BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 127—131 (1969)

On the Presence of Tetrafluoroborate Ions in Natural Waters[1]

Tomio ONISHI

The College of Liberal Arts, Kagoshima University, Kamoike-cho, Kagoshima

(Received February 27, 1968)

Tetrafluoroborate ions (BF_4^-) can be formed only in a strongly acid solution. Certain acid thermal waters and volcanic gases in the active volcanic zone can be expected to be the media of BF_4^- formation. When BF_4^- is supplied to natural waters, its rate of hydrolysis is relatively low, suggesting the possibility of the occurrence of BF_4^- in natural waters. The contents of BF_4^- have been determined in various thermal water samples from a volcano in Satsuma Iwo-jima, and the presence of BF_4^- confirmed. The BF_4^- content in the condensed water of volcanic gas from a fumarole with the high temperature of 745°C is 304 mg/*l*, which is 26% of the total F, and 79% of the total B content. The BF_4^- content in a sample of water from Kitabira Spa (pH 1.1) is 8.0 mg/*l*, which is about 50% of the total F or B. However, the presence of BF_4^- can not be confirmed in ordinary natural waters such as land and sea waters.

Ducret[2] reported a colorimetric method of analysis for B which consisted of the addition of a solution consisting of HF and NH_4F to a sample of water containing B, turning B into BF_4^-, and extracting the complex thus formed by the addition of methylene blue (MB) with 1,2-dichloroethane (DCE). Pasztor[3] and Utsumi *et al.*[4,5] have reported improved versions of this method. A series of these analytical methods aimed at determining the quantity of B by utilizing BF_4^- formation. Hosokawa and Morinaga,[6] and Muto,[7] taking the advantage of this method, attempted to make the complex of BF_4^- with MB directly, and to extract the BF_4^--MB complex with DCE. Hosokawa and Morinaga, and also Muto, then announced the presence of BF_4^- in sea and river waters and in hot spring water respectively.

On the other hand, in a preliminary study of natural water, a considerable quantity of material forming complexes with MB was extracted by the present author.[8] However, these complexes might consist of materials other than BF_4^-, such as alkylbenzenesulfonate ions (ABS^-) in river water and Cl^- in sea water. For this reason, the presence of BF_4^- in ordinary natural water is strongly suspected.

BF_4^- can be formed only in a strongly acid solution containing an amount of F larger than that of B.[1,2,4] If BF_4^- existed in ordinary natural waters, it could not have been formed in the present sea water, nor in land water. Certain acid thermal waters and volcanic gases in the active volcanic zone may be expected to have been the media of BF_4^- formation.

Actually, the formation of Avogadrite $(K,Rb)BF_4$ had been reported shortly after the eruption of Vesuvius in 1906.[9] Even if BF_4^- originatin in such volcanoes could exist in a stable state in natural waters, the presence of BF_4^- would be confirmed only in special areas. For the purpose of examining the survival of BF_4^-, KBF_4 was added to various kinds of natural waters, and its rate of hydrolysis was measured. It was found that BF_4^- was relatively stable in an aqueous solution. If there is any source of BF_4^-, BF_4^- may be expected to exist in natural waters under favorable conditions.

Volcanic gases from the volcano in Satsuma Iwo-jima contain a large quantity of the F compound. Large amounts of the H_3BO_3 sublimate were found around some fumaroles,[10,11] satisfying the requirements for the formation medium of

---

[1] I. Iwasaki, M. Kamada, T. Onishi and H. Sakamoto, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **89**, 324 (1968), Short communication.

[2] L. Ducret, *Anal. Chim. Acta,* **17**, 213 (1957).

[3] L. Pasztor and J. D. Bode, *Anal. Chem.,* **32**, 277 (1960).

[4] S. Utsumi, S. Ito and A. Isozaki, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 921 (1965).

[5] S. Utsumi and A. Isozaki, *ibid.*, **88**, 545 (1967).

[6] I. Hosokawa and T. Morinaga, Preprints for the Annual Meeting of The Geochemical Society of Japan, Tokyo (October, 1965), p. 153.

[7] K. Muto, *ibid.*, Kanazawa (October, 1966), p. 193.

[8] I. Iwasaki, T. Onishi, H. Sakamoto and M. Kamada, *ibid*, p. 195.

[9] V. M. Goldschmidt, "Geochemistry," ed. by A. Muir, Oxford University Press, Oxford (1954), p. 573.

[10] M. Yoshida, T. Ozawa and J. Ossaka, *Ganseki Koobutsu Kosho Gatsukaishi* (*J. Japan Assoc. Min. Petrog. Econ. Geol.*), **55**, 201, 262 (1966).

[11] M. Kamada, *Chinetsu* (*Geothermy*), **3**, 1 (1964).

BF_4^-. The BF_4^- contents have been determined in various samples from this volcano, and the presence of BF_4^- has been confirmed in all of these samples.

Experimental

Analysis of BF_4^-. When the MB complex method was directly applied to natural water in the presence of many interfering materials, the effects of those materials, particularly Cl^-, Br^-, I^-, and ABS^-, posed a problem. Utsumi *et al.*[5] removed the ABS^- in advance with DCE, and also removed the Cl^- by washing with a Ag_2SO_4 solution when the colorimetric method was adopted for the determination of the B in the water. The present author aimed at the direct determination of BF_4^-, but since considerable quantities of ABS^- and Cl^- were considered to exist in river and in sea waters respectively, the quantity of BF_4^- was determined by first extracting ABS^- with DCE only, adding MB to the sample water after removing the ABS^-, extracting the complexes with DCE, and backwashing the complex of F^- extracted with water, backwashing it again with a Ag_2SO_4 solution, and separating the halogen ions other than F^-. Further, it was found that BO_3^{3-} did not interfere because it did not form a complex with MB.

Procedure. A sample solution (20 m*l*) was taken in a polyethylene separating funnel, to which 10 m*l* of DCE was added, after the funnel had been shaken for 1 min, the organic phase was separated. Five milliliters of 0.001 M MB and 10 m*l* of DCE were then added to the water phase, and the mixture was shaken for 1 min. After it had then been left for 10 min, the organic phase was separated, washed with 5 m*l* of water and again with 5 m*l* of 0.01 M Ag_2SO_4, and then transferred into a glass-stoppered test tube. Then about 0.2 g of anhydrous Na_2SO_4 was added to the organic phase, and the mixture was shaken in order to remove the water completely. The optical absorbance of the organic phase was measured at the wavelength of 660 mμ using a blank test solution as a reference. The calibration curve is shown in Fig. 1.

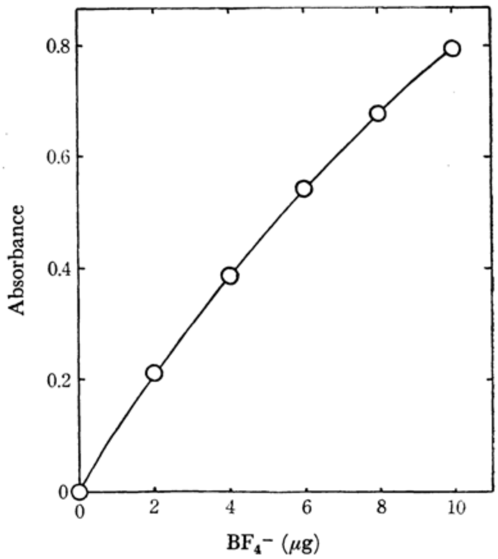

Fig. 1. Optical absorbance of BF_4^--MB complex at 660 mμ.

Sensitivity of BF_4^- in the Method of Analyzing F. Various methods of analyzing F which have been widely used do not pay any attention to the presence of BF_4^--type F. However, if BF_4^--type F exists in natural waters, attention should be paid to the behavior of F in any analytical procedure. Curves of the concentration *versus* the optical absorbances of F^-, SiF_6^{2-}, and BF_4^-, obtained by a method using "Azo-dye,"[12,13] are shown in Fig. 2.

TABLE 1. RECOVERY TEST OF F IN VARIOUS STATES

Sample	Given (μg as F)	Found (μg as F)	Recovery (%)
F^-	500	495	99.0
BF_4^-	500	495	99.0
$F^- + BF_4^-$	1000	988	98.8
$BF_4^- + H_3BO_3$†	500	486	97.2
$F^- + Al_2(SO_4)_3$†	500	486	97.2
$BF_4^- + H_3BO_3$†	500	490	98.0
$BF_4^- + Al_2(SO_4)_3$†	500	480	96.0
$BF_4^- + SiO_2$†	500	490	98.0

† With respect to the amounts of $Al_2(SO_4)_3$, H_3BO_3 and SiO_2, 1000 mg as Al, B and Si were added.

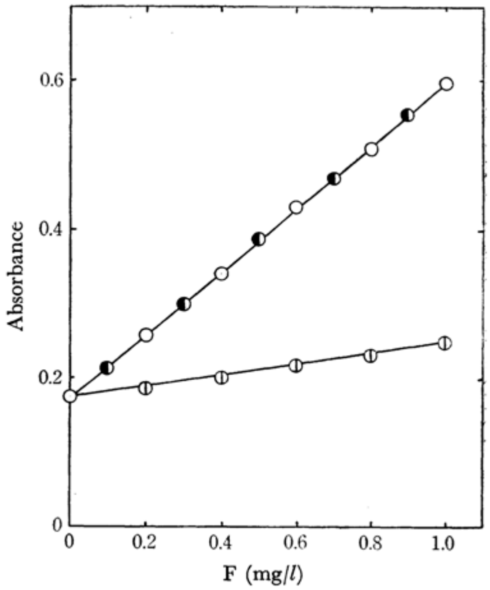

Fig. 2. Plot of F concentration *versus* optical absorbance of F-bearing ions.
○ F^- ◐ SiF_6^{2-} ⦶ BF_4^-

From Fig. 2, it is evident that the sensitivity with

---

[12] M. Kamada and T. Onishi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Scet.*), **80**, 275 (1959).

[13] M. Kamada, T. Onishi and M. Ota, This Bulletin, **28**, 149 (1955).

TABLE 2. NECESSARY INFORMATION ON SAMPLE WATERS

Sample water	Sampling date	pH	F (mg/*l*)	B (mg/*l*)	Locality
Rain	May 16 '64	6.2	0.100	0.06	Kagoshima city
River	Aug. 2 '65	6.7	0.060	0.05	Kotsuki-gawa
Well	Aug. 4 '65	7.0	0.101	0.13	Kagoshima city
Sea	July 29 '55	8.2	1.42	4.7	Okinoerabu Is.

respect to the optical absorbance of BF_4^- is only 15% of those of F^- and SiF_6^{2-}. Therefore, if BF_4^--type F exists in rain or river water, the conventional colorimetric method for F will give only a part of the F content.

On the other hand, in the case of samples containing much co-existing material, F is usually subjected to distillation in a strongly acid solution prior to the colorimetric determination to separate it from interfering materials. However, if BF_4^- is present in the water sample, or if B is also present, there is a question as to whether the complete recovery of F can be secured by means of distillation. To answer this question, the recovery test of F was conducted by distillation in the presence of interfering materials. The results are given in Table 1. As is shown in Table 1, BF_4^--type F could be sufficiently recovered and did not interfere with the analysis of F at all.

Stability of BF_4^-. The precious reports on hydrolysis have mentioned only its susceptibility to the decomposition of BF_4^-.[7,14] Thus, the experiment was conducted by adding freshly-prepared KBF_4 in pure water and various kinds of natural waters, immediately after the addition, the solutions in a polyethylene bottle were left in a bath with a constant temperature of 20°C. The rate of the decomposition of BF_4^- was traced by both the MB method and the indirect method using F formed through the decomposition of BF_4^-.

The necessary information on the water sample for the stability test of BF_4^- is given in Table 2, while the test results are shown in Fig. 3.

The results shown in Fig. 3 may be summarized as follows:

A. BF_4^- was relatively stable when left in an aqueous solution for one year at room temperature. Twenty percent of it remained in pure water, 25% in river water, and 30% in sea water. With respect the natural water, the higher the salt concentration, the more stable BF_4^- is.

B. As the concentration of BF_4^- increased, the stability also increased. An increase in the temperature of the solution from 5°C to 50°C caused a great increase in the rate of decomposition.

C. When BF_4^- was added to a solution of NaOH with the pH of 12, it was almost completely decomposed in 20 hr. Therefore, generally speaking, as the pH increased, the rate of decomposition increased.

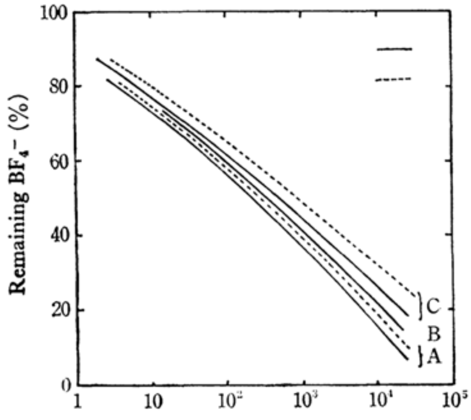

Fig. 3. Stability of BF_4^- in various natural waters.

A Pure water

B River and well waters

C Sea water

F as BF_4^- (1 mg/*l*) ——

F as BF_4^- (10 mg/*l*) -----

Results and Discussion

Confirmation of the Presence of BF_4^- in the Active Volcano Zone. The volcanic gases of Satsuma Iwo-jima contain a large amount of F compound, sometimes as much as 16.5% HF in vol% of gas excluding water vapor. Also, sublimates of B were found around the crater of the volcano. Thus, the BF_4^- contents were determined in various water samples from a volcano on Iwo-jima. The results are given in Table 3.

Condensed water from volcanic gas (No. 1) was collected on July 26, 1961, because of its high temperature (745°C), it was collected by means of quartz tubing instead of Teflon tubing. The cooling parts and sampling apparatus used were made of glass. There is a possibility of the contamination of B as well as of the reaction of BF_4^- with SiO_2 in galss, and also the possibility of a change in the state of the chemical species in the gas. To eliminate these defects, quartz tubing was inserted in a fumarole in the sampling of No. 2, and the gas was conducted through quartz tubing into chilled water in a polyethylene bottle. Here again, the reaction of BF_4^- with SiO_2 is possible. The No. 3 sample was obtained by using Teflon tubing since

---

14) C. A. Wamser, *J. Am. Chem. Soc.*, **73**, 409 (1951).

TABLE 3. CONTENTS OF BF_4^- IN SAMPLES FROM IWO-ZIMA

No.	Sample	F mg/l	B mg/l	B as BF_4^- mg/l	F as BF_4^- mg/l	(B as $BF_4^-/\Sigma B$) $\times 100$ %	(F as $BF_4^-/\Sigma F$) $\times 100$ %
1	Condensed water from a fumarole (Kamanokuchi)	1015	48.0	38.0	266	79	26
2	Condensed water from a fumarole (Kamanokuchi)	10.5	0.38	0.29	2.03	77	19
3	Condensed water from a fumarole (Kuromoe)	18.5	0.63	0.57	3.99	90	22
4	Hot spring water (Kitabira)	15	1.9	1.0	7.0	53	47
5	Hot spring water (Higashi)	16	1.7	0.4	2.8	24	18
6	Sea water (near Higashi hot spring)	1.6	5.1	0.005	0.035	0.1	2.2
7	Silica sublimate (Kamanokuchi)	11.6%	66 ppm	66 ppm	462 ppm	100	0.4

TABLE 4. CONTENTS OF BF_4^- IN NATURAL WATERS

No.	Sample	F mg/l	B mg/l	B as BF_4^- mg/l	F as BF_4^- mg/l
1	Rain water Oct. 30 '66 Kagoshima city	0.10	0.06	0.00	0.00
2	Rain water Aug. 25 '67 Kagoshima city	0.054	0.03	0.00	0.00
3	Lake water Sept. 23 '65 Okutama-ko	0.080	0.11	0.00	0.00
4	Lake water Oct. 3 '66 Ikeda-ko	0.085	0.04	0.00	0.00
5	River water May 1 '66 Kotsuki-gawa	0.08	0.045	0.00	0.00
6	Ground water Oct. 8 '65 Nishihodaka	0.022	0.017	0.00	0.00
7	Sea water Nov. 15 '66 Kagoshima bay	1.36	4.7	0.00	0.00
8	Sea water Aug. 16 '67 Okinoerabu Is.	1.40	4.38	0.00	0.00

the temperature of the fumarole was below 250°C; we thus avoided mixing the B compound in the solid form and conducting the gas into water.

In very case, BF_4^- was detected; the ratio of the BF_4^--type B against the total B was 77—90%, while that of the BF_4^--type F against the total F was 19—26%. In the subsurface part of fumaroles, no liquid phase is expected to exist. Therefore, the presence of BF_4^- in the condensed water indicates that most of the B is present in the form of BF_3 in the gas phase. The $BF_3(aq.)+F^- \rightarrow BF_4^-$ reaction may be responsible for the formation of BF_4^- in the liquid phase. The K_p (4×10^{11}, at 25°C) of this reaction indicates that this is highly probable.

A "unique sublimate"[*1] (No. 7) was obtained beneath the Kamanokuchi fumarole area. Yoshida *et al.*[10)] reported that this material contained a strongly acid aqueous solution consisting mostly of halogen compounds inside, and that its total F content reached 11.6%. If trace amounts of B are embodied in such a sublimate, the most suitable environment for the formation of BF_4^- is realized. The test results indicated that all of the B was present in the BF_4^- form.

BF_4^- was confirmed to exist also in some acid thermal waters near the volcano, such as Kitabira hot spring water (No. 4), with a pH of 1.1, and Higashi hot spring water (No. 5), with pH of 1.6. The change in the BF_4^- content during the storage of hot spring water in a bottle at room temperature for 1 year was pursued. There was no change at all for the No. 4 sample, but No. 5 indicated a 70% decrease in the BF_4^- content over a 10-day period. This may be attributed to the difference in stability caused by the difference in pH.

Sea water (No. 6) was a special sample, a mixture of hot spring water (No. 5) with coastal sea water; its pH was 4.0. There was formed a white suspension composed of amorphous $Al_2O_3\cdot xH_2O$ and $SiO_2\cdot xH_2O$ produced by hydrolysis. The filtrate was analyzed after the precipitates separated, and the presence of BF_4^-, though only a trace, was confirmed. However, sea water like this is extraordinary.

Presence of BF_4^- in Normal Natural Waters. For the purpose of ascertaining the presence of BF_4^-, normal natural water was also analyzed. The results are given in Table 4.

The presence of BF_4^- was not confirmed within the 0.00 mg/*l* detection limits of sea, river, and rain water. Although considerable quantities of F and B exist in sea water, these cannot be expected in the formation of BF_4^- because of the higher pH values of the water sample.[*2]

The author wishes to thank Dr. M. Kamada of Kagoshima University, Dr. I. Iwasaki, Dr. T. Ozawa and Dr. M. Yoshida of the Tokyo Institute of Technology, Dr. S. Utsumi of Nihon University, and Dr. T. Koh of Tokai University, for their many helpful discussions and suggestions during this work. Thanks are also due Mr. H. Sakamoto for his assistance in the experimental work.

[*1] Yoshida *et al.*[10)] have reported on the general chemical properties and formation mechanism of this sublimate.

[*2] Utsumi and Isozaki[5)] suspected the presence of BF_4^- while using the indirect method in analyzing the B in sea water.