

# THE ANALYST.

AUGUST, 1891.

## EXPERIMENTS ON THE ESTIMATION OF BORIC ACID.

By OTTO HEHNER.

(Read at Meeting, June 3rd, 1891.)

THE separation of boric acid by means of distillation with methyl alcohol in an acid solution has been recognised by a number of investigators as being capable of securing rapid and accurate results, and certainly furnishes the readiest analytical means for the determination of boric acid in articles of food. The method is at present generally attributed to Gooch; but it seems to have originated somewhat earlier, or possibly independently, with T. Rosenbladt (*Zeit. f. Anal. Chem.*, Vol. xxvi., p. 18), who distilled a sulphuric acid solution with methyl alcohol, fixed the boric acid contained in the distillate by the addition of a weighed quantity of magnesia, evaporating and igniting. Gooch, recognising that magnesia fixed boric acid only incompletely, or only after some hours of maceration, substituted for it caustic lime, a weighed quantity of which was placed in the receiver, the contents being afterwards transferred to a weighed platinum dish, and the residue obtained by evaporation ignited over the blow-pipe.

Penfield and Sperry (*Amer. Jour. of Sc.* xxxiv., p. 222), recognising the difficulty of igniting to constant weight a comparatively large quantity of caustic lime in a necessarily large platinum dish, modified the method by collecting the distillate, adding it to a weighed quantity of lime contained in a dish, evaporating, scraping out the contents of the dish into a weighed platinum crucible, dissolving adhering particles from the large dish with nitric acid, and adding the solution to the contents of the crucible, which is then ignited to constant weight. This method, clumsy as the transference of a dry residue from one vessel to another must necessarily be, is improved by Cassal (*ANALYST*, Vol. XV., p. 230), who collects the distillate at once into a weighed platinum dish containing the lime; but this modification of the process does not remove the obvious difficulty of igniting upwards of a gramme of lime to a constant weight in a large platinum basin.

I should here state that the use of lime for fixing boric acid is due to H. Gilbert (*Repert. Anal. Chem.*, Vol. v., p. 375), so that the Gooch method is really a combination of Rosenbladt's distillation method and Gilbert's ignition process.

In order to substitute for the lime other substances capable of fixing boric acid, the investigation was undertaken, of which the results are recorded in this paper. Although some of my results are negative, yet they may be worthy of being brought before you, as clearing up certain points in the chemistry of boric acid about which some difference of opinion existed.

### *Experiments to fix boric acid with ammonia.*

0.4807 gramme of pure boric acid ( $\text{H BO}$ ) were placed in a weighed platinum dish, dissolved in water; ammonia was added, the solution evaporated, and the residue

obtained first dried at  $100^{\circ}\text{C}$ ., afterwards ignited over an argand to constant weight.

Residue at  $100^{\circ}\text{C}$ . . . 0.4138, or 86.08 per cent.

Ignited residue . . . 0.2560, or 53.25 per cent.

Theory for  $\text{B}_2\text{O}_3$  56.45 per cent. 0.0898 gramme  $\text{H}_3\text{BO}_3$ , similarly treated with ammonia, yielded 0.0768 gramme at  $100^{\circ}\text{C}$ ., or 85.52 per cent. This residue, repeatedly evaporated with ammonia, diminished steadily in weight to 0.0620, 0.0432, 0.0340, and 0.0263 gramme, or 34.2 per cent., at which point the evaporation was not continued, it being demonstrated that boric acid is volatile in presence of ammonia.

This agrees with the observation of Bodewig (*Zeit. fur. Anal. Chem.*, Vol. xxiii., p. 149), who states that upon evaporation of a solution of ammonium borate on the water-bath a point is reached at which the vapours were alkaline, but the liquor acid.

*Experiments to fix with sodium carbonate.*

It is well known that boric acid can be completely fixed by sodium carbonate; but the statements as to the amount of carbonic acid driven out by the boric acid are very contradictory. According to Bloxam, one molecule of boric acid displaces on gentle ignition one molecule of carbonic acid, but at a strong red heat from 1.5 to 2.3 molecules; whilst according to Schaffgotsh one equivalent of  $\text{H BO}_3$  expels all carbonic acid from two molecules of sodium carbonate.

I could not obtain, in the few experiments I made in this direction, any results of sufficient accuracy for analytical purposes. To 0.5598 gramme pure boric acid ( $\text{H}_3\text{BO}_3$ ), 2.7824 grammes dry pure  $\text{Na}_2\text{CO}_3$  were added, and the mixture heated to constant weight. The loss, including 43.55 per cent. of water yielded by the boric acid amounted to 102.03 per cent. of the boric acid taken, corresponding to 58.48 per cent. of  $\text{CO}_2$ , or for one equivalent of  $\text{H}_3\text{BO}_3$ , 0.824 of an equivalent of  $\text{CO}_2$ .

In a second experiment the loss amounted to 104.89 per cent., or 61.34 per cent.  $\text{CO}_2$ , equal to 0.864 equivalents of  $\text{CO}_2$ .

As Bloxam's statements are doubtless for the old equivalents, his figures become comparable by halving them, when they are 0.75 to 1.15.

It is almost impossible to obtain constant weights, and I, therefore, abandoned the attempt.

*Experiments to fix with sodium phosphate.*

A solution of sodium phosphate was made, containing about 20 grammes pure crystallised sodium phosphate per litre.

25 c.c. of this were evaporated, the residue first very gently heated over the smallest possible argand flame (to avoid loss by spurting), and then gradually over a large argand flame, the residue never being permitted to become red-hot. The residue weighed 0.1856 gramme. According to the fifth edition of "Fresenius' Quantitative Analysis," at this temperature all water of crystallisation is driven off; but not constitutional water. This statement, however, is not correct, because on strong ignition of the above residue over a Bunsen flame, the weight remained perfectly constant. In the newest edition of Fresenius, I must add, this erroneous statement is omitted.

0.0632 gramme pure boric acid ( $\text{H}_3\text{BO}_3$ ) was evaporated with 10 c.c. of the phosphate solution, yielding 0.0742  $\text{Na}_2\text{P}_2\text{O}_7$ . The residue consisted of a perfectly transparent gummy mass, and was ignited most cautiously, as it is very apt to spurt, over a small

argand flame in a covered platinum basin, the heat being ultimately increased until the residue had fused. It weighed 0.1082 gramme, containing, therefore, 0.034 gramme  $B_2O_3$ , against 0.0356  $B_2O_3$  taken, loss 0.0016.

0.0691 gramme  $H_3BO_3$ , corresponding to 0.0390 gramme  $B_2O_3$ , plus 20 c.c. phosphate solution (0.1483 pyrophosphate), yielded 0.1863 gramme ignited residue, or 0.0380  $B_2O_3$  — loss 0.0010.

This residue was evaporated with repeated quantities of water, in all 200 c.c.; the dry mass was again ignited; loss of weight, none.

0.1100 gramme  $H_3BO_3$ , equal to 0.0621 gramme  $B_2O_3$ , was evaporated with 50 c.c. sodium phosphate solution (0.3712 pyrophosphate), yielded 0.4340 gramme residue, or 0.0628 gramme  $B_2O_3$  + 0.0007.

0.1008 gramme  $H_3BO_3$ , equal to 0.0569  $B_2O_3$ , evaporated with 35 c.c. sodium phosphate solution, containing 0.2598 gramme pyrophosphate, and then with 250 c.c. of distilled water in several portions. Ignited residue 0.3166, equal to 0.0568  $B_2O_3$ ; loss 0.0001.

To ascertain the minimum quantity of phosphate necessary to fix the boric acid a few experiments were made, which indicated, as far as they went, that one molecule of  $Na_2HPO_4$  is capable of binding 2 molecules of  $H_3BO_3$ , the resulting mass consisting of sodium metaphosphate and borax.

To 0.1785 gramme  $H_3BO_3$  a quantity of sodium phosphate was added, capable of yielding 0.1916 gramme of pyrophosphate, this being the above molecular proportion. Residue obtained, 0.2894 gramme, or 0.0978  $B_2O_3$ ; loss, 0.0029.

0.1792 gramme  $H_3BO_3$  (0.1015  $B_2O_3$ ) evaporated with 25 c.c. of water, without the addition of phosphate, and the residue ignited, yielded 0.0889 gramme  $B_2O_3$ , a loss of 0.0122 gramme, plainly showing the fixing influence of the sodium phosphate.

To ascertain whether this was in any way affected by the presence of alcohol, 0.1606 gramme  $H_3BO_3$  (0.0906  $B_2O_3$ ) were dissolved in 100 c.c. methylated spirit, 150 c.c. water added, and a quantity of phosphate solution, yielding 0.3832 gramme pyrophosphate; the mixture was then boiled in a covered beaker until all alcohol had evaporated; the remainder was transferred to a weighed platinum basin, evaporated, and the residue ignited. Obtained 0.4710, or 0.0878  $B_2O_3$ , a loss of 0.0028.

The advantage of adding a soluble salt, which easily parts with its water, and which combines by direct addition with the boric acid to be estimated over a substance like lime, which incrustates the vessels and attracts carbonic acid, which is difficult to remove, is obvious. I am not sure that sodium phosphate is the best possible salt that could be chosen; but the results yielded by its use are fairly satisfactory, and certainly very rapidly obtained. I only ascertained after the above analyses were completed that Stolba had long ago proposed to fix boric acid in solution by adding a weighed quantity of borax (about four times the weight), and igniting the residue (*Jour. f. Prac. Chem.*, xc., p. 479). I have made experiments in this direction and find that very good results may be obtained, but that the greatest caution is necessary to avoid loss by crepitation during the ignition of the residue.

Incidentally I may observe that boric acid cannot be alkalimetrically determined, as no indicator is at present known which allows of anything like a sharp titration;

and this in spite of the curious fact that Guyard (*Bullet. Soc. Chem.*, xl., p. 422) has recommended pure crystallised boric acid as an alkalimetric standard; logwood, which he recommends as an indicator, fails utterly to yield a sharp colour change with the acid.

I further wish to correct the statement found in books, that boric acid, when heated in a water-oven at  $100^{\circ}\text{C}$ . loses two-thirds of its water. Boric acid placed in a water-oven loses weight steadily, until the whole of it is volatilised, and no definite point at any stage can be observed.

Thus 0.0736 gramme  $\text{H}_3\text{BO}$  kept for three or four days at  $100^{\circ}\text{C}$ . diminished to 0.0179 gramme, or 24.3 per cent. of the original weight. This small residue ignited yielded 0.0108  $\text{B}_2\text{O}_3$ , or 60.34 per cent. of its weight. If the residue had consisted of  $\text{H}_2\text{B}_2\text{O}_4$ , as stated in the books, 72.7 per cent. ought to have remained. Of course, the determination cannot be very exact, seeing that it was made with a few milligrammes only; but the experiment proves sufficiently that by mere drying in the water bath no definite stage of composition can be reached.

Lastly, I record the observation, that if *anhydrous* boric acid is dissolved in cold water, the turmeric reaction is not obtained, or, at least, only exceedingly faintly, in comparison with an equivalent proportion of hydrated acid, whilst a strong reaction is at once obtained if a trace of mineral acid is added. This furnishes proof that boric anhydride dissolves as such, and does not immediately hydrate on being dissolved in water. The pieces of turmeric paper dried with solution of anhydrous boric acid gradually turn red when allowed to lie in the air of the laboratory.

This observation suggests some interesting speculations, with the testing of which I am at present engaged—namely, does there exist a series of pyroborates, just as there are pyrophosphates and pyrosulphates, and can their existence be analytically proved? In the case of the phosphates, the colour of the silver salts at once shows the difference, whilst in that of the pyrosulphates, two reactions are due to E. Drechsel (*Jour. f. Pract. Chemie*, v., p. 367), distinguishing pyro from acid sulphates. Anhydrous borax is, of course, pyroborate of sodium,  $\text{Na}_2\text{B}_4\text{O}_7$ ; but all the reactions of borates are those of the ortho acid  $\text{H}_3\text{BO}_3$ , and ordinary borax is certainly the acid ortho salt. The difficulty experienced in rendering boric acid anhydrous renders it most unlikely that by simple addition of soda in an aqueous solution, a molecule of anhydrous acid is produced, which combines with the neutral salt  $\text{Na}_2\text{B}_2\text{O}_4$ . Borax according to this view would be  $\text{Na}_2\text{H}_2\text{B}_3\text{O}_8 + 9 \text{H}_2\text{O}$ , and boric acid  $\text{H}_4\text{B}_4\text{O}_8 + \text{H}_2\text{O}$ . The evidence that boric acid is tribasic is exceedingly slight.

#### DISCUSSION.

MR. BLOUNT said that Mr. Hehner's method was extremely ingenious; but the objection to the lime process was not insuperable. He himself was in the habit of igniting lime to perfect causticity by the simple plan of using a muffle. It was the use of the blow-pipe, which he regarded as extremely unsuitable for this purpose, which caused all the trouble.

MR. CASSAL said that the substitution of phosphate of soda for lime, in the method suggested by Mr. Hehner, was certainly a valuable improvement, since under the most favourable circumstances, to get the lime to constant weight was very troublesome. He desired to take the opportunity of stating that in abstracts which had appeared of a

---

paper read some time ago by himself, the introduction of methyl alcohol to separate boric acid had been erroneously attributed to him. He could confirm what Mr. Hohner had said about the turmeric test; it was necessary to add hydrochloric acid when dealing with anhydrous boric acid.

---