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THE DETERMINATION OF BORIC ACID IN CIDER, FRUITS, ETC.

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THE natural occurrence of traces of boric acid in certain plants, trees, fruits, etc., has been pointed out by various observers,* and the presence of this acid in wine, cider, and allied products follows as a natural consequence. These facts were confirmed at the outset of our experiments upon the presence of preservatives in cider. All the ciders examined were found to contain a small but distinct amount of boric acid, and a similar result was obtained by the examination of various fruits, such as apples, pears, quinces, grapes, and pomegranates. Hence boric acid in cider, perry, wine, etc., cannot be regarded as an adulteration unless the amount is materially greater than can be fairly ascribed to natural causes. Our experiments have been chiefly made on cider and apples, and the following observations have special reference to these substances.

The *detection* of boric acid in cider and fruits can be readily effected by evaporating 20 c.c. of cider or apple-juice to dryness and igniting the residue, or by directly igniting 25 grammes of apple or other fruit. The ash is rendered distinctly acid to litmus with dilute hydrochloric acid, a piece of turmeric paper partially immersed in the liquid, and the whole evaporated to dryness on the water-bath in a flat porcelain dish. The residue is further dried in the water-oven for a short time. In the presence of boric acid the turmeric paper will acquire a brownish-red colour, which, on being moistened with a drop of caustic soda solution, is changed into a variety of colours, chiefly green and purple.

The *quantitative determination* of boric acid in cider and fruits, etc., we have found very troublesome, and this has been the subject of numerous experiments.

* The following is a summary of the chief papers on this subject. The English references only are given: Boric acid in trees and plants, E. Bechi, *J. C. S.*, lviii., 656; *J. C. S. I.*, ix., 635; in hops and (therefore) beer, but not in malt or barley, J. Brand, *ANALYST*, xviii., 135; in all parts of the vine, Baumert, Rising (reference not known); in peach-trees and peaches, Knorr (reference not known); in grapes and wine, apples, pears, radishes and lettuce, M. Gassend, *Pharm. Journ.*, xxiii., 6; *J. C. S.*, lxii., 93; in various fruits, A. Hebebrand, *ANALYST*, 1903, xxviii., 37; in fruits generally, E. Hotter, *J. C. S.*, 1890, lviii., 1338; in the ash of fruits and vine-leaves, H. Jay, *J. C. S.*, lxx., ii., 327; in wine, water-melon, etc., C. A. Crampton, *J. S. C. I.*, viii., 569; in wines, cider, perry and fruits, Jay and Dupasquier, *J. C. S.*, lxx., ii., 76, 327; absent from natural wines, Villiers and Fayolle, *J. C. S.*, lxx., ii., 75.

The difficulty of the analysis is enhanced owing to the minute quantity of boric acid present, and the determination is further complicated by the presence of phosphates. These salts render inapplicable the direct employment of R. T. Thomson's well-known process (*J. S. C. I.*, 1893, p. 433), in which the solution is first made neutral to methyl orange and then titrated with standard caustic soda solution and phenolphthalein in presence of glycerin, the end-point of the titration corresponding to the formation of NaBO_2 . The unsuitability of Thomson's method without modification in the presence of phosphates is due to the fact that while phosphates of the formula $\text{M.H}_2\text{PO}_4$ are neutral to methyl orange, they are acid to phenolphthalein. We have made a number of experiments with a view of overcoming the difficulty caused by the presence of phosphates in quantity, but without success. It does not seem possible to make an allowance for the disturbing action of the phosphates; nor does the addition of glycerin after the aqueous liquid has been rendered neutral to phenolphthalein overcome the difficulty, owing to the fact that boric acid is distinctly, but indefinitely, acid to phenolphthalein, even in the absence of glycerin.

F. Parmentier (*Comptes rend.*, 1891, cxiii., 41; *abst. J. C. S.*, lx., 1551) has devised a process for the determination of small quantities of boric acid, based on the solubility of borates in a solution of ammonium nitrate. The method has been found quite useless for our special purpose, owing to the fact that it is impossible to titrate boric acid with alkalis in the presence of large quantities of ammonium nitrate, since ammonia is set free during the titration. Boric acid is, moreover, more or less volatile when heated with ammonia or ammonium nitrate.

After a large number of experiments, the following method for the determination of boric acid in cider, etc., based on the moderate solubility of calcium borate in water, was devised: About 100 c.c. of cider or other liquid is evaporated to dryness with a few cubic centimetres of a 10 per cent. solution of calcium chloride; or, in the case of fruits, about 50 grammes weight is cut up into small pieces, and the solution of calcium chloride poured over the mass, which is then evaporated to dryness. The dry residue is well charred, boiled with about 150 c.c. of distilled water, and the liquid filtered. The carbonaceous residue is thoroughly incinerated at a moderate temperature, and when cold boiled with a further quantity of 150 c.c. of water, and allowed to stand in the cold for some hours, or preferably overnight. The liquid is then filtered cold, and the filtrate added to the first extract.* The mixed aqueous extracts are next evaporated to a volume of 25 or 30 c.c., and after cooling neutralized by decinormal acid, using methyl orange as indicator.† An equal volume of glycerin is next added, and the liquid titrated with phenolphthalein and $\frac{N}{20}$ caustic soda solution (free from carbonate). About 10 c.c. more glycerin should now be added, when, if the titration is complete, the red coloration will remain. Each c.c. of the $\frac{N}{20}$ normal solution of caustic soda required represents 0.00175 gramme of boric anhydride, B_2O_3 ; 0.0031 gramme of crystallized boric acid, H_3BO_3 ; or 0.004775 gramme of crystallized borax, $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$. The above process gives good results when the amount of boric acid present in the sample taken is not less than 0.005 gramme.

* It is desirable to extract the residue for a third time with hot water, allowing the liquid when cold to stand for some time before filtration. This third extract, when titrated separately, will generally be found to be free from boric acid. If not, the amount found must be added to that already extracted.

† Care should be taken that all the borate is in solution before the titration is begun.

We have also examined the well-known method for the determination of boric acid based on the volatility of methyl borate, and find the following to be the best method of operating: A suitable quantity of the substance under examination is treated with calcium chloride solution as already described, and well charred, and the main portion of the salts extracted with about 50 c.c. of water. This aqueous extract is transferred to a distillation flask of about 100 c.c. capacity, and cautiously evaporated nearly to dryness over a naked flame. Meanwhile the charred residue is incinerated, the ash (nearly white) moistened with 2 c.c. of strong sulphuric acid, and the mixture warmed. When the evolution of hydrochloric acid gas is nearly at an end, the acidified residue is transferred to the distilling-flask containing the evaporated aqueous extracts. The last portions are washed in with 10 c.c. of methyl alcohol,* the flask immersed in a boiling water-bath, and the liquid distilled almost to dryness. A further addition of 10 c.c. of methyl alcohol is then made, and the distillation repeated. As many as six such treatments are usually required. Between each distillation the residue in the flask should be allowed to cool before the next addition of methyl alcohol is made. The residue finally contained in the distilling flask should be tested by the flame reaction with alcohol to insure that the whole of the boric acid has been volatilized. If this is not found to be the case, the distillation should be repeated once or twice more.

The alcoholic vapours are passed into 25 c.c. of water contained in a flask, the end of the condenser-tube dipping into the liquid. When the process is completed, the distillate is evaporated over a water-bath until free from alcohol. By this treatment the methyl borate is hydrolysed, and the boric acid left in a free state. The residual liquid is diluted with a little water and rendered exactly neutral to methyl orange. An equal volume of glycerin is then added, and the liquid titrated with $\frac{1}{20}$ normal caustic soda and phenolphthalein as already described. The glycerin used in these processes should be rendered neutral to phenolphthalein just before use, as it is generally slightly acid in reaction.

In many of the processes already in use for the separation of boric acid by distillation the methyl borate is distilled into a solution of caustic soda, and after evaporation of the alcohol the aqueous liquid is titrated in the usual way. In our experience, however, when an alkali was used, the results were always above the truth, even when specially purified methyl alcohol was employed. For this reason the use of caustic soda is not to be recommended, and, as previous experiments have shown, is quite unnecessary (see Allen's "Commercial Organic Analysis," vol. iv., footnote to p. 178).

The following results were obtained in a series of experiments made to test the accuracy of the processes here described. A known weight of crystallized borax was added either to a mixture of calcium chloride, magnesium sulphate and sodium phosphate, or to a known weight of apple. In the latter case, an exactly similar portion and weight of the same apple was treated with calcium chloride, and the boric acid determined and deducted from that found in the other portion to which borax had been added:

* Ordinary wood-spirit of good quality, purified by redistillation over caustic potash, is suitable for this purpose.

	Number of Experiment.	Substances Added to the Borax.	Borax Taken.	Borax Found.
Extraction method	1. }	Calcium chloride, magnesium sulphate, and sodium phosphate	Gramme. { 0.200	Gramme. 0.198
	2. } ...		{ 0.200	0.204
	3. } ...		{ 0.020	0.019
	4. } ...		{ 0.020	0.020
Distillation method	5. ...	None	0.200	0.197
	6. ...	None	0.020	0.022
	7. ...	Sodium phosphate	0.200	0.201
	8. ...	Sodium phosphate	0.020	0.023

Richmond and Harrison's method (ANALYST, 1902, xxvii., 197) for the determination of boric acid in butter is rapid and accurate for its intended purpose, but the presence of phosphates in fruits and fruit products renders the process unsuitable for the determination of boric acid in these substances.

A colorimetric method for the determination of boric acid in milk and other foods has been devised by Cassal and Gerrans (*British Food Journal*, October, 1902). The process is based upon the fact that in the presence of oxalic acid the colouring-matter of turmeric forms with boric acid an intense magenta-red colour more delicate than the ordinary turmeric reaction (that is, when obtained in the absence of oxalic acid), and permanent for many hours. The alcoholic solution of the colour formed in the reaction is compared with that from a known weight of boric acid. The method is said to be reliable and accurate, but appears to be rather lengthy and tedious.

The two processes described at the beginning of this paper are obviously applicable to a considerable number of other substances besides cider and fruits; and their employment will, we believe, be found to result in a large saving of time, while the accuracy attained will at least equal that of other more tedious methods now in use.

The following table shows the proportion of boric acid contained in various fruits and ciders, etc., examined by us:

Fruits, etc.	Boric Acid, H ₃ BO ₃ .
1. Apple (Norfolk)	0.009 per cent.
2. Apple (Fox Whelp)	0.013 "
3. Apple (Old Fox Whelp)	0.011 "
4. Pear, No. 1	0.007 "
5. Pear, No. 2	0.016 "
6. Quince	0.016 "
7. Pomegranate	0.005 "
8. Grapes	0.004 "
9. Norfolk Cider	0.009 gramme per 100 c.c.
10. Hereford Cider	0.017 " " "
11. Devonshire Cider	0.004 " " "
12. Apple Juice (Devon)	0.004 " " "

NOTE.—In Mr. Allen's paper on "Cider" (ANALYST, xxvii., p. 183) the quantities of boric acid are stated in terms of B₂O₃, and not H₃BO₃, as might be supposed.