The Determination of Boric Acid in Foodstuffs

BY ROBERT S. ALCOCK, M.A., PH.D.

THE volumetric method of Thomson[1] for the determination of boric acid in foodstuffs has been shown to be liable to considerable errors when applied to samples of food containing large proportions of phosphates or of fat and small proportions (such as those found naturally in certain fruits) of boric acid. The errors were traced to co-precipitation of calcium borate during removal of phosphates, incomplete removal of phosphate, or volatilisation of boric acid with glycerol derived from fat during the ashing of the food in an alkaline condition. Monier-Williams[2] modified the process by removal, first, of calcium salts and, secondly, of phosphoric acid as magnesium phosphate, so as to avoid the first two causes of error. These causes of error were reduced to a minimum by another modification of the process,[3] based on work in this laboratory, in which the exact conditions of alkalinity required for precipitation of calcium phosphate and retention in solution of calcium borate were specified; the removal of fat before ashing the sample was a part of this modification, of which other later investigators have made slight changes.

As the conditions for removal of phosphate require great care and the results obtained by titration of the boric acid may be vitiated by accidental presence of phosphoric acid or carbonic acid, it is desirable to have a confirmation of the results by some test specific for boric acid. At one time all results obtained in this laboratory[4] were confirmed by a method involving ashing of the sample with excess of alkali, solution of the ash in a known excess of hydrochloric acid, addition of alcohol and turmeric solution in definite proportions, and comparison with known amounts of boric acid treated in the same way. This method was generally satisfactory, but failed when applied to meat products or to articles containing appreciable proportions of iron.

The present method was developed for the determination of boric acid in phosphate-rich ashes and makes use of the ready esterification of boric acid with methyl alcohol, distillation of the methyl borate and final titration of the boric acid as in the Thomson process.

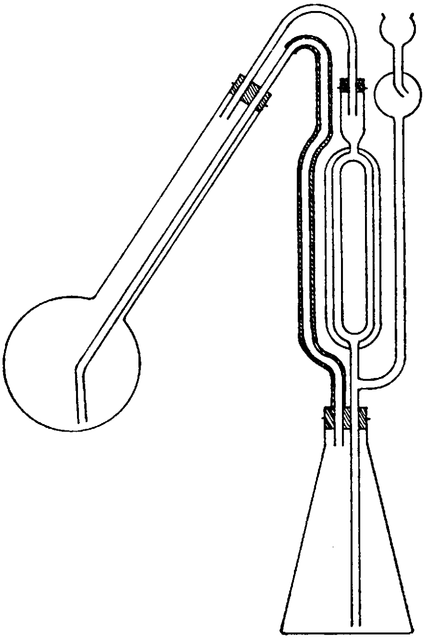

Fig. 1

APPARATUS.—The distillation is carried out in the apparatus here illustrated (Fig. 1). The acidified ash is boiled with methyl alcohol in a 300-ml. Kjeldahl flask, and the vapours are carried over into a double-surface condenser, the condenser being in a vertical position and the Kjeldahl flask inclined at 30° to it. The exit tube is elongated and dips below the surface of alkaline methyl alcohol in a 400-ml. conical flask. This flask stands on a tripod and gauze, and is strongly heated by a Bunsen burner. It is closed with a rubber stopper which carries, besides the condenser exit, another wide glass tube passing through a second hole in the bung of the Kjeldahl flask down into the methyl alcohol. The ascending limb of this tube must be lagged. This is conveniently done by enclosing it in a rubber tube.

Immediately above the stopper of the conical flask is a side-tube sealed on to the condenser outlet. This runs up close to the condenser and carries a splash-bulb and funnel. It serves to maintain atmospheric pressure inside the apparatus, to prevent possible losses through bumping in the receiver flask, and to make possible the washing out of the lower part of the condenser outlet.

PROCEDURE.—From 40 to 50 g. (or less when large amounts of boric acid are anticipated) of the sample are moistened with 10 ml. of 2 N sodium hydroxide solution. If much fat is present, it should be removed by solution in ether, as previously described.[3] The water is evaporated on a steam-bath, and the sample is ashed; there is no need to burn away all the carbon. The ash is transferred from the dish into the Kjeldahl flask, as little water as possible being used. The dish is finally washed with a few ml. of dilute sulphuric acid, and the ash in the flask is dissolved in a further quantity of the acid by warming. This removes most of the carbon dioxide and dissolves the lumps of ash. Methyl red is added, and 30 per cent. sodium hydroxide solution is run in until the colour changes to yellow. The liquid is concentrated to one or two ml. over a Bunsen flame, with continuous agitation. After cooling, 60 ml. of methyl alcohol and 1 ml. of methyl red solution are added.

Conc. sulphuric acid is then dropped in until, after shaking, the solution is strongly acid to the indicator. The flask is then attached to the apparatus, as is also the 400-ml. conical flask containing 0·5 ml. of *N* sodium hydroxide solution and a few drops of phenolphthalein solution. The Kjeldahl flask is heated and, when sufficient alcohol has collected in the conical flask, that too is strongly heated, so that the vapour bubbles vigorously through the acid liquid in the Kjeldahl flask. The flame beneath that flask is then adjusted so that 15 to 20 ml. of alcohol remain. If during the distillation the colour of the phenolphthalein in the conical flask is discharged, a further 0·5 ml. of sodium hydroxide solution is added.

After half-an-hour the flame beneath the Kjeldahl flask is replaced by a beaker of cold water, and as much of the methyl alcohol as possible is distilled up into it, and may be recovered later. The conical flask is removed, and the condenser tube, both inside and out, is washed into it with water. The remaining methyl alcohol is boiled off, and the solution is then made just acid to methyl red with $N/10$ sulphuric acid and boiled for a further five minutes to remove carbon dioxide. After cooling, the acidity is re-adjusted with $N/20$ sodium hydroxide solution until it is just not acid to methyl red. More phenolphthalein is added, and, after addition of 1 g. of mannitol, the titration is carried to the phenolphthalein change. A blank determination is made with water in place of a distillate. This result is usually of the order of 0·1 ml. of $N/20$ sodium hydroxide solution (1 ml. of sodium hydroxide solution $\equiv$ 0·0031 g. boric acid).

Conditions of Distillation.—The conditions governing the distillation are illustrated in the following tables:

TABLE I

30 mg. of boric acid; 60 ml. of methyl alcohol; distilled 30 minutes

Acid	Methyl alcohol strength Per Cent.	Boric acid recovered Per Cent.
H_2SO_4	90	99·5
H_2SO_4	95	99·5
H_2SO_4	100	99·5
H_3PO_4	90	82·0
H_3PO_4	100	96·0

Table I shows that, given a sufficient strength of acid (excess of sulphuric over phosphate in the ash) amounts up to 10 per cent. of water in the alcohol do not influence the rate of distillation. When phosphoric acid is used the rate is affected.

TABLE II

1 g. of "artificial ash" plus boric acid; 60 ml. of methyl alcohol; excess of sulphuric acid; distillation 30 minutes

Boric acid mg.	Titration (less blank) $N/20$ NaOH ml.	Apparent boric acid mg.	Percentage error
0	0·05	0·15	—
5	1·65	5·12	2·4
10	3·28	10·15	1·5
30	9·77	30·18	0·6

Table II indicates the error likely to arise from phosphoric acid being carried over in the vapour. An artificial ash was made of equal weights of calcium chloride, kieselguhr, sodium sulphate and disodium phosphate. One g. of this mixture was placed in the distillation flask for each experiment. The phosphate coming over corresponds to some 0·15 mg. of boric acid (3 p.p.m. on 50 g. of sample). In practice, the figures for actual ashes seem to be less than this. Such a degree of accuracy is seldom required, but when very small amounts of boric acid are involved—of the order of 1 mg.—the distillation should be followed by the usual precipitation, after adding a drop or two of 10 per cent. calcium chloride solution. The phosphate comes over as a result of esterification, not through splashing, as more appears when a small amount of phosphate, acidified with sulphuric acid, is in the distillation flask, than when syrupy phosphoric acid itself (2 ml.) is used for acidification. Sulphuric acid is used, as the lower *p*H accelerates the distillation.

TABLE III

Boric acid; 60 ml. of methyl alcohol; sulphuric acid

Boric acid mg.	Time Minutes	Boric acid recovered mg.	Recovery Per Cent.
10	5	8·1	81
10	15	10·0	100
20	15	19·8	99
20	15	20·0	100
30	15	25·7	86
30	20	28·8	92
30	20	29·5	98
30	30	29·8	99·3
30	30	30·0	100

Table III summarises the experiments on the time required for distillation. In every instance the liquid in the receiver flask was boiled as vigorously as possible. It is seen that up to 20 mg. come over quantitatively in 15 minutes, while 30 mg. require longer. Half-an-hour's distillation is a usual routine time, as amounts of more than 30 mg. are seldom met with. If, however, on titration, more than 10 ml. of $N/20$ sodium hydroxide solution are required, the distillation can be carried on for a further half-hour period, when the remainder, if any, will be recovered.

TABLE IV

Sample	Weight g.	Boric acid added mg.	Titration (less blank) $N/20$ NaOH ml.	Boric acid found mg.	Recovery Per Cent.
Currants A	40	0	1·55	4·8	—
,, A	40	20	8·00	24·8	100
Flour B	50	0	0·3	0·9	—
,, B	50	20	6·7	20·8	99·5
,, B	50	40	13·3	41·2	100·7

Table IV gives two examples of the many determinations that have been made on various materials. It will be seen that the boric acid added to the sample before ashing was quantitatively accounted for in the final titration.

SUMMARY.—A method for the determination of boric acid in foodstuffs, using the distillation of methyl borate followed by a mannitol titration, is described.

A continuous steam-distillation apparatus, used in the method, is illustrated.

My thanks are due to Dr. J. J. Fox, the Government Chemist, for permission to publish this work.

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