Semi-Micro Analysis of Soap. II. Semi-Micro Determination of Borax

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THIS paper describes a semi-micro procedure for the determination of borax in soaps adapted from a macro method described recently by Blank and Troy (1). In brief, the method consists in the separation of borates from soluble silicates, carbonates, and orthophosphates by means of strontium chloride. Strontium metaborate is soluble in an excess of strontium chloride solution whereas both strontium orthophosphate and silicate are quantitatively precipitated. Carbonates are destroyed during the preparation of the sample. The insoluble strontium salts are removed by filtration, the strontium metaborate in the filtrate converted into boric acid by acidification with hydrochloric acid, and the boric acid titrated in the presence of mannitol.

The Semi-Micro Determination of Borax in Soap

Reagents Required

Following is a list of the reagents used in the procedure:

- N/50 Sodium Hydroxide solution, carbonate-free.
- 25% by weight Sodium Hydroxide solution, carbonate-free.
- 33⅓% by weight Strontium Chloride solution ($SrCl_2 \cdot 6H_2O$).
- 1:5 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

Weigh accurately a sample of 30 to 40 milligrams and transfer to a 5-ml. beaker. Add approximately 3 ml. of water and warm on a steam bath until the soap is dissolved. Add a drop of methyl red indicator solution and sufficient 1:5 hydrochloric acid (added with a fine dropper) to completely hydrolyze the soap and slightly acidify the solution. The excess of acid added must not be large. To reduce possible slight losses of boric acid by volatilization, cover the beaker at once and cool in a shallow container of cold water.

Filter through a No. 40 Whatman paper in a 25-mm. funnel. Wash the fatty acids with approximately 5 ml. of hot water added in small portions at a time.

To the filtrate add, dropwise, 25% sodium hydroxide solution until the methyl red indicator shows the solution to be slightly alkaline. Add approximately 0.1 ml. of 25% sodium hydroxide solution in excess. Reduce the volume of the solution to about 5 ml. by evaporation on a steam bath.

Heat the solution to incipient boiling and add with stirring approximately 0.15 ml. of 33⅓% strontium chloride ($SrCl_2 \cdot 6H_2O$) solution. Allow the contents of the beaker to boil for two minutes. Avoid spattering of the contents of the beaker by stirring continuously throughout the boiling period. Filter hot through a No. 40 Whatman filter paper into a 25-ml. Erlenmeyer flask using a funnel somewhat larger than the 25-mm. funnel used before, in order to accommodate easily the bulky precipitate. Wash the precipitate with approximately 3 ml. of hot water added in small portions, allowing the filter to drain completely after each addition.

To the filtrate add sufficient 1:5 hydrochloric acid with a fine dropper to decompose any precipitated strontium carbonate. Agitate vigorously by swirling to expel carbon dioxide. Continue adding 1:5 hydrochloric acid with a fine dropper until the solution is distinctly acid to methyl red indicator. Titrate with N/50 Sodium Hydroxide to the pure yellow endpoint of methyl red employing a micro-buret. Record the buret reading.

TABLE I

Recovery of Borax Added to Sprayed Soap

Sample No.	Composition of Sample		Total Weight of Sample	$Na_2B_4O_7 \cdot 10H_2O$ Present	
	Sprayed Soap	$Na_2B_4O_7 \cdot 10H_2O$		Calculated	Found
	mg.	mg.	mg.	%	%
1	34.304	0.080	34.384	0.23	0.26
2	35.120	0.249	35.369	0.70	0.73
3	35.719	0.498	36.217	1.38	1.39
4	35.119	0.995	35.614	2.79	2.82
5	35.830	1.493	37.323	4.00	3.96
6	36.283	2.098	38.381	5.47	5.45
7	35.400	2.488	37.388	6.57	6.53
8	36.234	2.985	39.219	7.61	7.59
9	36.256	4.810	41.066	11.72	11.68

Add 0.1 gram of mannitol and agitate with rotary motion until dissolved. Add 3 or 4 drops of α-naphtholphthalein indicator solution and titrate the boric acid complex with N/50 Sodium Hydroxide to a green-yellow end-point. The temperature of the solution at the time of titration should not markedly exceed room temperature because the stability of the complex decreases sharply with rise in temperature.

A blank should be run on a quantity of mannitol equal to that employed in the titration of the sample. The blank titration should not exceed 0.020 ml., and is usually less than 0.010 ml.

If the borax content of the soap is less than 2%, it may be found advantageous to use N/100 sodium hydroxide instead of N/50 sodium hydroxide for the titration. In case the weaker solution is used, extra care must be taken to avoid error due to absorption of CO_2. The titration of the sample should be performed rapidly; and the titration of the mannitol blank should include not only the volume of the N/100 sodium hydroxide necessary to reach the end-point, but also that which is necessary to keep it at the end-point for a total titration time equal to the time required in the titration of the sample.

The N/50 sodium hydroxide may be standardized against $Na_2B_4O_7 \cdot 10H_2O$ or anhydrous borax as described by Kolthoff and Sandell (2).

The per cent of borax may be calculated from the titration values as follows:

$$\frac{\left[\left(\begin{array}{l}\text{ml. N/50}\\ \text{NaOH to}\\ \text{titrate}\\ \text{sample}\end{array}\right) - \left(\begin{array}{l}\text{ml. N/50}\\ \text{NaOH to}\\ \text{titrate}\\ \text{blank}\end{array}\right)\right] \times \begin{array}{l}\text{Value of 1 ml.}\\ \text{N/50 NaOH in}\\ \text{terms of}\\ Na_2B_4O_7 \cdot 10H_2O\end{array} \times 100}{\text{Weight of sample in grams}} = \%\ Na_2B_4O_7 \cdot 10H_2O$$

Results

Table I presents data proving that the recovery of borax added to soap is quantitative within the experimental limitations of the method. The sprayed soap employed in the recovery experiments contained 3.8% H_2O, 61.2% anhydrous soda soap, 10.2% Na_2SiO_3, 4.7% $Na_4P_2O_7$, and 12.4% Na_2CO_3

Table II presents a comparison of values obtained in the analysis of various commercial products containing borax by the Poetschke method, and both the macro and semi-micro strontium methods.

Summary

A semi-micro procedure for the determination of borax in soap has been developed based on the fact that strontium metaborate is soluble in an excess of strontium chloride solution, whereas both strontium orthophosphate and silicate are quantitatively precipitated. The strontium metaborate is acidified and the liberated boric acid titrated to α-Naphtholphthalein in the presence of mannitol.

TABLE II

Determination of Borax in Commercial Soap Products

Product	Borax Present as % $Na_2B_4O_7 \cdot 10H_2O$		
	Poetschke Method (3) (4)	Macro Strontium Chloride Method	Semi-Micro Strontium Chloride Method
	%	%	%
Borax Soap Flakes A	0.77	0.87	0.89
Borax Soap Flakes B		0.76	0.76
Borax Soap Flakes C		1.53	1.50
Borax Bar Soap A	0.65	0.83	0.85
Borax Bar Soap B		1.62	1.59
Borax Bar Soap C		2.10	2.10
Borax Soap Powder A		0.67	0.67
Borax Soap Powder B	1.29	1.31	1.35
Borax Soap Powder C	2.35	2.36	2.45

REFERENCES

1. Blank and Troy, Oil and Soap *23*, 50 (1946).

2. Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," Revised Edition, p. 560, The Macmillan Co., New York (1943).

3. Poetschke, J. Ind. Eng. Chem. *5*, 645 (1913).

4. Official and Tentative Methods of the American Oil Chemists' Society: Sampling and Analysis of Soap and Soap Products, 2nd Ed., Edited by V. C. Mehlenbacher, Method Da 17-42, American Oil Chemists' Society, Chicago (1946).

Partial Hydrogenation of Linseed Oil by a Continuous Process*

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Summary

Alkali refined linseed oil was partially hydrogenated, using both continuous and batch processes. The continuous process was carried out in a series of Votator machines, using Rufert nickel catalyst, pressures up to 145 psig. and temperatures up to 400°F.

The continuous hydrogenation of linseed oil under the most selective conditions possible, using the Votator equipment, shows little selectivity between the linolenic and linoleic acid radicals. A pronounced selectivity is observed between oleic and the more unsaturated acid radicals. Under selective conditions of hydrogenation of linseed oil about 31% of the hydrogenated linolenic acid radical is transformed into 9-15 linoleic acid while the remainder of the linolenic acid goes to oleic acid in either one or two steps.

Batch hydrogenation yields oils of superior non-yellowing characteristics over comparable oils prepared by the continuous process.

The hydrogenated linseed oils were tested in both clear and pigmented alkyds where they displayed superior non-yellowing characteristics over the original linseed oil and, in many instances, over that of soya bean oil.

The yellowing of oils and alkyds appears to be a function of both 1) the quantity of fatty acids more unsaturated than oleic present in the oil and 2) the ratio of the quantity of linolenic acid radicals to linoleic acid radicals present.

WHEN it looked as if the supply of soya bean oil would be sharply curtailed for use in paints and alkyds, it appeared possible to hydrogenate selectively the linolenic acid in linseed oil to linoleic acid without reducing the linoleic or oleic acids present to more saturated acids to obtain a drying oil, with high linoleic acid content, with better drying qualities than soya bean oil, and with non-yellowing characteristics as satisfactory as soya bean oil.

Yellowing

The yellowing of oil films or oil-containing vehicles upon aging is an important problem in the paint and varnish industry, especially in white paints and enamels. It has been shown that the free fatty acid content does not affect the yellowing tendency of an oil (1). The unsaponifiable matter, while affecting the yellowing, is not believed to be the prime cause. The relative susceptibilities of the various vegetable oils to yellowing appear to be more or less proportional to their degree of unsaturation (1, 7, 8, 9, 10). Oils which contain only small proportions of any fatty acids more unsaturated than linoleic (soya bean oil, poppyseed oil, dehydrated castor oil, etc.) are relatively free from this defect (2). Holman (6, 7, 8, 9) *et al.*, believe that colored substances formed in the oxidation of fatty acids arise primarily from oxidation products of the fatty acids themselves and not from the oxidation products of trace substances present in natural fats.

Eibner and others believe that the yellowing of oils is a function of the amount of free or esterified α-linolenic and α-linoleic acid present. It is known that the hexabromide number is a quantitative measure of the linolenic content of an oil while the iodine number is a quantitative measure of the total unsaturation. Elm (1) and co-workers, however, have been unable to find any simple proportionality between these constants and the degree of yellowing in oils.

It is Scheiber's theory that the colored compounds are polyketones formed through oxidation of the double bonds.

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