0.1016	0.0818	80.5	......	......
3A	3:1	0.5189	0.4864	93.7	94.7	0.7
3B	3:1	0.5124	0.4869	95.0	......	......
3C	3:1	0.5113	0.4884	95.5	......	......
4A	1:3	1.5502	1.2712	82.0	82.9	3.8
4B	1:3	1.5436	1.2031	78.0	......	......
4C	1:3	1.5390	1.3637	88.6	......	......
5A	......[3]	2.0448	1.6100	78.8	88.2	6.3
5B	......	2.0534	1.9665	95.8	......	......
5C	......	2.0490	1.8449	90.0	......	......

[1] Represents weight of borax in a 200-ml. aliquot of the sample.
[2] Samples marked 1 are all soap and contain no borax.
[3] Samples marked 5 are all borax and contain no soap.

Add enough distilled water to make the volume in the beaker approximately 100-ml. (Note: Distilled, carbon dioxide-free water should be used throughout this procedure.)

Add 2 ml. of 25% sodium hydroxide solution, heat the solution almost to boiling, and add, with stirring, 10 ml. of either the strontium chloride or strontium nitrate solution to precipitate the soap and any phosphate or silicate which may be present. Heat the solution for an additional five minutes, stirring frequently and avoiding vigorous boiling.

Filter through a No. 41 Whatman paper, collecting the filtrate in a 400-ml. beaker. Wash the precipitate thoroughly with hot, distilled water (approximately 100 ml.).

Make the filtrate and washings just acid to methyl purple indicator with 1:1 hydrochloric acid and add 0.5 ml. of acid in excess. Place a cover glass on the beaker and heat to simmering temperature for 10 minutes.

Cool the solution in a cold water bath to room temperature and rinse the watch glass into the beaker. Titrate with 0.1N sodium hydroxide solution to the methyl purple endpoint (bright green). Record the burette reading.

TABLE IV

Determination of Borax in Soap-Borax-Alkali Mixtures by Blank and Troy Method (3)

Sample No.	Soap-Borax-Alkali Ratio[1]	Borax Added (Grams)[2]	Borax Found (Grams)	% Recovery	Average % Recovery	Average Deviation
1A	3:9:1	1.3903	1.3476	96.9	92.5	4.9
1B	3:9:1	1.3771	1.3143	95.4	......	......
1C	3:9:1	1.3890	1.1834	85.2	......	......
2A	2:3:3	0.7671	0.6330	82.5	80.9	1.9
2B	2:3:3	0.7649	0.6288	82.2	......	......
2C	2:3:3	0.7636	0.5951	78.0	......	......
3A	3:9:1	1.3836	1.2675	91.6	90.0	3.7
3B	3:9:1	1.3850	1.1693	84.4	......	......
3C	3:9:1	1.3827	1.2982	93.9	......	......
4A	2:3:3	0.7680	0.5072	66.0	70.0	3.6
4B	2:3:3	0.7627	0.5753	75.4	......	......
4C	2:3:3	0.7694	0.5265	68.5	......	......

[1] Samples marked 1 and 2 contain trisodium phosphate; samples marked 3 and 4 contain sodium metasilicate, pentahydrate.
[2] Represents weight of borax in a 200-ml. aliquot of the sample.

Add 1 ml. of phenolphthalein indicator and 5 grams of mannitol and titrate to a definite reddish pink with 0.05N or 0.1N sodium hydroxide solution depending on the percentage of borax expected. Add 1 gram of mannitol, stir, and continue the titration if the color of the solution reverts to green. When the phenolphthalein endpoint has been reached once more, add an additional gram of mannitol and proceed as before. The endpoint is reached when the addition of mannitol at the phenolphthalein endpoint does not change the color of the solution back to green and an additional drop of alkali increases the pink color considerably.

A blank is conducted using the same weight of mannitol as that used in the analysis. Dissolve mannitol in a volume of boiled, distilled water corresponding to the volume of solution at the end of the titration. Add methyl purple indicator and make the solution just acid with 1:1 hydrochloric acid. Titrate with 0.1N sodium hydroxide solution to the methyl purple endpoint. Add 1 ml. of phenolphthalein indicator and titrate with 0.05N or 0.1N sodium hydroxide to the phenolphthalein endpoint. The blank is the volume of alkali used between the two endpoints. Generally the blank does not exceed 0.1 ml.

Results of the titration are calculated as follows:

$$Na_2B_4O_7 \cdot 10H_2O, \% = \frac{(A - B) \times N \times 9.536}{(C/250) \times D}, \text{ where}$$

A = ml. standard alkali to titrate sample,
B = ml. standard alkali to titrate blank,
C = weight of sample,
D = ml. of aliquot taken, and
N = normality of standard alkali.

Results

Results of analyses are given in Tables I to VI, inclusive. Tables I and II illustrate the low and erratic results obtainable with the federal specification method. The Blank and Troy method, results for which are presented in Tables III and IV, also give low results of poor reproducibility. Results by the Industrial Test Laboratory method given in Tables V and VI show essentially complete recovery of borax in soap-borax mixtures of varying ratios of soap to borax. The reproducibility of the method is considered good. In mixtures containing trisodium phosphate or sodium metasilicate, the method also gives satisfactory recovery except for samples containing more than about 10% of silicate. Low recovery of borax in samples containing much silicate is probably due, as previously pointed out by Blank and Troy, to occlusion of borax by the voluminous strontium silicate precipitate. Samples 4A, 4B, and 4C of Table VI illustrate the low results obtained for borax when the silicate content is high.

TABLE V

Determination of Borax in Soap-Borax Mixtures by ITL[1] Method

Sample No.	Soap-Borax Ratio	Borax Added (Grams)	Borax Found (Grams)	% Recovery	Average % Recovery	Average Deviation
1A	19:1	0.1032	0.1041	100.9	99.6	0.9
1B	19:1	0.1051	0.1040	99.0	......	......
1C	19:1	0.1036	0.1025	98.9	......	......
2A	3:1	0.2553	0.2589	101.4	101.1	0.3
2B	3:1	0.2569	0.2584	100.6	......	......
2C	3:1	0.2573	0.2604	101.2	......	......
3A	1:3	0.3833	0.3833	100.0	100.0	0.4
3B	1:3	0.3851	0.3828	99.4	......	......
3C	1:3	0.3864	0.3886	100.6	......	......
4A	......[2]	0.4112	0.4118	100.1	100.3	0.2
4B	......	0.4069	0.4089	100.5	......	......
4C	......	0.4106	0.4115	100.2	......	......

[1] Industrial Test Laboratory.
[2] Samples marked 4 are all borax and contain no soap.

TABLE VI

Determination of Borax in Soap-Borax-Alkali Mixtures by *ITL[1] Method*

Sample No.	Soap-Borax-Alkali Ratio[2]	Borax Added (Grams)	Borax Found (Grams)	% Recovery	Average % Recovery	Average Deviation
1A	3:8:1	0.3422	0.3418	99.9	99.8	0.3
1B	3:8:1	0.3470	0.3448	99.4	......	......
1C	3:8:1	0.3471	0.3474	100.1	......	......
2A	2:3:3	0.2899	0.2873	99.1	97.6	1.0
2B	2:3:3	0.2900	0.2806	96.8	......	......
2C	2:3:3	0.2850	0.2763	96.9	......	......
3A	3:8:1	0.3473	0.3448	99.3	99.2	0.1
3B	3:8:1	0.3466	0.3438	99.2	......	......
3C	3:8:1	0.3484	0.3448	99.0	......	......
4A	2:3:3	0.2887	0.2599	90.0	90.2	0.2
4B	2:3:3	0.2906	0.2629	90.5	......	......
4C	2:3:3	0.2882	0.2595	90.0	......	......

[1] Industrial Test Laboratory.
[2] Samples marked 1 *and* 2 contain trisodium phosphate; samples marked 3 and 4 contain sodium metasilicate, pentahydrate.

Summary

Based on the data presented, it is considered that the present method is superior to both the federal specification and Blank and Troy procedures in terms of more complete recovery of borax, better reproducibility, and shorter time required for analysis.

The present method differs from the Blank and Troy method in two essential features, namely, simultaneous removal of soap and silicates, phosphates, and carbonates by precipitation with strontium ion, and use of methyl purple instead of methyl red indicator during adjustment of the acidity of the solution prior to final titration with standard alkali. These differences are believed responsible for the more accurate and reproducible results obtainable by the present method as compared with those given by the Blank and Troy procedure.

It should be noted that the above procedure is limited to soaps and/or alkaline builders and cannot be applied to synthetic detergents that do not precipitate with strontium.

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