Analytical Studies of Boron. VI. Determination of Boron Using Ion Exchange Resin

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Introduction

When boric acid was treated with a cation exchange resin, it could be separated quantitatively from cations which coexisted with boric acid. Such a separation procedure was reported by the author[1] and applied to the determination of boron in steels[2], silicon[3] and silicate rocks[4]. For the determination of boron, a sample solution was passed through a cation exchange resin column and the effluent was titrated with an alkaline solution. However, weak acids such as phosphoric and silicic interfere with the titration.

After a solution containing a small amount of boron was treated with an ion exchange resin column, a colorimetric procedure was applied to the effluent. The results were satisfactory.

Treatment of Boric Acid Solution with an Ion Exchange Resin Column

Reagents and Chemicals: *Resins*; Cation exchange resins, Amberlite IR-120 and Diaion K in Na- or H-form.

Anion exchange resins, Amberlite IRA-400 and Diaion A in Cl- or OH-form.

Washing solution; Three normal aqueous solution of chemically pure grade sodium hydroxide, hydrochloric acid and sodium chloride.

Sodium carbonate; Guaranteed grade sodium carbonate.

pH regulating solution; One normal guaranteed grade sodium hydroxide. One normal guaranteed grade hydrochloric acid.

Standard boric acid solution; Guaranteed grade boric acid was recystallized and a solution containing 1.1mg. B/cc. was prepared. This solution was diluted to the given concentration before use.

Preliminary Experiment: Standard boric acid solutions containing 1 γ—20 mg. B were taken, and made up to 20 cc. with distilled water. These solutions were divided into 3 groups. The first group, (a), contained 1—20 mg. B, the second, (b), 10—500 γB, and the third, (c), 1—9 γB.

One normal hydrochloric acid and 1 N sodium hydroxide solution were added to 20 cc. of the boric acid solution and its pH was adjusted to various values. The resulting solution was passed through a cation exchange resin column. The column was washed with distilled water, and a titration method was applied to the (a) group. To the (b) group containing 10—500 γB was applied the colorimetric procedure using acetone-curcumin. The effluent and the washing solution were combined together and diluted to 100 cc. The resulting solution was made alkaline with solid sodium carbonate, evaporated on a water bath,

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1) S. Muto, *J. Chem. Soc. Japan, Pur. Chem. Sec.*, **72**, 976 (1951).

2) J. R. Martin and J. R. Hays, *Anal. Chem.*, **24**, 182 (1952).

3) C. L. Luke, ibid., **27**, 1150 (1955).

4) H. Kramer, ibid., **27**, 144 (1955).

and then the colorimetric procedure was applied. The same procedure was applied to the (c) group. The results are shown in Table I, II and III.

TABLE I
DETERMINATION OF BORON IN (a) GROUP. (mg. B)

Taken	0.0	1.1	5.5	11.	22.
Found	0.01	1.14	5.50	10.9	22.1
	−0.02	1.14	5.47	10.9	22.2
	0.02	1.08	5.51	11.0	21.7
Mean	0.00 ±0.01	1.12 ±0.01	5.49 ±0.01	10.9 ±0.0	22.1 ±0.3

TABLE II
DETERMINATION OF BORON IN (b) GROUP. (γB)

Taken	11.	55.	110.	220.	550.
Found	11.3	54.6	110.	215.	554.
	10.1	54.6	107.	281.	546.
	11.4	55.2	105.	221.	546.
Mean	10.9 ±0.3	54.8 ±0.2	107. ±1.	218. ±1.	548. ±2.

TABLE III
DETERMINATION OF BORON IN (c) GROUP. (γB)

Taken	0.0	1.1	2.2	5.5	9.9
Found	0.04	1.07	2.24	5.45	9.90
	−0.02	1.05	2.15	5.50	9.84
	−0.02	1.14	2.15	5.48	9.92
Mean	0.00 ±0.01	1.09 ±0.02	2.18 ±0.02	5.48 ±0.01	9.89 ±0.02

These results indicate that boron is not adsorbed on the cation exchange resin and separated from cations quantitatively. For the second place, the pH of the boric acid solution, whose volume was diluted to 20 cc., was adjusted by adding hydrochloric acid and sodium hydroxide solutions, for the resulting solution to be passed through an anion exchange resin column of Cl- or OH- form. The direct titration method was applied to the effluent. The content of boron in the effluent is shown in Fig. 1.

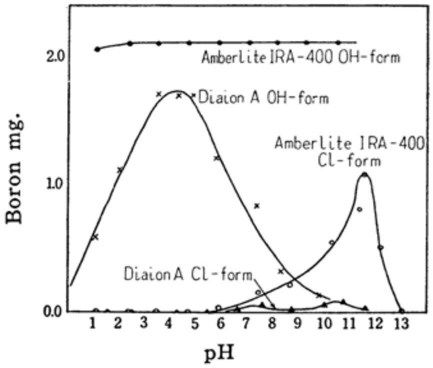

Fig. 1. Boron adsorbed by various forms of anion exchange resins. (The original solution contained 2.12 mg. B.)

Boron was adsorbed to some extent on a weak-base resin, like Diaion A. The adsorption on the resin of OH-form was most marked at pH 3 to 4. The resin of Cl-form did not adsorb boron from acidic solution. When the pH was higher than 5, however, the resin adsorbed boron slightly. A strong-base resin, Amberlite IRA-400, of Cl-form showed the highest adsorption value at pH 11 to 12. When the pH value is higher than 12, the adsorption decreased. Boron was not adsorbed on the resin and separated quatitatively when the pH of solution was lower than 4. This fact makes it possible to separate boron from other anions. When the pH value was higher than 2, Amberlite IRA-400 of OH-form adsorbed boron quantitatively.

A solution containing 5 γ boron was prepared from the standard boric acid solution. The solution was treated with the resin column, and the boron in the effluent was determined colorimetrically by the acetone-curcumin method. The results are shown in Fig. 2. The curve has a similar tendency to that in Fig. 1. Boron can be adsorbed to some extent by the Amberlite IRA-400 of Cl-form in the pH range of 11 to 12. It flows down quantitatively when the pH is lower than 5.

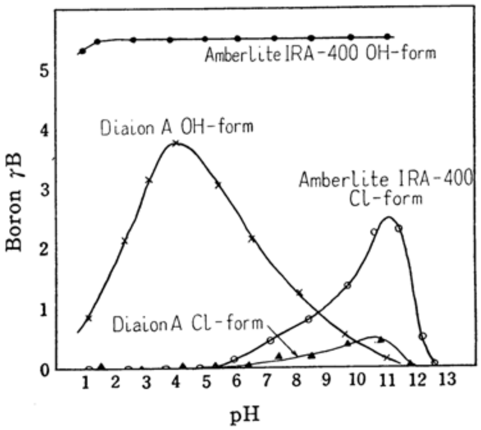

Fig. 2. Boron adsorbed by various forms of anion exchange resins. (The original solution contained 5.5 γB.)

Experimental

Decomposition of Samples: Since the samples are treated with resin column, acid decomposition is better than alkaline fusion. When the samples are decomposed with acid and heated, however, a considerable amount of boric acid volatilizes with water vapor. For this reason, the author placed the sample in a 100 cc. round flask, a slight excess of 6 N hydrochloric acid was added, and the sample was decomposed on a water bath with a reflux condenser. Samples which could not be decomposed by acids were fused with sodium carbonate of guaranteed grade. The melts were dissolved in a slight excess of 6 N hydrochloric acid.

In order to examine this decomposition method, the guaranteed grade sodium carbonate was added to the standard boric acid solution to make the solution alkaline, and evaporated on a water bath. The residue was dissolved with a small amount of water and the solution was poured into a 100 cc. round flask. This solution was neutralized with 6 N hydrochloric acid and 1 cc. excess of the acid added. The flask was connected to a reflux condenser and heated on a water bath for 1 hour. The solution was diluted with 50—100 cc. of water and passed through the cation and the anion exchange resin column using the apparatus as shown in Fig. 3. The effluent was analyzed by either titrimetric or colorimetric procedure.

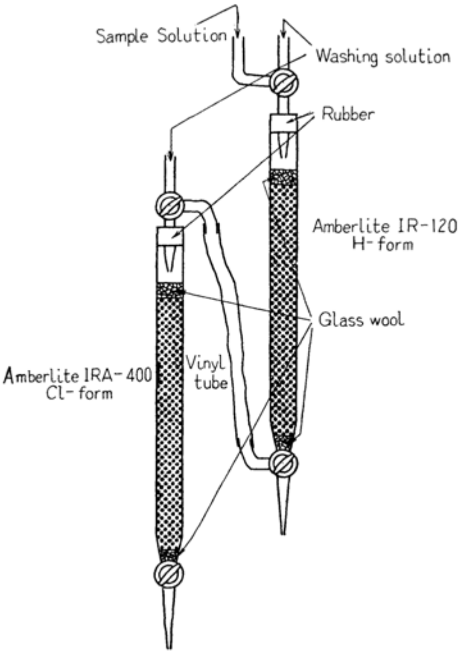

Fig. 3. Resin columns.

Titrimetric Procedure:

Reagents and Chemicals: Standard sodium hydroxide solution (N/20); Guaranteed grade sodium hydroxide was dissolved in carbonate-free distilled water. The factor of the solution was 1.165.

Sodium hydroxide solution (1 N); Guaranteed grade sodium hydroxide was dissolved in carbonate-free distilled water.

Hydrochloric acid (1 N); Distilled hydrochloric acid was diluted to 1 N.

p-Nitrophenol indicator; 0.1% ethanolic solution.

Phenolphthalein indicator; 0.1% ethanolic solution.

Mannitol; Analytical grade reagent in solid.

Procedure: After a sample solution was treated with a resin column, 1—5 mg. B was pipetted out and poured into a 300 cc. conical flask and the volume of the solution was adjusted to 100 cc. To this solution was applied an improved Foote's titrimetric procedure[5]. One drop of *p*-nitrophenol solution was added as indicator and the solution was neutralized with 1 N sodium hydroxide solution until yellow color of the indicator just appeared. One drop of 1 N hydrochloric acid was added to this solution to make the yellow color vanish, then the flask was connected to an aspirator. The solution was heated and boiled at a low pressure. Carbon dioxide gas being bubbled out, the pH of the solution became higher. When the yellow color of the indicator appeared again, one drop of 1 N hydrochloric acid was added and then the boiling was continued. After 2 to 3 minutes of boiling, the aspirator was removed and the solution was cooled by cold water. One twentieth normal sodium hydroxide solution was added to the solution until the yellow color of *p*-nitrophenol was just visible. This is the starting point of the titration. Two grams of mannitol and 5 drops of phenolphthalein were added to the solution, which was titrated with N/20 sodium hydroxide solution. At the end point, the color of the solution was yellowish brown. The color of phenolphthalein appears at pH 8.0, and the neutralization point of mannitol-boric acid complex lies at pH 7.6. Therefore, the end point of the titration is shown by the appearance of yellowish brown color in the solution.

TABLE IV

DETERMINATION OF BORON BY TITRIMETRIC PROCEDURE. (mg. B)

Taken	0.0	1.1	5.5	11.	22.
Found	−0.04 0.03 −0.03	1.05 1.09 1.13	5.50 5.45 5.54	10.7 11.3 10.9	21.6 22.0 22.4
Mean	−0.01 ±0.01	1.09 ±0.02	5.50 ±0.02	11.0 ±0.04	22.0 ±0.02

When the yellowish brown color changes to yellow or sometimes disappears on the addition of 2 grams of mannitol, the titration should be continued. The results on the experiment with known amounts of boron is shown in Table IV.

Colorimetric Procedure:

Reagents and Chemicals: Sodium carbonate; Guaranteed grade sodium carbonate (solid).

Hydrochloric acid-oxalic acid solution; Mix one volume of distilled 6 N hydrochloric acid with four volumes of saturated solution of guaranteed grade oxalic acid.

Acetone-curcumin solution; Dissolve 0.0625 g. of curcumin in 5 cc. of carbitol (monomethyl ether of diethyl glycol), then dilute to 500 cc. with acetone. The solution is stable for 2 to 3 months.

Acetone; Distilled with calcium oxide.

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[5] F. J. Foote, *Ind. Eng. Chem., Anal. Ed.*, **4**, 39 (1932).

Procedure: The Naftel's[6] and the Silverman's[7] method were modified and the following procedure was applied to the sample. After the sample solution was treated with resin, a portion containing 1 to 5 γB was pipetted out and poured into a 50 cc. porclain dish, to which 0.2 g. of sodium carbonate was added. The resulting solution was evaporated on a water bath and acidified with 2 cc. of the hydrochloric acid-oxalic acid solution. The product was evaporated on a water bath at 55±2°C. The heating was continued for 30 min. after the solution was dried. The red color of rosocyanine appeared in the presence of boron. After the colored residue was cooled, it was treated with acetone. The colored acetone solution was centrifuged for 20 minutes at 3000 r. p. m. The clear solution was poured into a 10 mm cell of Hitachi APO-I photocolorimeter equipped with No. G (520 $\mathrm{m}\mu$) filter. This method was applied to solutions containing a known amount of boric acid, which were not treated with the resin columns. A known amount of the standard boric acid solution was treated by the above mentioned procedure and the scale of photocolorimeter was plotted in Fig. 4. The results are shown in Table V.

TABLE V

DETERMINATION OF BORON BY COLORIMETRIC PROCEDURE. (γB)

Taken	0.0	1.1	2.2	5.5	11.
	0.04	1.10	2.18	5.43	10.8
Found	0.02	1.08	2.18	5.51	10.6
	0.00	1.06	2.18	5.49	11.3
Mean	0.02	1.08	2.18	5.48	10.9
	±0.01	±0.01	±0.00	±0.02	±0.1

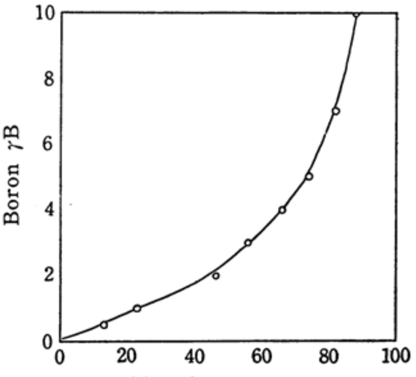

Fig. 4. Standard curve of boron-absorbancy.

This procedure could be applied to a sample containing a small quantity of boron within the error of ±5%.

As shown in Table VI and VII, iron and aluminium interfered with this colorimetric procedure.

TABLE VI

INTERFERENCE OF IRON. (γ)

B (taken)	Fe^{3+}	B (found)	Error γB
0.0	0	0.02	0.02
0.0	9	0.02	0.02
0.0	45	0.05	0.05
0.0	90	0.05	0.05
0.0	900	0.14	0.14
0.0	9000	0.00	0.00
3.3	0	3.33	0.03
3.3	9	3.40	0.07
3.3	45	3.40	0.07
3.3	90	3.65	0.35
3.3	900	3.85	0.55
3.3	9000	0.08	−2.22
5.5	0	5.45	0.05
5.5	9	5.54	0.04
5.5	45	5.55	0.05
5.5	90	5.63	0.13
5.5	900	6.00	0.45
5.5	9000	0.11	−4.39

TABLE VII

INTERFERENCE OF ALUMINIUM. (γ)

B (taken)	Al	B (found)	Error γB
0.0	0	−0.01	−0.01
0.0	0.5	0.00	0.00
0.0	1	−0.02	−0.02
0.0	10	0.04	0.04
0.0	100	−0.01	−0.01
0.0	1000	−0.02	−0.02
3.3	0	3.32	0.02
3.3	0.5	3.29	−0.01
3.3	1	3.18	−0.12
3.3	10	3.10	−0.20
3.3	100	3.09	−0.21
3.3	1000	3.05	−0.25
5.5	0	5.48	−0.02
5.5	0.5	5.50	0.00
5.5	1	5.36	−0.14
5.5	10	5.24	−0.26
5.5	100	5.24	−0.26
5.5	1000	5.08	−0.42

When the ferric ion exists in small quantities, the error tends to become larger. The presence of the aluminium ion gives negative error. Sodium chloride does not interfere with this method.

Application

Kotoite, paigeite and tourmaline were sampled. Kotoite and paigeite were decomposed with hydrochloric acid in a flask connected with a reflux condenser. Tourmaline was fused with sodium carbonate and the melt was dissolved in hydrochloric acid. When the samples were rich in

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[6] J. A. Naftel, *Ind. Eng. Chem., Anal. Ed.*, **11**, 407 (1939).

[7] L. Silverman and K. Trego, *Anal. Chem.*, **25**, 1264 (1953).

TABLE VIII

BORON IN BORON MINERALS

(Determined on the regulated volume of the effluent as explained before)

	Determined		Added		Determined (total)		Recovered	
	Tit. (i) mg. B	Colo. (ii) γB	Tit. mg. B	Colo. γB	Tit. (iii) mg. B	Colo. (iv) γB	(iii)-(i) mg. B	(iv)-(ii) γB
Kotoite	1.77	1.75	1.1	0.11	2.90	1.82	1.3	0.07
(Miyako, Iwate.)	1.72	1.82	5.5	1.1	7.21	2.89	5.4	1.1
5.38±0.06% B_2O_3	1.80	1.73	11.	5.5	12.85	7.17	11.	5.4
Paigeite	5.67	5.55	1.1	0.11	6.82	5.61	1.2	0.06
(Kamaishi, Iwate.)	5.65	5.80	5.5	1.1	11.05	6.86	5.4	1.1
16.00±0.12% B_2O_3	5.67	5.65	11.	5.5	16.80	11.25	11.	5.6
Tourmaline	5.13	5.20	1.1	0.11	6.17	5.28	1.0	0.08
(Shima, Gunma.)	5.22	5.16	5.5	1.1	10.62	6.30	5.4	1.1
7.93±0.04% B_2O_3	5.19	5.14	11.	5.5	16.20	10.57	11.	5.4

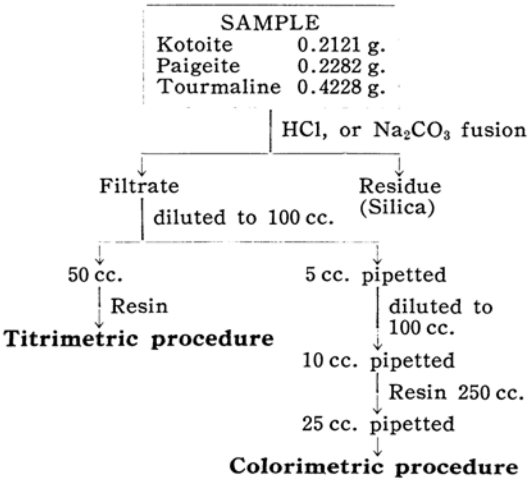

Fig. 5. Decomposition of samples

silica, the acidic solution had to be filtered. The solutions were treated with resin columns, as shown in the Fig. 5. The results in Table VIII were obtained when boron in the effluent was determined by the titrimetric and the colorimetric procedure. The errors of the colorimetric procedure were greater than those of the titrimetric procedure, but less than ±5%. The accuracy of the procedures was examined by adding a known amount of the standard boric acid solution to the minerals. The results were satisfactory as shown in Table VIII. The boron could be determined by the titrimetric procedure, but the colorimetric procedure gave more satisfactory results for micro amounts of boron.

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