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The Spectrophotometric Determination of Boron in Condensed Water from Fumaroles*

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Synopsis. A simple and accurate spectrophotometric method for determining boron in condensed water from fumaroles has been developed. The proposed method is based on the methylene blue-tetrafluoroborate ion pair. It was possible to determine micro amounts of boron with satisfactory results without any interference of foreign ions.

The tetrafluoroborate ion (BF_4^-) forms an ion pair with methylene blue, which may be easily extracted by 1,2-dichloroethane. The present authors have investigated this method in greater detail[1] and applied it to the determination of micro amounts of boron in natural waters[2] and rocks.[3] The determination of boron in condensed water from fumaroles[4-6] has been almost always performed by a titration method using a sodium hydroxide solution and mannitol. However, it seems difficult to determine boron at lower concentrations such as 0.1 ppm. Onishi[7] has determined the BF_4^- in natural waters by a spectrophotometric method on the basis of the methylene blue ion-pair. However, he has not reported in detail about the total boron. There are also some problems regarding the pretreatment of the sample. In the present work, the authors investigated a simple and accurate method for the determination of total boron in condensed water.

Results and Discussion

Reagents and Apparatus. *Standard Boric Acid Solution* (0.25 and 2.5 ppm as boron). *Standard Tetrafluoroboric Acid Solution* (0.25 ppm as boron): Add 50 ml of a standard boric acid solution (2.5 ppm as boron) and 5 ml of 5% hydrofluoric acid to a 500 ml polyethylene measuring flask. After the mixture has been allowed to stand for 24 hr, dilute to exactly 500 ml with water. *Silver Sulfate Solution* (0.01 M): Dissolve 1.5 g of silver sulfate in water and dilute to 500 ml. This solution contains 10 mg of silver ions per 5 ml. A Hitachi double-beam spectrophotometer (Model 124) and 10 mm cells were used to measure the absorbance. The other reagents and apparatus used in this investigation were the same as those described in a previous paper.[1]

Sampling. Fumarolic gas is collected by means of a quartz tube inserted into a fumarole. The cooling parts and sampling flask were also made of quartz.

Procedure. In a 100 ml platinum dish, place the condensed water so that it contains below 1.0 μg of boron, add 1.0 ml of a 0.5 M potassium hydroxide solution and 0.5 ml of a 30% hydrogen peroxide solution, and then dilute to 10 ml with water. Place the platinum dish in a water bath at boiling. After evaporation to dryness, dissolve the cake with 4 ml of a 0.5 M sulfuric acid solution. Transfer the solution to a polyethylene separatory funnel and wash the platinum dish with 13 ml of water. Into the separatory funnel, add 3 ml of a 5% hydrofluoric acid and allow the mixture to stand for 30 min at room temperature. Then add 3 ml of a 0.001 M methylene blue solution and 10 ml of 1,2-dichloroethane, and shake the separatory funnel for 1 min. Transfer the organic layer into another separatory funnel containing 5 ml of a 0.01 M silver sulfate solution and shake it for 1 min. After it has stood for about 20 min, measure the absorbance of the dichloroethane phase at 660 nm, using dichloroethane as the reference. The calibration curve was prepared by taking 0.0, 1.0, 2.0, 3.0, and 4.0 ml of a 0.25 ppm standard boric acid solution. It was reproducible within an error of ±0.02 μg of boron.

Effect of Foreign Ions. In order to confirm the effect of foreign ions, which are usually present in condensed water from fumaroles, and eliminate the interfering ions, the experiments were made both in the presence of 0.5 μg of boron and in its absence. The experimental results are given in Table 1. Sulfide and sulfite ions interfered with the determination of boron under masking with 10 mg of silver ions. However, by this procedure these ions could be decomposed by oxidation with hydrogen peroxide in an alkaline solution. It was found suitable from several experiments to use 0.5 ml of 30% hydrogen peroxide for the oxidation.

Effect of the Volatilization of Boron. When a solution containing borate ions is concentrated or evaporated to dryness, an alkaline solution has been used. On the other hand, BF_4^- exists in a strongly acid-condensed water containing a larger amount of fluo-

Table 1. Effect of foreign ions

Ions added (mg)	Absorbance			
	Masking with 10 mg Ag^+		This procedure	
	Blank	0.5 μg B	Blank	0.5 μg B
None	0.109	0.493	0.123	0.498
S^{2-} 1, Cl^- 1	0.206	0.546	0.134	0.507
SO_3^{2-} 1, Cl^- 1	0.150	0.488	0.122	0.490
$S_2O_3^{2-}$ 0.1	0.138	0.519	0.119	0.484
$S_2O_6^{2-}$ 0.1	0.095	0.488		
$S_4O_6^{2-}$ 0.1	0.124	0.529		
CO_3^{2-} 1	0.101	0.495		
Cl^- 10	0.112	0.503		

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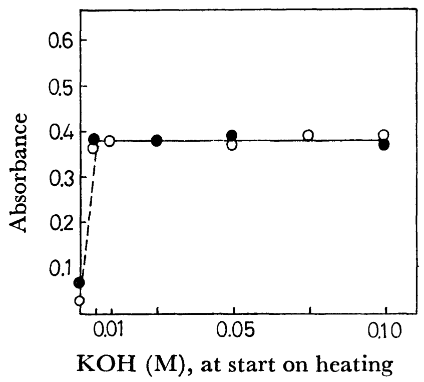

Fig. 1. Effect of volatilization of boron.
○: H_3BO_3 (0.5 μg as B), ●: HBF_4 (0.5 μg as B); against reagent blank

Table 2. Determination of boron in condensed water from fumaroles

Sample	Boron found ppm	Relative std. devn. %	Titration ppm
Hakone Ōwakudani, 122.5 °C (December 26, 1972)	3.9 3.8 4.0 4.0 4.0 3.7	3.3	3.9 3.8
Iwate-san, 402 °C (July 20, 1972)	1.2 1.2 1.2 1.3 1.2 1.1	5.2	1.1 0.6
Kagoshima Iō-Jima, 97°C (August 25, 1973)	0.21 0.18 0.20 0.20 0.22	7.5	

ride;** therefore, it is necessary to examine the volatilization of BF_4^-. Several experiments were made in order to examine the volatilization of boron by using a standard boric acid solution or tetrafluoroboric acid solution and by changing the amount of potassium hydroxide, according to the above procedure. As can be seen in Fig. 1, the loss of boron in both cases was insignificant except in the absence of alkali. Therefore, 1 ml of 0.5 M potassium hydroxide was added in the present work.

The Determination of Boron in Condensed Water from Fumaroles. The boron in some condensed waters was determined by the present method. The results listed in Table 2 show good agreement within the limits of experimental error. A colloidal sulfur sometimes exists in condensed water. It was found that the amount of boron adsorbed on sulfur was negligible. The analytical results obtained by a titration method[8] are also shown in Table 2. It was difficult to determine less than 1 ppm of boron by the titration method. Further, it was found that when a sample is rich in BF_4^-, the titration method gives a considerable error in the results because of trouble at pH adjustment from the fundamental experiment. The present method may be applied not only to condensed water from fumaroles, but also to hot spring water and thermal water in active volcanic areas.

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** Onishi[7] reported that in some cases the ratio of the BF_4^--type boron against the total boron is 90%.