

## Calculations:

$$\% \text{ glycerol} = \frac{(B-S) \times N \times 3.07}{W}$$

B = ml. of alcoholic potassium hydroxide required to titrate blank.

S = ml. of alcoholic potassium hydroxide required to titrate sample.

N = Normality of alcoholic potassium hydroxide.

W = Weight of sample in gm.

## Summary

A method for the determination of glycerol has been presented in which the acetylation is performed

with a reagent consisting of acetic anhydride in pyridine. Typical data obtained by this procedure and other accepted methods are shown. The proposed procedure is simpler, more rapid, and more accurate than the conventional acetin method.

## REFERENCES

1. Bradford, Pohle, Gunther, and Mehlenbacher, *Oil & Soap* 19, 189, (1942).
2. Glycerin Analysis Committee, Am. Oil Chemists' Soc. Report, *Oil & Soap*, 10, 71, (1933); 11, 53, (1934).
3. Official and Tentative Methods of the Am. Oil Chemists' Soc., page D-3, (1938).
4. West, Hoagland, and Curtis, *J. Bio. Chem.*, 104, 627, (1934).

## Determination of Borax in Soap and Synthetic Detergents\*

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THE usual method employed for the determination of borax in soap and soap products is that described by Poetschke (1, 2). The procedure is accurate but tedious. It includes a lengthy fusion that requires constant attention and care. In addition, repeated operations of filtration and refluxing are required to remove, respectively, the excess of calcium carbonate over that required to neutralize the solution prior to titration of the boric acid and the carbon dioxide liberated during neutralization. The presence of calcium carbonate during the final titration, as recommended in the method, tends to obscure the phenolphthalein endpoint.

Scott (3) describes a method for the determination of borax in soap in which the soap is acidified, the fatty acids removed by filtration, and the boric acid titrated with normal sodium hydroxide solution in the presence of mannitol. The excess of acid remaining from splitting the soap is previously neutralized to methyl orange with sodium hydroxide. If silicate is present, it is removed by dehydration with concentrated hydrochloric acid employing a distillation flask and collecting the volatile boric acid in a receiving flask. If phosphates are present, a correction must be applied to the titration since a portion of the phosphate titrates as borate.

The method described in this paper is both accurate and rapid. The presence of phosphate or silicate does not interfere with the determination. Carbonates are destroyed during the course of the procedure.

### Principle of the Method

The method to be described is based upon the fact that soluble silicates, carbonates, and orthophosphates can be quantitatively precipitated by strontium chloride whereas strontium metaborate is soluble in an excess of strontium chloride solution. After the insoluble strontium salts are removed by filtration, the strontium metaborate is converted into boric acid by acidification with hydrochloric acid, and the boric acid titrated in the usual manner in the presence of mannitol.

The solubility of strontium carbonate ( $\text{SrCO}_3$ ) is given as 0.0011 grams per 100 ml. of water at 18°C. and 0.065 grams per 100 ml. of water at 100°C. (4). The same source lists strontium metasilicate ( $\text{SrSiO}_3$ ) and strontium orthophosphate ( $\text{SrHPO}_4$ ) as insoluble. It has been found by experiment that meta- or pyrophosphates do not interfere in the determination.

Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) is slightly soluble in ethyl alcohol. For this reason determined values for borax in the alcohol insoluble material obtained from the original sample tend to run low. In the procedure described in this paper the borax is determined on the original sample to avoid errors due to the solubility of borax in ethyl alcohol.

### Solubility of Boric Acid in Ethyl Ether and Petroleum Ether

During the development of the method the question arose as to the degree of solubility of boric acid in ethyl ether and petroleum ether. This question merits consideration since in the procedure to be described the fatty acids are normally removed from the sample solution by use of petroleum ether. The solubilities were determined by employing a modification of the apparatus devised by Bahr (5). Figure 1 shows the constructional details of the modified apparatus. The apparatus was maintained at  $25 \pm 0.01^\circ\text{C}$ . by immersion in a thermostatically controlled water bath.

The method of procedure was essentially as follows: Boric acid was placed in contact with the ether and stirred by a stream of dry nitrogen for six hours. Nitrogen was passed through the ether by closing stopcock B and opening stopcocks A and C. Stopcock D was oriented in such a manner as to permit passage of the nitrogen while sealing off the measuring pipet. A slight amount of refluxing took place in the condenser. Some ether was lost by volatilization. Due to the latter loss the solubility is determined in a solution that is being slowly concentrated. Super-saturation is prevented due to the agitation of the solution by the stream of nitrogen. The nitrogen was dried by passage over anhydrous calcium sulfate.

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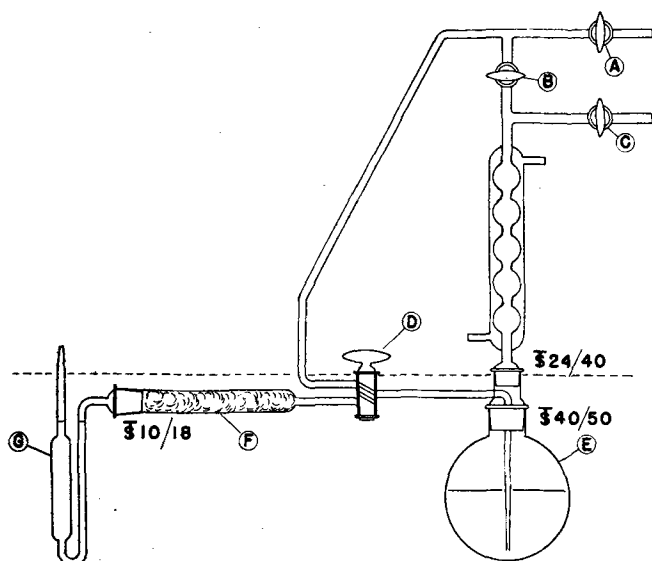


FIG. 1. Constructional details of apparatus employed for the determination of the solubility of boric acid in petroleum ether and ethyl ether.

Stopcocks are designated as A, B, C, and D. The letter E represents the flask containing the boric acid and ether; F is a filter tube containing cotton, and G is a measuring pipet. The apparatus is immersed to the level of the broken line in a thermostat.

When equilibrium had been reached (approximately six hours in the case of ether-boric acid), stopcock D was turned to connect the pipet with the flask and B opened (C is already open). By gradually closing C sufficient pressure was developed in the apparatus to force the saturated solution of boric acid in ether through the filter plug (cotton) and into the measuring pipet. The contents of the measuring pipet were then transferred to a flask and titrated electrometrically employing a weight buret for the titrating solution.

The values given in Table I are typical of the magnitude of the solubilities. On the basis of the determined solubilities it is recommended that petroleum ether be employed for the extraction of fatty acids.

TABLE I.

Solubility of Boric Acid in Ethyl and Petroleum Ether at 25°C.

Solubility of Boric Acid in Ethyl Ether	Solubility of Boric Acid in Petroleum Ether
Grams per 100 ml. of Solution	Grams per 100 ml. of Solution
0.1109	0.00183
0.1135	0.00150
0.1106	0.00167
0.1097	0.00181
0.1089	0.00165

### Reagents Required

The following reagents are required for use in the procedure:

N/20 Sodium Hydroxide solution, carbonate free.

25% by weight Sodium Hydroxide solution, carbonate free.

33½% by weight Strontium Chloride solution (SrCl<sub>2</sub>·6H<sub>2</sub>O).

1:1 Hydrochloric Acid.

Methyl Red indicator solution prepared by dissolving 0.10 grams of methyl red in 100 ml. of a 50/50 mixture of ethyl alcohol and water.

α-Naphtholphthalein indicator solution prepared by dissolving 0.10 grams of α-naphtholphthalein in 100 ml. of a 50/50 mixture of ethyl alcohol and water.

### Procedure

Accurately weigh a sample of 2.5 to 3.0 grams and transfer to a 250-ml. beaker. If the sample contains over 20% of borax, reduce the weight of sample taken for analysis to 1.5 to 2.0 grams. Add approximately 200 ml. of water and warm on the steam bath until the sample has dissolved. Transfer the solution to a 500-ml. glass-stoppered extraction cylinder, add several drops of methyl red indicator and sufficient 1:1 hydrochloric acid solution to completely liberate the fatty acids and slightly acidify the solution. Avoid adding a large excess of the acid. After acidifying, quickly stopper the extraction cylinder and cool to room temperature under the tap. This operation will prevent the possible loss of slight amounts of boric acid by volatilization.

Extract the acidified solution five times with 100-ml. portions of petroleum ether. When oxidized fatty acids are present, they should be removed by a sixth extraction with a 50/50 mixture of petroleum and ethyl ether. If preferred, the fatty acids may be removed by filtration.

Transfer the extracted solution to a 600-ml. beaker and add dropwise 25% sodium hydroxide solution until the solution is slightly alkaline. Add approximately 5 ml. in excess of the 25% sodium hydroxide solution. Evaporate the solution on the steam bath to a volume of approximately 300 ml. Wash down the inside walls of the beaker with a small volume of hot water using a rubber policeman to facilitate solution of encrusted salts.

Bring the solution to incipient boiling and add drop-wise, with vigorous stirring, 10 ml. of 33½% strontium chloride (SrCl<sub>2</sub>·6H<sub>2</sub>O) solution. Boil the contents of the beaker for two minutes.

Filter through a No. 40 Whatman paper. Vacuum filtration can be employed if desired. In the event vacuum is employed, a platinum cone should be used to prevent rupturing the paper.

Wash the precipitate with approximately 150 ml. of hot water added in small volumes at a time. Transfer the filtrate to a 500-ml. volumetric flask. Add sufficient 1:1 hydrochloric acid to decompose any precipitated strontium carbonate. Shake vigorously to remove carbon dioxide. Finally bring to the volume mark with water at room temperature.

By means of a pipet, withdraw a 200-ml. aliquot from the volumetric flask and transfer to a 400-ml. beaker. Add 1:1 hydrochloric acid dropwise until the solution is distinctly acid to methyl red indicator and titrate with N/20 sodium hydroxide to the methyl red endpoint (pure yellow). Record the burette reading. Add 5 grams of mannitol and stir until dissolved. Add 3 ml. of α-naphtholphthalein indicator solution, and titrate the boric acid complex with N/20 sodium hydroxide to a green yellow endpoint. The titration should be carried out in cold solution (room temperature or less) because the stability of the boric acid complex decreases sharply with a rise in temperature. The use of invert sugar instead of mannitol is more economical. Directions for its preparation are given by Gilmour (6).

A blank should be run on the amount of mannitol used in the titration. The blank should not exceed 0.1 ml. and is usually less than 0.05 ml.

If the sample is a mixture of alkaline salts and does not contain soap, dissolve the weighed sample in 200 ml. of hot water, cool the solution to room tem-

perature, add 1:1 hydrochloric acid to slight acidity, make alkaline by the cautious addition of 25% sodium hydroxide solution, and then add approximately 5 ml. in excess of the 25% sodium hydroxide solution. Finally add 10 ml. of 33 $\frac{1}{3}$ % strontium chloride solution as directed above.

The N/20 sodium hydroxide may be standardized against  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  or anhydrous borax as described by Kolthoff and Sandell (7). A procedure for crystallizing borax with ten formula weights of water is given by Kolthoff and Furman (8). Young has described three methods for the preparation of borax containing exactly 10 mols. of water of crystallization (9). These methods comprise drying over a saturated solution of sodium bromide, drying over a saturated solution of sugar and salt, and washing recrystallized borax with alcohol and ether.

If a continuous pH recorder is available the titration may be made electrometrically. The potentiometric titration of boric acid has been described by Hildebrand (10). Figure 2 represents a graph of a typical potentiometric titration of borax.

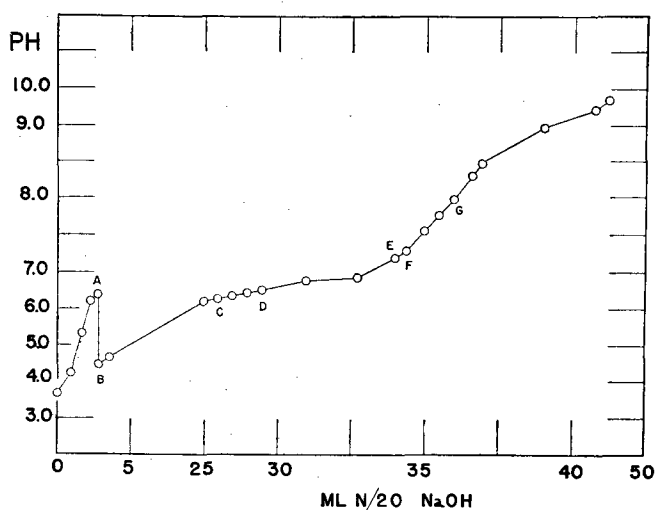


FIG. 2. Graph of a typical electrometric titration of borax.

- A == Yellow endpoint of Methyl Red  
 A to B == Drop in pH due to addition of Mannitol  
 C == Second yellow endpoint of Methyl Red  
 D == Addition of  $\alpha$ -Naphtholphthalein: orange colored solution  
 E == Initial  $\alpha$ -Naphtholphthalein transition: green yellow  
 F == Green endpoint (pH 7.40) of  $\alpha$ -Naphtholphthalein  
 G == Strong brilliant green endpoint of  $\alpha$ -Naphtholphthalein

In the potentiometric titration the solution should be brought approximately to a pH of 6.3 by the dropwise addition of 25% sodium hydroxide solution. It should then be titrated to exactly pH 6.3 with N/20 sodium hydroxide solution and the burette reading recorded. Add 5 grams of mannitol and titrate to a pH of 8.0. The same pH range should be employed in the standardization of the N/20 sodium hydroxide solution.

The titration values can be expressed as per cent borax by use of the following calculation:

$$\left[ \left( \frac{\text{ml. N/20 NaOH to titrate sample}}{\text{ml. N/20 NaOH to titrate blank}} \right) - 1 \right] \times \frac{\text{Value of 1 ml. N/20 NaOH in terms of Na}_2\text{B}_4\text{O}_7}{\text{weight of sample}} \times 100$$

= %  $\text{Na}_2\text{B}_4\text{O}_7$   
 %  $\text{Na}_2\text{B}_4\text{O}_7 \times 1.8942 = \text{ % Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

## Results

Some of the results obtained with this procedure are recorded in Tables II to IV. The results presented in Table II attest to the accuracy of the method since the recoveries of added amounts of borax are satisfactory.

TABLE II.  
Recovery of Borax Added to Soap and Soap Products.

Type of Product	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ Originally Present	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ Added	Total $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ Present	
			Calculated	Found
Sprayed Soap.....	0.00	6.41	6.41	6.45
Sprayed Soap.....	0.00	18.50	18.50	18.46
Sprayed Soap.....	0.00	33.49	33.49	33.49
Sprayed Soap.....	0.00	49.71	49.71	49.77
Sprayed Soap.....	0.00	77.41	77.41	77.35
Borax Washing Powder (A)*.....	1.85	3.58	5.43	5.39
Borax Washing Powder (A)*.....	1.85	5.86	7.71	7.66
Borax Washing Powder (B)*.....	1.42	1.60	3.02	3.00
Borax Washing Powder (B)*.....	1.42	3.15	4.57	4.57
Borax Washing Powder (B)*.....	1.42	6.78	8.20	8.16
Borax Bar Soap (A).....	0.80	0.74	1.54	1.51
Borax Bar Soap (A).....	0.80	2.16	2.96	2.89
Borax Bar Soap (B).....	0.86	1.11	1.97	1.96
Borax Bar Soap (B).....	0.86	2.22	3.08	3.03
Lather Shave Cream.....	0.99	0.93	1.92	1.94
Lather Shave Cream.....	0.99	1.48	2.47	2.50
Hand Lotion.....	0.64	0.75	1.39	1.42
Hand Lotion.....	0.64	1.09	1.73	1.71
Hand Lotion.....	0.64	1.71	2.35	2.33

\*Consisting of borax and sodium carbonate.

Table III presents a comparison of the results obtained when various indicators are employed in the titration of boric acid. The salt concentrations present in the titrated mixtures were equivalent to those encountered in the method. It was found that  $\alpha$ -naphtholphthalein and phenolphthalein indicator give comparable results. The mixed indicator Cresol red-Thymol blue (11) gives slightly higher results. Use of the mixed indicator Phenolphthalein-Methylene Green resulted in values definitely too high (12).

TABLE III.  
Comparison of Results Obtained in the Titration of Boric Acid With Various Indicators.

Titration No.	Boric Acid Present	Boric Acid Found		
		$\alpha$ -Naphtholphthalein Indicator	Phenolphthalein Indicator	Cresol Red Thymol Blue Indicator
	Grams	Grams	Grams	Grams
1.....	0.0500	0.0501	0.0502	0.0510
2.....	0.0500	0.0505	0.0502	0.0509
3.....	0.0500	0.0506	0.0504	0.0508
4.....	0.0500	0.0506	0.0506	0.0506
5.....	0.0500	0.0504	0.0505	0.0508
6.....	0.0500	0.0506	0.0506	0.0508
7.....	0.0500	0.0504	0.0505	0.0506
Average.....		0.0504	0.0504	0.0508

The results given in Table IV are of interest in revealing that perborates require no special treatment when analyzed according to the described procedure. During preparation of the sample for precipitation perborates decompose into hydrogen peroxide and metaborate.

Figure 3 shows the effect of phosphates, carbonates, and silicates on the determination of borax. Carbonates, of course, are destroyed during the course of the procedure. However, they exert an indirect influence inasmuch as the sodium chloride concentra-

TABLE IV.  
Determination of Boron Compounds in Admixture  
With Various Substances

Sample No.	Composition of Mixture Taken for Analysis	Found
	Grams	Grams
1	0.0826 gms. NaBO <sub>3</sub>	0.0821 gms. NaBO <sub>3</sub>
2	0.0596 gms. NaBO <sub>3</sub> 0.2923 gms. Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> 0.1401 gms. Na <sub>2</sub> CO <sub>3</sub>	0.0611 gms. NaBO <sub>3</sub>
3	0.0592 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O 0.3794 gms. Na <sub>2</sub> CO <sub>3</sub> 3.0349 gms. 95% Glycerol	0.0604 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O
4	0.0803 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O 0.2150 gms. Na <sub>2</sub> CO <sub>3</sub> 0.4549 gms. Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> 0.1228 gms. Na <sub>2</sub> SiO <sub>3</sub>	0.0790 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O
5	0.1966 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O 0.1966 gms. Na <sub>3</sub> PO <sub>4</sub> 0.1514 gms. Na <sub>2</sub> SiO <sub>3</sub>	0.1968 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O
6	0.1301 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O 0.3645 gms. Na <sub>5</sub> F <sub>3</sub> O <sub>10</sub> Penta-Sodium Tripolyphosphate	0.1305 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O
7	0.1554 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O 0.5553 gms. (Na <sub>6</sub> F <sub>6</sub> O <sub>18</sub> ) Sodium Hexa-metaphosphate	0.1517 gms. Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O

tion is increased when they are present. In each determination shown in Figure 3 exactly 0.0500 gram of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O was present.

The plots indicate that silicate is an interfering substance to a slight extent. Results are not seriously in error until the silicate content becomes very high. As the concentration of silicate increases, the amount of borax recovered falls off rapidly. By analyzing the strontium silicate precipitates for borax, it has been determined that the strontium silicate occludes borax. This is not surprising in view of the physical characteristics of silicate precipitates.

#### Reproducibility of Results

In order to determine the reproducibility of results a homogeneous mixture of soap and borax was analyzed eight times. The endpoints were determined potentiometrically and by use of  $\alpha$ -naphtholphthalein. The results obtained are given in Table V.

TABLE V.  
Reproducibility of Results.

Mixture of Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O and Sprayed Soap*	Per Cent Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O Found			
	Per Cent Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O Present	Electrometric Titration	$\alpha$ -naphtholphthalein Indicator Titration	
8.00	8.15	+ 0.029	8.04	-- 0.135
	8.18	+ 0.059	7.96	-- 0.215
	8.16	+ 0.039	8.12	-- 0.055
	8.11	-- 0.011	8.16	-- 0.015
	8.15	+ 0.029	8.27	+ 0.095
	8.04	-- 0.081	8.42	+ 0.245
	8.12	-- 0.001	8.24	+ 0.065
	8.06	-- 0.061	8.19	+ 0.015
	Mean 8.121	0.0388	Mean 8.175	0.105
	Mean Deviation		Mean Deviation	
Average deviation of the mean is $\frac{0.0388}{\sqrt{8}} = \pm 0.0137$		Average deviation of the mean is $\frac{0.105}{\sqrt{8}} = \pm 0.0371$		
Most probable % Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O = 8.12 $\pm$ 0.01		Most probable % Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O = 8.18 $\pm$ 0.04		

\*Eight per cent Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O and 92% of sprayed soap containing 7.18% Na<sub>2</sub>SiO<sub>3</sub>, 1.05% Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and 12.70% Na<sub>2</sub>CO<sub>3</sub>.

Values obtained by use of  $\alpha$ -naphtholphthalein as indicator are slightly higher than those obtained elec-

trometrically. In addition the average deviation of the mean is approximately four times as great when  $\alpha$ -naphtholphthalein indicator is employed.

#### Discussion

During the course of this investigation the question arose as to the magnitude of the effect exerted by borax when present during the oxidation of glycerol with potassium dichromate. It was found that borax has only a slight disturbing effect in the determination of glycerol by potassium dichromate.

In one experiment a glycerol sample assaying an average 94.60% purity and weighing 0.1172 gram was oxidized in the usual manner in the presence of 0.0504 gram of borax. In the presence of the borax the glycerol assayed an average 95.10%. Considered on the basis of the amount of glycerol that is ordinarily present in soap the presence of borax has a negligible effect on the determination.

A number of indicators were tested for use in this procedure.  $\alpha$ -naphtholphthalein was found entirely satisfactory and is recommended. The values obtained using this indicator check closely the values obtained electrometrically. Phenolphthalein or the mixed indicator Cresol Red-Thymol Blue may be employed if the endpoints are more readily discernible by the person running the determination.  $\alpha$ -naphtholphthalein has been recommended by Strecker and Kannappel as an indicator in the titration of boric acid (13). This indicator has a transition interval in pH of 7.3 to 8.7. It exhibits the following sequence of colors in passing from a pH of 7.3 to 8.7:

pH 7.3	Red-yellow red	(Value 7, Chroma 8) (14),
↓	Green yellow	(Value 3, Chroma 4),
pH 8.7	Purple blue	(Value 3, Chroma 12).

This indicator is subject to a salt error (15). For this reason the N/20 sodium hydroxide used in the titration of the boric acid complex should preferably be standardized under conditions of equal salt concentration as directed under procedure.

After a few preliminary trials the green yellow endpoint of  $\alpha$ -naphtholphthalein was adjudged the most satisfactory discernible endpoint and all of the results reported in this paper were obtained by using this endpoint. It has been the experience of this laboratory that the green yellow endpoint is easier to distinguish than the more usual purple blue.

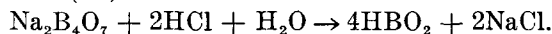
Boric acid should not be employed for the standardization of the N/20 sodium hydroxide employed in this procedure unless the results are reported as boric acid. A factor of 6.1680 is involved in calculating boric acid to Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O and any error in the determination is magnified six times.

It has been pointed out in a previous paragraph under *Principle of the Method* that borax is slightly soluble in ethyl alcohol. On account of its solubility in ethyl alcohol borax should be determined on a separate portion of the original sample. In a complete analysis of a soap the analysis of the alcohol insoluble portion involves the determination in many cases of silicate, carbonate, and phosphate in addition to some undissolved borax.

Silicate, carbonate, and phosphate should be determined on separate portions of the alcohol insoluble material in the usual manner. Borax should be determined on a portion of the alcohol insoluble

material as described under *Procedure* for alkaline salt mixtures.

The total alkali content of a portion of the alcohol insoluble material should be determined by titration to the methyl orange endpoint with N/2 hydrochloric acid. Borax titrates to acid according to the following equation (16):



The usual corrections for untitrated  $\text{Na}_2\text{O}$  in phosphate should also be applied. It is necessary to add one-third of the %  $\text{Na}_2\text{O}$  present in the form of  $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$  and one-half of the %  $\text{Na}_2\text{O}$  present in the form of  $\text{Na}_4\text{P}_2\text{O}_7$  to the titration for total alkali determined as described above. Factors for other phosphates that may be encountered can be readily determined by titration of a portion of the pure phosphate.

The sum of the amounts of  $\text{Na}_2\text{O}$  required to satisfy the  $\text{CO}_2$ ,  $\text{P}_2\text{O}_5$ , and  $\text{HBO}_2$  present subtracted from the total  $\text{Na}_2\text{O}$  present leaves the amount of  $\text{Na}_2\text{O}$  in combination with the  $\text{SiO}_2$ .

If the ratio of  $\text{Na}_2\text{O}$  to  $\text{SiO}_2$  is arbitrarily taken as 1:3.25, it is obvious that the total alkali content of the alcohol insoluble material need not be determined. Neither will it be necessary to determine the amount of borax remaining in the alcohol insoluble.

In presenting the analysis of a soap or soap product containing borax, the latter is usually reported as anhydrous borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ) or hydrated borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ). It has been found by Trusler (17) that fully hydrated borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) loses approximately 80.00% of its water of crystal-

lization when subjected to Xylol distillation. The final product remaining in the distillation flask has a formula corresponding to approximately  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$ . Moisture results should be corrected on this basis.

#### Borax in the Presence of Synthetic Detergents

In extending the work on the determination of borax in soap to borax in admixture with synthetic detergent, it was found that the presence of synthetic detergents had an adverse effect on the indicator endpoint. This was expected on the basis of reports already published (18). In an effort to avoid the use of indicators to determine the endpoint, recourse was had to potentiometric titration. However, the precipitate formed with strontium chloride in the preliminary preparation of the sample was characterized by undesirable filtering qualities. Accordingly recourse was had to an entirely different mode of preparation of sample in which the synthetic detergent was destroyed by ashing.

Martin (19) has described the titration of borax in soap after ignition to destroy the organic matter present. No provision is made for the possible presence of silicate and phosphate. In the following scheme synthetic detergents are removed by ashing; silicates and phosphates are removed by precipitation with strontium chloride.

#### Ash Procedure for the Determination of Borax in the Presence of Synthetic Detergents

Weigh accurately about 1 to 1.5 grams of the sample into a platinum dish. Add 5 mls. of 50% sodium hydroxide solution and sufficient water to wet the

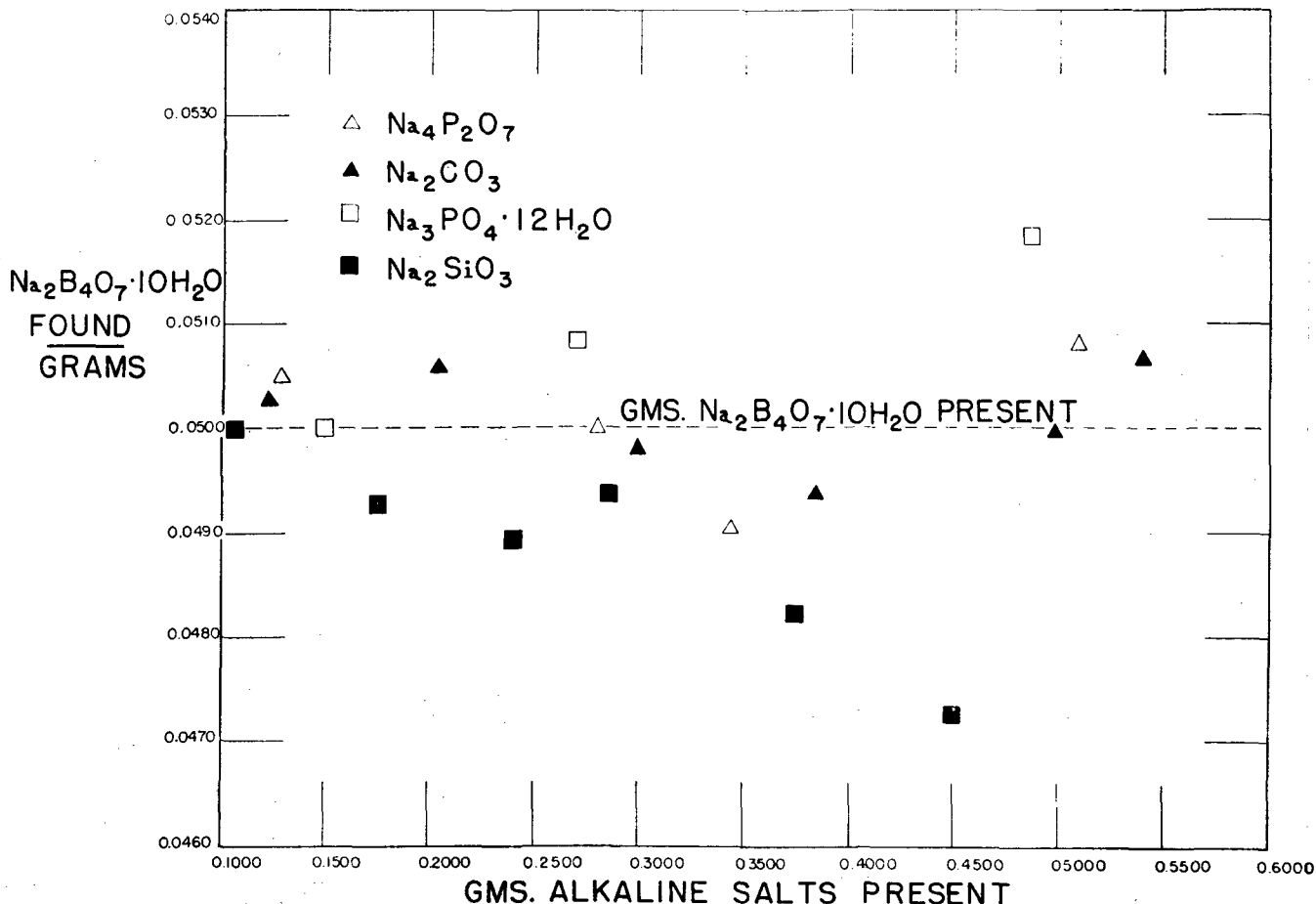


FIG. 3. Plot showing the effect of phosphates, carbonates and silicates on the determination of borax.

contents of the dish. Evaporate to dryness on the steam bath. Ignite the contents of the dish over a bunsen flame until the organic matter is destroyed. Allow to cool.

Transfer the dish to a 600-ml. beaker and add 200 ml. of water. Warm on a hot plate to facilitate solution of the fused mass. When solution is complete remove the dish with forceps and wash with water adding the washings to the solution already in the beaker.

Add 5 ml. of 50% NaOH solution and proceed to precipitate with  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  as previously directed. Titrate with N/20 NaOH in the presence of mannitol.

Table VI shows some of the results obtained by this procedure. All samples contained approximately 10% of  $\text{Na}_2\text{SiO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ; approximately 55% of the detergent and the indicated amounts of hydrated borax.

## REFERENCES

- Poetschke, J. Ind. Eng. Chem., 5, 645 (1913).
- Official and Tentative Methods of the American Oil Chemists' Society: Standard Methods for the Sampling and Analysis of Soap and Soap Products, p. A-7b (1943).
- "Scott's Standard Methods of Chemical Analysis," edited by N. H. Furman, 5th Ed., Vol. 2, Chapter on "Methods for Analysis of Soaps and Soap Products," compiled by the Chemical Division of the Procter & Gamble Co., p. 2035, D. Van Nostrand Co., Inc., New York (1939).
- Handbook of Chemistry and Physics, 28th Ed., p. 467, Chemical Rubber Publishing Co., Cleveland (1944).
- Bahr, Z. anorg. Chem. 71, 79 (1911).
- Gilmour, Analyst 46, 3 (1921); 49, 576 (1924). Quoted by Kolthoff and Furman, "Volumetric Analysis," Vol. 2, p. 122, John Wiley & Sons, Inc., New York (1929).

TABLE VI.

Recovery of Borax Added to Synthetic Detergents.

Type of Synthetic Detergent*	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ Added	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ Recovered
	%	%
Aliphatic Sulfate—Sample I.....	13.00	12.78
Aliphatic Sulfate—Sample II.....	10.00	10.10
Aliphatic Sulfate—Sample II.....	10.15	10.24
Aliphatic Sulfate—Sample II.....	10.34	10.37
Fatty Acid Amide.....	8.50	8.52
Alkyl Aryl Sulfonate.....	11.55	11.70
Non-Ionic Compound.....	9.24	9.44
Cation-Active Compound.....	6.53	6.60

\*All samples contained approximately 55% of the synthetic detergent; approximately 10% of  $\text{Na}_2\text{SiO}_3$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  and the indicated amounts of hydrated borax.

- Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," Revised Edition, p. 560, The Macmillan Co., New York (1943).
- Kolthoff and Furman, "Volumetric Analysis," Vol. 2, p. 94, John Wiley & Sons, Inc., New York (1929).
- Young, Can. J. Research 17, B, 192 (1939).
- Hildebrand, J. Am. Chem. Soc. 35, 861 (1913).
- Kolthoff and Sandell, loc. cit., p. 451.
- Ibid., p. 451.
- Strecker and Kannappel, Z. analyt. Chem. 61, 378 (1922). Cf. Kolthoff and Furman, loc. cit., Vol. 1, p. 100; Vol. 2, p. 123.
- Colors are designated by I.S.C.C.-N.B.S. color names. Cf. Bie-feld and Griffing, J. Chem. Ed., 19, 282, 307 (1942); Munsell Book of Color, Standard Edition, Munsell Color Co., Inc., Baltimore (1929).
- Kolthoff and Furman, "Indicators," p. 173, John Wiley & Sons, Inc., New York (1926).
- Snell and Biffen, "Commercial Methods of Analysis," p. 271, McGraw-Hill Book Co., Inc., New York (1944).
- Trusler, Oil & Soap 19, 1 (1942).
- Smith and Jones, J. Phys. Chem. 38, 243 (1934).
- Martin, "The Modern Soap and Detergent Industry," 2nd Edition, Vol. II, Section IX, p. 21, Crosby Lockwood and Son, London (1931).

## Flavor Reversion in Edible Fats<sup>1</sup>

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FLAVOR reversion in fats is probably defined most satisfactorily as the appearance of objectionable flavor from less oxidation than is required to produce true rancidity. The degree to which reversion and rancidity are separated—in terms of oxygen absorbed by the fat—is widely different for different fats. In the broadest sense, no fat is altogether free of a tendency toward reversion, i.e., there is none which will remain completely neutral in flavor up to the point of incipient rancidity. Most fats, however, do not develop markedly objectionable flavors or odors until oxidation has become relatively far advanced. In these the onset of reversion and of rancidity are so nearly coincidental that reversion constitutes no special problem. There are some fats, however, including particularly fish oils and vegetable oils containing linolenic acid, which revert with extremely slight oxidation. It is almost impossible to prepare edible products from such fats and get them to the consumer before they have suffered some loss of palatability. It is the reversion occurring in these fats which is of greatest present interest and will be principally treated in this discussion.

It has been pointed out previously (1, 4, 11) and should be repeated that the term "flavor reversion" is to a large degree a misnomer. Probably the term originated in reference to marine oils, which have a fish-like flavor and odor until they are deodorized and upon reversion again assume a decidedly fishy character. Most other fats which are given to reversion, particularly hydrogenated fats, have flavors and odors in the reverted state which bear little or no resemblance to the flavor or odor of the unprocessed fat. Thus, unhydrogenated soybean oil which has reverted badly is more "fishy" than "beany." Hydrogenated soybean oil in the reverted state has a flavor which is reminiscent of hay or straw. The reverted taste of hydrogenated linseed oil is more or less similar to that of hydrogenated soybean oil, but more pronounced. Hydrogenated rapeseed oil develops a peculiar nauseous taste, suggestive of an animal odor.

### Amount of Oxygen Required to Produce Flavor Reversion

The extremely small amount of oxidation which may be required to produce reversion is well illustrated by certain experiments carried out on hydrogenated lard (2). Slightly hydrogenated lard (i.e., lard hydrogenated from an iodine value of about 70 to about 60) has the peculiarity of quickly developing a muttoney flavor only when stored in a sealed can

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