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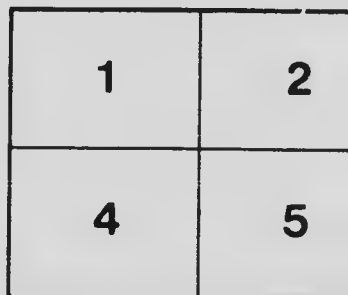
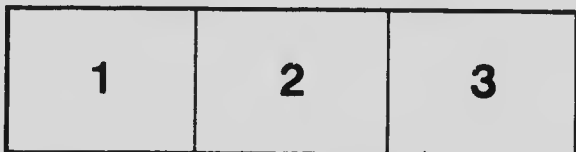
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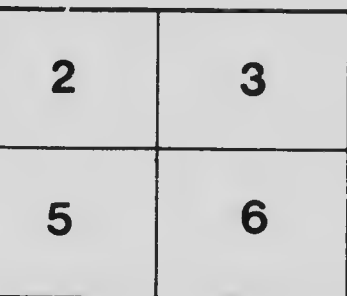
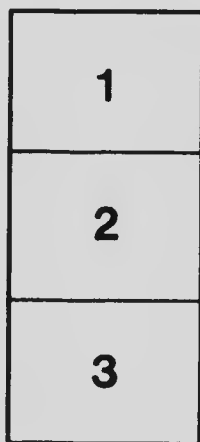
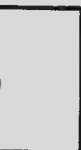
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AND IN THE PRESENCE OF PHOSPHORIC ACID, BY R. J.
MANNING AND W. R. LANG

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**THE DETERMINATION OF BORIC
ACID, ALONE AND IN THE
PRESENCE OF PHOSPHORIC
ACID.**

BY

RODGER J. MANNING AND WILLIAM R. LANG.

LONDON :

VACHER & SONS, WESTMINSTER HOUSE, GREAT SMITH STREET, WESTMINSTER, S.W.

1906.



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Canadian Section.

Meeting held at Toronto, on Friday, April 6th, 1906.

DR. F. J. SMALE IN THE CHAIR.

THE DETERMINATION OF BORIC ACID, ALONE AND IN THE PRESENCE OF PHOSPHORIC ACID.

By RODGER J. MANNING AND WILLIAM R. LANG.

In a recent paper in this Journal, by Dr. Milton F. Schick (1) on methods of estimating boric acid, mention is made of the compound formed by this acid and methyl alcohol in mixtures thereof, its distillation and collection over a weighed quantity of calcium oxide by which the ester is decomposed and the boric acid becomes fixed and, after ignition, is calculated by increase of weight (2).

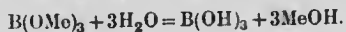
Berzelius' method, used and recommended by Thaddeeff (3), depends on the formation of potassium borodihydroboride from the distilled trimethyl borate: its accuracy is, however, found to be doubtful owing to the imperfect insolubility of the compound (4). Other methods, such as that of Partheil and Bose (5) and that of Mylius and Meusser (6), are pronounced "unsatisfactory," "complicated" and "tedious."

This paper deals primarily with the separation of boric acid as the trimethyl compound and its subsequent gravimetric estimation as the barium salt. The first series of experiments is connected with this, the second has reference to volumetric methods of estimating boric acid in the distillate, and the last deals with its direct titration in mixtures of other acids.

1.—In order to determine, first, if boric acid is completely expelled as the trimethyl salt by distillation, quantities of from 0.5 to 1.5 grms. of boric acid (7) were placed in a retort, 250 c.c. of methyl alcohol added and the mixture distilled at a temperature of from 66° to 67° C., when it was found that after distillation at this temperature for an hour the residue in the retort contained only a small proportion of boric acid and, after one and a-half hours, none could be detected.

The estimation of the boric acid, thus expelled as the trimethyl compound, with barium chloride solution was proceeded with. Known amounts of boric acid were dissolved in methyl alcohol (8), placed in a retort, and the

distillate allowed to mix with a concentrated aqueous solution of barium chloride. The trimethyl borate reacts with the water according to the equation—



The boric acid thus liberated reacts with the barium chloride to form barium borate and free hydrochloric acid in which the former dissolves. Caustic alkali was then added and the resulting precipitate of barium borate, $\text{Ba(BO}_2)_2$, washed with alcohol till free from all traces of chlorides, dried at 110°C. and weighed on a tared filter. The resulting weights of precipitate were in all cases too high and this was found to be due to the presence of barium hydroxide which was precipitated on concentrating the solution from filtration (9). The proceeding was then modified to obviate this, and the liberated hydrochloric acid in the reaction—



neutralised accurately by means of semi-normal sodium hydroxide with phenolphthalein as indicator. The use of this strong solution of sodium hydroxide—and also of barium chloride—was necessary to prevent the solution of part of the barium borate in water, in which it was found to be appreciably soluble. Weighing the precipitated barium salt gave results corresponding to 99.68 per cent. of the theoretical.

Being now fully satisfied with the accuracy of this method, determinations of the boric acid in pure borax were undertaken. Amounts of borax of about 1 gm. were weighed out, mixed carefully with from 20 to 30 c.c. of concentrated sulphuric acid and added to 350 c.c. of methylated spirit (8) contained in a retort. An excess of sulphuric acid was found to be necessary to prevent the reprecipitation of the salt by the alcohol. The mixture was then subjected to distillation at a temperature of from $65^\circ\text{--}70^\circ\text{C.}$ and it was found advisable to keep the bulk of the alcoholic solution approximately constant by leading into the retort from a distilling flask a further supply of spirit. About 30 minutes sufficed to carry over most of the boron compound, but results showed it to be necessary to continue the distillation much longer. A period of one and a half hours was therefore chosen as the best time for the operation. The determination of the boric acid was done as described previously, and a number of estimations showed that the borax could be estimated in this way with only a very small error.

Wt. of borax taken. Wt. of $\text{Ba(BO}_2)_2$. Percentage found.

0.9728 gm.	1.1262	99.0
0.9700 "	1.1270	99.4
0.9364 "	1.0900	99.6

The presence of any appreciable comparative amount of water in the retort is to be avoided, as the trimethyl borate would then be decomposed, yielding the alcohol and boric acid, which would not distil over; the result would then be too low.

This method was further applied to mixtures containing phosphates and sulphates in addition to borates with perfectly satisfactory results.

2. *Volumetric estimation with previous distillation.*—As boric acid can be titrated with standard sodium hydroxide in the presence of glycerine, and the end-points in the formation of sodium borate indicated by phenolphthalein, several determinations were tried after decomposing the borate in alcoholic solution with sulphuric acid. The apparatus used was the same as in the previous experiments: the distillate was collected in water, made up to a litre and aliquot portions taken for titration. To each portion thus taken it was found necessary to have about one-third of the bulk of the solution glycerine⁽¹⁰⁾. The results of the titration gave 99.75 per cent. of the boron compound, this error—0.25 per cent.—being considerably less than the literature on the subject would lead one to expect.

3. *Direct volumetric estimation in the presence of phosphates and sulphates.*—A mixture of a phosphate, a sulphate⁽¹¹⁾ and a borate were treated with decinormal sulphuric acid till acid to Methyl Orange, thus setting free phosphoric and boric acids. Decinormal sodium hydroxide was then run in until the solution was neutral to Methyl Orange, which was found only to indicate the end of the formation of the sodium dihydrogen phosphate; a still further amount of alkali had to be added before the solution began to react alkaline with phenolphthalein showing that the disodium compound had been formed⁽¹²⁾. The boric acid not being neutralised at once in aqueous solution by alkali, glycerine was then added, and the titration of the boric acid completed. The results are given below from which the accuracy of the method may be seen:—

Amounts of $\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$.	Amount formed by titration as above.	Per cent.	Error.
0.2390 grm.	0.2385 grm.	99.82	0.18
0.2990 ..	0.2985 ..	99.85	0.15
0.3824 ..	0.3823 ..	99.95	0.05
	Average	99.88	0.126

An error avoided here by titrating the solution previously with the sodium hydroxide till neutral or faintly alkaline, is the quantity of alkali of necessity absorbed by the water before the first trace of alkalinity is apparent. Experiments showed this to be an appreciable

amount : in the case of 50 c.c. alcohol and 50 c.c. water, 0.0016 gram. potassium hydroxide was required.

The authors intend applying these methods to the determination of boric acid in food stuffs.

(1) 1905, 609.

(2) See Gooch. Ann. Chem. J., 9, 23—33, and Montemartini Gazz. chim. ital., 28, 344—348.

(3) This J., 1898, 953.

(4) See (2) and (3).

(5) Ber., 1901, 3611.

(6) Ber., 1904, 397, and this J., 1904, 269.

(7) The composition of the boric acid employed—whether $B(OH)_3$, HBO_2 or $H_2B_4O_7$ —was determined by estimating the amount of B_2O_3 contained in it. A weighed amount of boric anhydride, formed by fusing the boric acid to a clear glass, was dissolved in water and titrated against potash with phenolphthalein as indicator. A weighed amount of boric acid was also titrated against the same potash. Hence the percentage of B_2O_3 in the acid used was found. In these titrations—and all subsequent ones in the second part of this paper—25 to 30 per cent. of glycerine was used, as it is found that the neutralisation of boric acid by alkali cannot be done with any degree of accuracy except in the presence of glycerine or other polyatomic alcohol. (R. T. Thomson, this J., 1893, 432.)

(8) Ordinary methylated spirits (free from mineral oil) were found to act equally well.

(9) Pure sodium hydroxide was used, prepared from metallic sodium.

(10) See note (7). Also J. Amer. Chem. Soc., 1898, 288. The determinations were done before the above papers were noticed.

(11) The sulphate might have been omitted, as it took no part in the subsequent reaction.

(12) A strong solution of disodium hydrogen orthophosphate is slightly alkaline to phenolphthalein. Comparative experiments were made with varying amounts of a saturated solution of this salt and equal quantities of water; phenolphthalein added to each and decinormal potassium hydroxide added to the water till the shades of pink were identical:—

Phosphate solution in c.c.	Alkali required for 50 c.c. of water.
0.00	0.02 c.c.
0.50	0.06 ..
1.00	0.08 ..
2.00	0.09 ..
3.00 made up	0.10 ..
4.00 to 50 c.c.	0.11 ..
5.00	0.12 ..
6.00	0.12 ..
7.00	0.12 ..
8.00	0.12 ..

For most solutions of this salt, therefore, a deduction of 0.1 c.c. would be the maximum correction necessary.

