

# Volumetric determination of boric acid in the medium of anhydrous acetic acid

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Boric acid can be determined in the medium of anhydrous acetic acid after its transformation to tetrafluoroboric acid by titrating with the volumetric solution of sodium or potassium acetate, diethylaniline or pyridine in anhydrous acetic acid. A potentiometric or conductometric indication is to be used. The amounts of 1—10 millimoles of boric acid were determined with a relative error which did not exceed 0.3%.

Борную кислоту можно определить в среде безводной уксусной кислоты после перевода первой на тетрафторборную кислоту, титрованием растворами ацетата натрия или калия, диэтиланилина или пиридина в безводной уксусной кислоте при помощи потенциметрического или кондуктометрического определения. Количества 1—10 ммоль борной кислоты были определены с относительной ошибкой не больше 0,3%.

The determinations of boric acid in nonaqueous media by titration have been given little attention. *Moss* and coworkers [1] titrated boric acid with sodium alcoholate in the medium of ethylenediamine. *Bork* [2] determined boric acid by titrating with the volumetric solution of calcium chloride in the medium of anhydrous acetic acid. The medium of anhydrous acetic acid is most frequently used for the determination of bases [3, 4]. *Kreshkov* [4] used this medium for the determination of strong acids, too. Boric acid, however, does not exhibit sufficiently acid properties usable for its alkalimetric determination in this medium. On the other hand, in this medium we can alkalimetrically determine tetrafluoroboric acid which arises from boric acid and hydrogen fluoride in the presence of acetic anhydride.

## Experimental

### *Chemicals and solutions*

Anhydrous acetic acid, acetic anhydride, and boric acid were anal. grade chemicals purified by distillation, freezing, and recrystallization. The solutions of hydrofluoric acid

were prepared from the 38% (w/w) aqueous solution of this acid by adding acetic anhydride and diluting with anhydrous acetic acid. The content of water in acetic acid and its solutions was checked by the method of K. Fischer and was not greater than 0.02% (w/w).

### *Instruments and equipment*

The manipulation with the solutions of hydrofluoric acid was carried out in polypropylene vessels. The titrations were performed in a closed four-necked polytetrafluoroethylene (teflon) vessel in the atmosphere of dried argon. A gold or chloranil [5] electrode was used for potentiometric indication. It was connected with a modified calomel electrode filled with the saturated solution of NaCl in water. The conductive connection with the titrated solution was ensured by a bridge filled with the saturated solution of sodium perchlorate in anhydrous acetic acid. The conductivity cell consisted of a couple of platinized platinum electrodes. The liquid junction and electrode holders were made of teflon or polypropylene in order to prevent the reaction of glass with fluorides. The conductivity was measured with an instrument Konduktomat (Polymetron, Switzerland). The potentiometric measurements were carried out with an instrument Potentiometer E 353 (Metrohm, Switzerland).

### *Working procedure*

The weighed amount of boric acid or its solution in anhydrous acetic acid in the amounts 1—10 millimoles was put into the titration vessel containing 30 ml of 0.4 M solution of hydrofluoric acid in acetic acid with 10% (w/w) of acetic anhydride. After a few seconds the electrodes were inserted and the mixture was titrated with 0.05—1.0 M solution of the volumetric agent. In most cases, the solution of sodium acetate in anhydrous acetic acid was used as volumetric agent. But the solutions of potassium acetate, diethylaniline, and pyridine

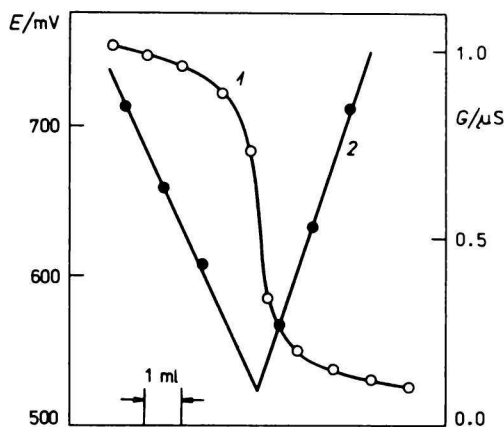


Fig. 1. Titration curve for 3 millimoles of tetrafluoroboric acid.

1. Potentiometric indication; 2. conductometric indication.

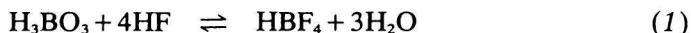
Initial volume 50 ml, titrating agent 0.5 M sodium acetate. The chloranil indication electrode was used for potentiometric indication.

were also used. The equipment rendered possible simultaneous potentiometric and conductometric indication. The titration curves are represented in Fig. 1. The end point was found by calculation or usual graphical methods [6]. The end point found potentiometrically and conductometrically gave identical values of the consumption of titrating agent.

### Results and discussion

The alkalimetric determination of the weak boric acid in the protogenic medium of anhydrous acetic acid is feasible by transforming boric acid to the monobasic strong tetrafluoroboric acid using excess hydrogen fluoride and acetic anhydride.

The formation of tetrafluoroboric acid and dehydration of its solution can be described as follows



The equilibria of exothermic reactions (1) and (2) are considerably shifted in favour of the formation of reaction products and are rapidly established. The dehydration reaction is catalyzed by the presence of the proton from the dissociated tetrafluoroboric acid. The existence and properties of tetrafluoroboric acid were investigated in aqueous medium [7—9] as well as in the medium of anhydrous acetic acid [10—12]. Tetrafluoroboric acid reacts with water at increasing pH in aqueous medium to give trifluorohydroxyboric acid and other products of gradual hydrolysis. Its determination in aqueous medium by alkalimetric titration does not afford analytically usable results. Neither boric acid nor hydrofluoric acid can be alkalimetrically titrated in the protogenic medium of anhydrous acetic acid because of their slight dissociation as we have found by potentiometric and conductometric measurements. An excess of acetic anhydride up to 10% (w/w) does not affect the correctness of determination and, on the contrary, it may be used for dehydration of the solutions of boric acid. The use of potassium acetate as a volumetric agent results in the formation of a little soluble potassium salt —  $\text{KBF}_4$ . The more basic acetates of pyridine and diethylammonium give titration curves with greater overall change in EMF and greater slope, but these benefits in estimation of correctness are suppressed by the inaccuracy due to indirect standardization and tedious preparation of the volumetric solution.

As to the indication electrodes, the chloranil electrode proved to be the best. Its potential was established rapidly enough and was well reproducible. The overall change in EMF during titration and slope in the point of inflexion were greater than those obtained with gold electrode. The graphite electrode modified according to [3] may be also used for indication. The glass electrode is not suited to indication.

The determination is impaired by the presence of basic substances and strong mineral acids in the titration medium.

The results obtained by titrating 1—10 millimoles of boric acid are given in Table 1. The boric acid used may be regarded as an alkalimetric standard [13].

As the volumetric solutions of sodium acetate were prepared from sodium carbonate possessing purity of a reference material, the accuracy of the method could be tested.

Table 1

Results of the determination of boric acid

Given, mg	Found <sup>a</sup> , mg
61.8	61.7 ± 0.3
185.4	184.8 ± 0.4
309.0	308.4 ± 1.0
494.4	493.0 ± 2.1
618.0	617.7 ± 2.4

a) The results are average values of 5 determinations with the interval of reliability calculated for 95% probability by procedure according to [13].

The equation of the linear relationship between the determined amount and the given amount of boric acid is calculated from the data given in Table 1 and has the form

$$y = 0.999x - 0.33 \quad [\text{mg}]$$

where  $y$  is the determined amount of boric acid and  $x$  is the given amount of boric acid. The method has a small negative systematic additive error and a very small negative systematic proportional error. The reproducibility of the method is good and by the use of the described equipment and working procedure the standard deviation of individual determination was not greater than 0.6%. The precision of determination may be enhanced by perfect thermostating of the titration equipment.

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