温泉科学（J. Hot Spring Sci.），75，2-18（2025）

原　　著

Simple, Quick, and Precise Determination of Fluoride Ions in High-Aluminum Volcanic Hydrothermal Water by Ion Selective Electrode with Complexing Agent-added TISAB: A Case Study of Yugama Crater Lake, Kusatsu-Shirane Volcano

Yifan CHEN[1)]*, Kazuki AKIMOTO[1)] and Yoshikazu KIKAWADA[2)]

(Received November 21, 2024, Accepted March 3, 2025)

錯形成剤添加 TISAB を用いたイオン選択電極法による高アルミニウム濃度火山性熱水中のフッ化物イオンの簡便・迅速・高精度な定量法：草津白根山湯釜火口湖を例として

陳　怡帆[1)]*，秋元和輝[1)]，木川田喜一[2)]

要　　旨

フッ素は温泉法の別表に示されている温泉の定義に関わる溶存成分である．一方，火山性熱水中のフッ化物イオンの濃度やその変動は，火山活動や熱水環境の変化を知るための重要な指標となる．しかし，通常，フッ素の分析は蒸留などの煩雑な操作を伴うため，火山活動モニタリングではフッ化物イオンは定量されないことも多い．我々は，高アルミニウム濃度火山性熱水中のフッ化物イオンの簡便・迅速・高精度な定量法を目指し，金属イオンに対する錯形成剤を含む全イオン強度調整剤（TISAB）を用いたイオン選択性電極（ISE）による簡便なフッ化物イオン直接定量法の火山熱水試料への適用性を，草津白根山の活動的火口湖である湯釜の湖水に適用した際の定量確度と精度に基づいて評価した．その結果，錯形成剤として Tris（hydroxymethyl）aminomethane（THAM）を含む TISAB を用いることで，フッ化物と強く錯体を形成するアルミニウムや他の金属が高濃度で共存していても，ISE 法により十分な精度・確度にフッ化物イオンを直接測定できることが示された．THAM はアルミニウムイオンと安定な錯体を形成するため，THAM を含む TISAB は高アルミニウム濃度の試料の ISE 測定にきわめて有効である．適切な錯形成剤を含む TISAB を用いた ISE によるフッ化物イオンの直

[1)] Chemistry Division, Graduate School of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo, 102-8554, Japan. [1)] 上智大学大学院理工学研究科理工学専攻化学領域　〒102-8554 東京都千代田区紀尾井町 7-1. *Corresponding author：E-mail y-chen-4n5@eagle.sophia.ac.jp
[2)] Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo, 102-8554, Japan. [2)] 上智大学理工学部物質生命理工学科　〒102-8554　東京都千代田区紀尾井町 7-1.

接測定は，前処理を必要とせず操作が簡便であり，高アルミニウム濃度の火山性熱水試料中のフッ化物イオンを迅速かつ正確に測定することが可能である．

キーワード：フッ素，フッ素定量分析，熱水流体，イオン選択電極，全イオン強度調整剤

Abstract

Fluorine is a dissolved component related to the definition of a hot spring, as listed in the Japanese Hot Spring Law. On the other hand, the concentration and fluctuations of fluoride ions in volcanic hydrothermal fluids are essential indicators for monitoring volcanic activity and changes in the hydrothermal environment. However, in many cases, fluoride ions are not determined because the analytical procedure usually involves complicated operations such as distillation. We aimed at a simple, quick, and precise direct determination method to analyze fluoride ions in high-aluminum volcanic hydrothermal water and investigated the applicability of the simple direct determination methods of fluoride ions using the ion-selective electrode (ISE) with total ion strength-adjusted buffers (TISABs) containing several complexing agents for metal ions to volcanic hydrothermal water samples. The effectiveness of these analytical methods was evaluated based on the analytical accuracy and precision when applied to the water of Yugama, an active crater lake of the Kusatsu-Shirane volcano. The results showed that when the TISAB, which contains the complexing agent Tris(hydroxymethyl) aminomethane (THAM), was used, it was possible to directly determine fluoride ions with sufficient accuracy and precision using the ISE method, even when there were high concentrations of aluminum and other metals that strongly form complexes with fluoride. Because THAM forms a stable complex with aluminum ions, TISAB containing THAM is very effective for ISE measurement of samples with high aluminum concentrations. Directly determining fluoride ions by ISE using the TISAB with an appropriate complexing agent is simple to operate without any pretreatment, making it possible to quickly and accurately determine the fluoride ions in high-aluminum volcanic hydrothermal water samples.

Key words : fluorine, fluoride determination, hydrothermal fluids, ion selective electrode, total ion strength-adjusted buffer

1. Introduction

Fluorine is a dissolved component that is related to the definition of hot spring as listed in the appendix of the Japanese Hot Spring Law and is one of the essential components to be analyzed in hot spring analysis based on the Law. The “Standard Methods of Analysis for Mineral Springs, Japan” (Ministry of the Environment, 2014), which provides the official method for analyzing hot spring water, lists the ion-selective electrode method and the lanthanum alizarin complexone method (colorimetry) as methods for analyzing fluorine. Both methods are assumed to be combined with sample pretreatment by steam distillation with sulfuric acid for fluorine isolation. On the other hand, fluorine is also a vital component that should be focused on in chemical volcanic activity monitoring. In chemical monitoring of volcanic activity using fumarolic gases and water from hot springs and active crater lakes, chemical species of fluorine are critical components as important as chlorine for detecting changes in volcanic activity and volcanic hydrothermal environment.

Both as halogens, fluorine and chlorine are original substances of volcanic activity, but they also behave differently in actual volcanic activities. Fluorine and chlorine derived from magma

volatiles are mainly contained as HF and HCl in high-temperature volcanic gases, and dissolved as fluoride and chloride ions and their complex ions in the liquid phase generated by condensation of volcanic gases and their mixing with meteoric water. Changes in the concentration ratios of fluorine and chlorine in shallow hydrothermal systems are helpful for understanding changes in the state of deep magma-associated hydrothermal systems because fluorine and chlorine behave differently due to their different properties in the path of magma volatiles from depth to the surface via volcanic hydrothermal systems (Hirabayashi 1982 ; Yoshida 1990 ; Nogami and Onizawa, 2020) in addition to differences in their dissolution and degassing behavior in magma melts (Aiuppa *et al.*, 2002 ; 2004). At the same time, these differences result in a significant disparity in the concentrations of dissolved fluorine and chlorine in hydrothermal systems. In general, the concentration of chloride ions is considerably higher than fluoride ions. Chloride ion is one of the most critical analytical components in monitoring volcanic hot springs and crater lake waters, so a large amount of observational data has been accumulated at volcanic hydrothermal systems and geothermal areas worldwide. Chloride ion is recognized the monitoring items that should never be excluded from the chemical analysis of such sample water. On the other hand, the reporting and accumulation of observational data on fluoride ions is minimal because obtaining reliable quantitative values for fluoride ions is more complicated than for chloride ions. This may be due to the lower concentration of fluoride ions in the sample water compared to chloride ions, and the analytical methods are much more complicated than chloride ions. However, the importance of fluoride content as a monitoring item needs to be better understood.

Fluoride ions form highly stable complexes with various coexisting ions in the liquid phase due to the strong electronegativity of the fluorine atom. When using ion chromatography (IC) or ion selective electrode (ISE), which are widely used methods for anion analysis, the chemical species to be detected is a specific dissolved ionic species, which in the case of fluorine determination is usually a free fluoride ion. Therefore, if fluoride ions form chemically stable complexes with coexisting ions in the analytical samples, the IC and ISE methods will not provide adequate analytical values. Volcanic fluids usually contain coexisting ions that readily form complexes with fluoride ions, such as aluminum and iron. Therefore, for the determination of fluoride ions by the IC and ISE methods, it is necessary to dissociate dissolved metal-fluoride complex ions in the samples by an appropriate pretreatment method. The typical pretreatment technique for this purpose is a series of fluoride distillation methods. Several fluoride distillation methods have been developed and improved over the years ; the most representative of them are the sulfuric acid steam distillation method (e.g., Willard and Winter, 1933 ; Hoskins and Ferris, 1936 ; Smith and Parks, 1955) and the fluorosilane distillation method (e.g., Taves, 1968 ; Yoshida *et al.*, 1978 ; Tsuchiya *et al.*, 1985). Such pretreatment complicates routine analysis and is an obstacle to automation since it requires a certain amount of labor and specific equipment (distillation line) for the distillation operation.

On the other hand, it is also known that a metal ion complexing reagent is added as a masking reagent to the total ion strength adjustment buffer (TISAB) added to the sample during ISE measurement to inhibit the formation of metal fluoride complexes, and free fluoride ions are determined directly by ISE. Adding such a masking reagent is also effective in preventing the sorption of fluoride ions to colloidal aluminum in a neutral pH range in the ISE measurement

(Pickering, 1986). For example, Deng *et al.* (2011) reported the results of this method applied to Yellowstone hydrothermal water to study its fluoride geochemistry. This method does not require any complicated pretreatment, and fluoride ions can be determined quickly and easily. This paper calls such a measurement method without pretreatment to isolate fluorine, such as distillation, "direct determination." According to the "Standard Methods of Analysis for Mineral Springs, Japan" (Ministry of the Environment, 2014), the direct determination of fluoride ions by ISE with a TISAB to which citric acid has been added as a complexing agent is only applicable when the aluminum concentration in the hot spring water is 100 mg/L or less. However, there are not many examples of applying this type of technique to samples associated with volcanic hydrothermal systems, and it is difficult to say that it is a widely used method. The effectiveness of the complexing reagent in masking coexisting metal ions and releasing fluoride ions, which is the core of this technique, should be highly dependent on the type and concentration of the complexing reagent and the coexisting ion species. Therefore, the type and concentration range of effective complexing reagents differ depending on the chemical composition of the sample to be analyzed, and it may be necessary to optimize the type and concentration of complexing reagents according to the composition and physicochemical properties of the sample water to be analyzed. If this analytical method for fluoride ion can be reliably applied to more varied hydrothermal water samples, it could become a valuable option for many researchers in the field of chemical volcanology as a simple, rapid, and practical method for the determination of fluoride ions in volcanic hydrothermal water that does not require distillation operation. Therefore, more reports on fluoride ion concentrations in volcanic hydrothermal fluids are expected to be published, and discussions on fluorine in volcanic hydrothermal systems will be further deepened.

To explore the applicability of direct determination method for high-salinity, strongly acidic volcanic hydrothermal samples, we selected the "Yugama", known as an active crater lake, as the subject of this study. Yugama is filled with highly acidic lake water (pH is around 1.0), which is defined as acidic sulfate-chloride waters based on its water chemistry (Taran and Kalacheva, 2020). Yugama water contains significant concentrations of various metal ions, especially high concentrations of aluminum ion, which easily forms complexes with fluoride ions. Volcanic gas fumaroles and hydrothermal vents are present at the lake bottom, and molten sulfur is found around the fumaroles (Takano, 2001). Changes in the concentrations of dissolved chemical components in Yugama water have been reported since the 1960s, and changes in chloride ion concentration have been discussed in relation to the rise and fall of volcanic activity (Ohba *et al.*, 2000 ; 2008 ; Ossaka *et al.*, 1997 ; Yaguchi *et al.*, 2021). However, in the large amount of analytical data accumulated on Yugama water samples, we could find only a few reported values of fluoride ion concentration.

In this study, by using Yugama lake water as an example, we aimed at a simple, quick, and precise ISE direct determination method to analyze fluoride ions in high-aluminum volcanic hydrothermal water. We investigated the optimal conditions on the type and concentration of TISAB reagents, and verified the accuracy and precision of the analytical results by comparing them with the results analyzed with traditional methods.

2. Samples and Methods

In this study, we collected Yugama lake water as a representative example with strong acidity and high aluminum concentration for experiments. By comparing with traditional analytical methods and conducting spike and recovery test, we evaluated the accuracy of ISE direct determination results when using different TISAB, and found out the most suitable type of TISAB.

The samples, reagents, apparatus, and analytical methods used in this study are as follows.

2.1 Preparation of samples, reagents and apparatus

2.1.1 Yugama water samples

The target analyte in this study is fluoride dissolved in the water of Yugama, an active crater lake of Kusatsu-Shirane Volcano. Kusatsu-Shirane Volcano is an active volcano in the center of Japan's main island (Fig. 1), consisting of three pyroclastic cones named Shirane, Ainomine, and Moto-Shirane. The crater lake, Yugama, is located at the summit of the Shirane pyroclastic cone.

The surface water of Yugama collected at the "U-1" point (Fig. 1) at the southwest shore of crater lake was subjected to this study. The collected water samples were stored in polypropylene bottles until the analysis without filtration, degassing, or other chemical treatments. Samples were collected between July 29, 2002, and June 3, 2024. The specific sampling dates are documented in the "Sampling Date" column of the analysis result tables (Tables 1, 2, and 4). The volume collected for each sampling was from 500 to 1,500 mL, depending on the situation while sampling.

In the following, the sulfuric acid steam distillation and IC measurements were performed within one month after collection in November 2015. The ISE measurements were performed in June 2022 and September 2024. The main dissolved components of Yugama water in Table 2 were re-analyzed in February 2024. Na and K were analyzed by Flame Emission Spectroscopy (Thermo Electron, SOLAAR M6) and Ca, Mg, Fe, Al, Mn, Si, Cl, SO_4^{2-} were analyzed by ICP-OES (SII, SPS3520UVDD). SO_4^{2-} is calculated from the ICP-OES analysis value after being separated by an anion exchange resin. Water temperature and pH were measured using temperature meter (Anritsu Meter, HD-1200E) and pH meter (Yokogawa Electric, PH72SN, with PH82 electrode) at the time of collection.

2.1.2 Reagents and apparatus

The reagents used in this study were basically of JIS special grade or equivalent. All solutions were prepared using distilled water except for the eluent in the IC measurement, which was prepared using ultra-purified water (Milli-Q water, prepared with Merck Millipore Simplicity UV system and the resistance is 18.2 MΩ·cm). The standard solutions of fluoride ion for fluoride determination were prepared by dissolving NaF with distilled water.

ISE measurements were conducted using the Combination Ion Selective Electrode (Thermo Fisher Scientific Inc., ORION 9609BNWP) with the pH/ISE Benchtop Meter (Thermo Fisher Scientific Inc., ORION Dual Star). IC measurements were conducted using the ion chromatography system (Metrohm, 883 Basic IC plus) installed with the separation column (Metrohm, Metrosep A Supp 4-250/4.0). Sulfuric acid steam distillation of fluoride ions was conducted using fluorine

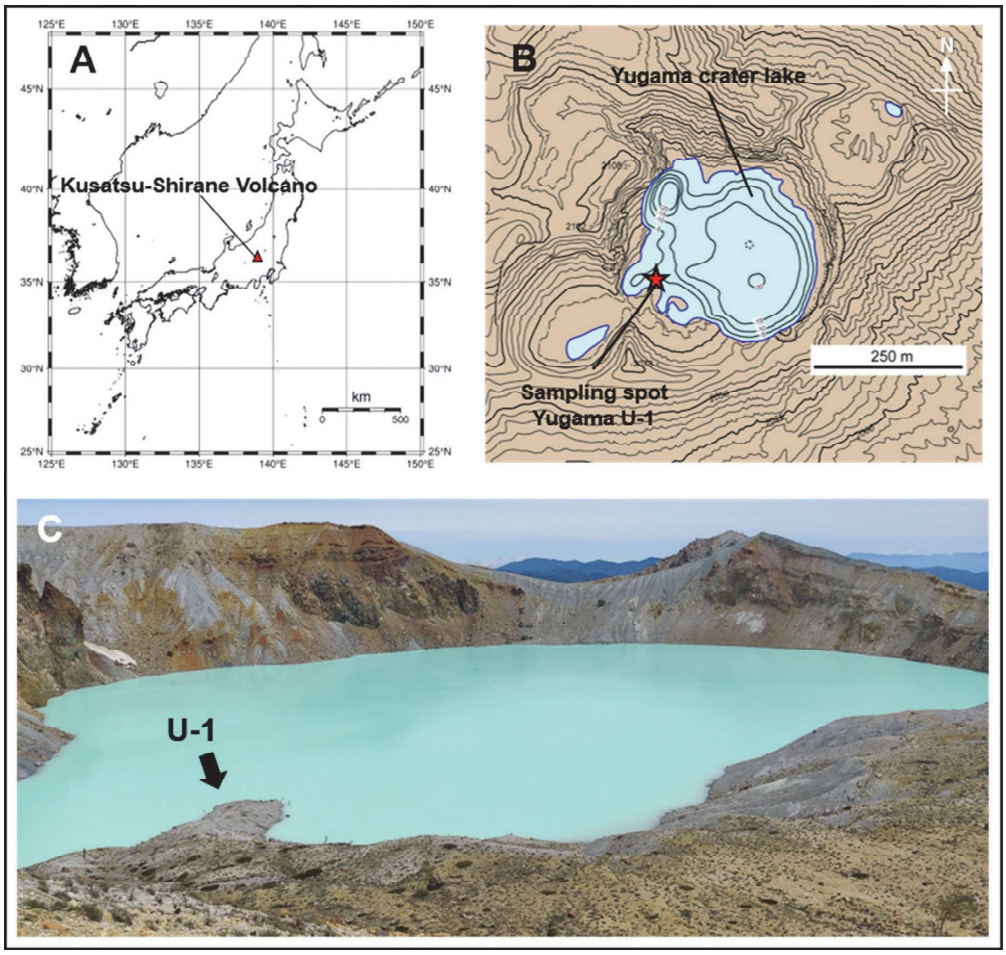

Fig. 1　Map and photo of Yugama, crater lake of Kusatsu-Shirane volcano. A : Location of Kusatsu-Shirane Volcano in the Japanese Islands. This map was generated using Generic Mapping Tools (GMT ; Wessel *et al*., 2019). B : Enlarged map around Yugama crater lake. Contours are given in meters. Created by editing the 1 : 25,000 Topographic Map of Geospatial Information Authority of Japan. C : Overview of Yugama. The sample waters were collected from "U-1" located at the southwest shore. This photograph was taken on June 13, 2022.

distillation equipment (Sugiyama-Gen Co., Ltd., EHP-341-ELC). The distillation of fluoride ions was conducted utilizing the distillation apparatus made of glass described in Tsuchiya *et al.* (1985).

2. 1. 3　TISABs preparation

Referring to the previous papers (Frant and Ross, 1968 ; Peters and Ladd, 1971 ; Buck and Cosofret, 1993 ; Corbillón *et al*., 1995 ; Petrenko *et al*., 2021), we used three types of TISABs and here named them "TISAB-B," "TISAB-C" and "TISAB-D."

TISAB-B was prepared as follows (Frant and Ross, 1968 ; Buck and Cosofret, 1993) : 170 g of sodium nitrate, 68 g of sodium acetate trihydrate, and 92.4 g of sodium citrate dihydrate were added to 500 mL of distilled water and mixed well by stirring. The mixture's pH was adjusted between 5.0 and 5.5 by adding 5 M NaOH dropwise. After the solution was cooled to room

temperature, the solution was finally adjusted to one liter by adding distilled water.

TISAB-C was prepared as follows (Peters and Ladd, 1971 ; Buck and Cosofret, 1993) : 17.65 g of trans-1,2-Cyclohexanediamine-N,N,N',N'-tetraacetic acid monohydrate (CyDTA) was added to 500 mL of distilled water, and 40% NaOH sol. was dropped until the salt was dissolved. 300 g of sodium citrate dehydrate and 60 g of sodium chloride were added to the solution and mixed well by stirring. The solution was finally adjusted to one liter by adding distilled water.

TISAB-D was prepared as follows (Corbillón *et al.*, 1995) : 84 mL of concentrated hydrochloric acid (36–38 %), 242 g of tris(hydroxymethyl)aminomethane and 230 g of sodium tartrate dihydrate were added to 500 mL of distilled water and dissolved by stirring. After the solution was cooled to room temperature, it was finally adjusted to one liter by adding distilled water.

2. 2　Analytical methods and analytical accuracy test

2. 2. 1　Sulfuric acid steam distillation followed by IC measurement (IC/SFC method)

Sulfuric acid distillation is a conventional technique for isolating fluoride ions from matrix in sample water as a pretreatment for fluoride determination. The distillation operation here conforms to the "Standard Methods of Analysis for Mineral Springs, Japan" (Ministry of the Environment, 2014).

Twenty-five mL of the sample water was added with a volumetric pipette in the distillation flask and placed in an ice bath, and 40 mL of sulfuric acid was added. Then, the distillation apparatus was assembled, and fluorine distillation was performed. When the temperature of the solution in the distillation flask reached 140℃, steam was introduced into the distillation flask. Then, 200 mL of the distillate was collected in a 250 mL volumetric flask. The solution was fixed to 250 mL, and then the fluoride ion was determined by IC.

2. 2. 2　Trimethylsilylating distillation (HMDS distillation) followed by ISE measurement (ISE/HMDS method)

Here, trimethylsilylating distillation using 1,1,1,3,3,3-Hexamethyldisilazane (HMDS, also known as Bis(trimethylsilyl)amine, structural formula : $(CH_3)_3Si\text{-}NH\text{-}Si(CH_3)_3$) was performed according to the distillation procedure by Tsuchiya *et al.* (1985). After assembling the distillation apparatus, 5 mL of sample water, 3 mL of diphosphoric acid, and 1 mL of perchloric acid were added to the reaction tube, and 10 mL of 0.1 mol/L NaOH solution was added to the absorption tube. Then 85 mL of HMDS was dropped into the reaction tube to start the reaction, while N_2 gas flowed for at least 40 min from the reaction tube to the absorption tube. The solution in the absorption tube was transferred into a 25 mL volumetric flask with a suitable volume of 0.5 mol/L nitric acid to neutralize the solution. Then, the volume was constituted at 25 mL with Milli-Q water to make a sample solution. Twenty-five mL of the fluoride ion standard solution containing the same NaOH and nitric acid concentrations as the sample solution was also prepared. Next, 2 mL of TISAB-B was added to the prepared sample and standard solutions, and ISE measurements were conducted using the calibration curve method.

2. 2. 3　ISE measurement without distillation (Direct ISE determination, ISE/TISAB method)

The method here involves mixing the sample with a TISAB containing metal masking reagents and analyzing it with ISE. The sample solutions mixed with the same volume of sample

water and the selected TISAB (e.g., Five mL sample and 5 mL TISAB) were subjected to the ISE measurements using the calibration curve method. Standard solutions for ISE measurements were made by mixing the fluoride standard solution and the TISAB in the same way as the sample solutions. TISABs C and D were used here to verify their applicability.

2.2.4 Spike and Recovery Test for ISE measurements

The spike and recovery tests were performed to confirm the accuracy of fluoride determination methods. The sample solution spiked with a known amount of fluoride standard solution was subjected to the ISE measurement, and then the recovery of the spiked fluoride ion was calculated. The test solutions here were prepared by adding 1.0–4.0 mL of 100 mg/L fluoride standard solution in 1.0 mL increments each to 20 mL of sample water, and then, they were made up to 25 mL with pure water using a 25 mL volumetric flask. Thus, the test solutions were prepared by adding +0, +4.0, +8.0, +12.0, and +16.0 mg/L of fluoride.

3. Results and Discussion

Table 1 summarizes the fluoride ion determination values for Yugama samples obtained by the different analytical methods applied in this study. Figure 2 shows an example of a calibration curve for ISE determination. As shown in the figure, the linearity of the calibration curves was good for all TISABs tested in this study, and there were no problems with the stability of the measurement potentials and response time.

3.1 Analytical consideration

Figure 3 shows the results of determining fluoride ion concentrations in Yugama water collected in 13 July 2015 using different analytical methods. Figure 3 shows that the IC/SFC and ISE/HMDS methods yielded nearly equal determination values of approximately 20 mg/L. In contrast, the direct determination by the IC or ISE/TISAB-B methods without distillation yielded determination values that were 40–50% smaller than those obtained by IC/SFC and ISE/HMDS. The ISE/HMDS method uses TISAB-B for ISE determination after distillation ; the only difference between the ISE/HMDS and ISE/TISAB-B methods is whether HMDS distillation was performed as a pretreatment. The analytical results shown in Fig. 3 indicate that directly determining fluoride ions by IC or ISE/TISAB-B does not yield the correct concentration because fluoride ions form stable complexes with coexisting metal ions at high concentrations in the Yugama sample. Yugama water contains several hundred mg/L of aluminum ions (Table 2). It is well-known that the presence of aluminum ions greatly hinders the determination of fluoride ions. In addition to aluminum ions, Yugama water also contains high concentration of iron ions that can form complexes with fluoride ions. Taking Yellowstone National Park as an example, Deng *et al.* (2011) mentioned that the Al-F complexes AlF^{2+}, AlF_2^+, AlF_3 and the Fe-F complexes FeF^{2+}, FeF_2^+, may be widely exist in the water samples. Therefore, the fluoride ion concentration of Yugama water cannot be uncritically accepted as determined directly by IC or ISE without pretreatment.

Next, comparing the results of three direct determinations by ISE using different TISABs in Fig. 3, the ISE/TISAB-D method gave determination values consistent with the two analytical

Table 1　Analytical results of fluoride ion concentrations in Yugama water using different analytical methods. "Mean" column lists the average F concentration with the error at the 95% confidence limits. "SD" represents the standard deviation, and "CV" represents the coefficient of variation. "*n*" shows the number of parallel experiments.

Sampling Date	Analytical Methods	F Conc. (mg L^{-1})			Mean	SD	CV(%)	*n*
July 2, 2014	ISE/HMDS	12.66	11.26	12.58	12.16±1.96	0.787	6.47	3
	ISE/TISAB-B	6.64	6.55	6.55	6.58±0.32	0.053	0.81	3
	ISE/TISAB-C	11.17	11.21	11.17	11.18±0.07	0.028	0.25	3
	ISE/TISAB-D	12.94	12.40	12.65	12.66±0.67	0.269	2.13	3
July 13, 2015	IC		10.74		-	-	-	1
	IC/SFC		19.64		-	-	-	1
	ISE/HMDS	17.19	17.90	17.10	17.40±1.08	0.437	2.51	3
	ISE/TISAB-B	7.61	7.37	7.49	7.49±0.26	0.338	1.57	3
	ISE/TISAB-C	12.64	12.53	12.58	12.58±0.61	0.800	0.44	3
	ISE/TISAB-D	19.27	18.73	18.18	18.73±1.35	0.544	2.90	3
November 22, 2015	ISE/HMDS	19.42	20.63	19.74	19.93±1.56	0.629	3.16	3
	ISE/TISAB-B	6.91	6.80	6.78	6.83±0.42	0.070	1.03	3
	ISE/TISAB-C	15.31	14.56	13.99	14.62±1.64	0.659	4.51	3
	ISE/TISAB-D	19.22	19.29	18.85	19.12±0.59	0.237	1.24	3
November 14, 2016	ISE/HMDS	20.38	22.16	20.98	21.17±2.25	0.904	4.27	3
	ISE/TISAB-B	6.19	6.09	6.11	6.13±0.46	0.056	0.91	3
	ISE/TISAB-C	14.13	14.27	13.15	13.85±1.52	0.613	4.43	3
	ISE/TISAB-D	22.11	21.89	21.15	21.72±1.25	0.502	2.31	3

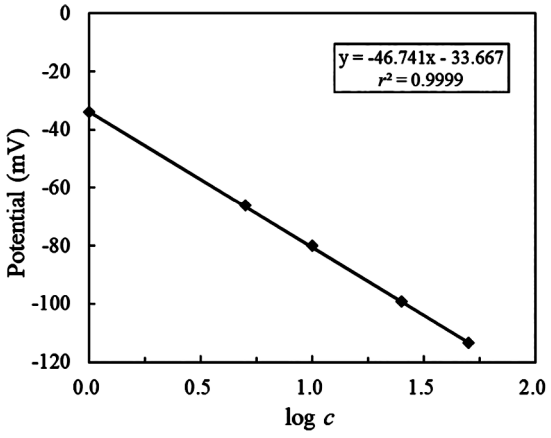

Fig. 2　An example of a calibration curve using the ISE/TISAB-D method. Measured potential values for the prepared standard solutions are plotted against the logarithm of *c* (log *c*), where *c* represents the fluoride concentration (mg L^{-1}) of the standard solutions.

Table 2　Some examples of the water quality of Yugama water in recent years.

Sampling Spot	Sampling Date	Water Temp. (°C)	pH	dissolvable components concentration (mg L^{-1})									
				Na	K	Ca	Mg	Fe	Al	Mn	Si	Cl	SO_4^{2-}
Yugama U-1	September 22, 2006	23.9	1.44	27.1	15.6	86.8	16.9	69.4	124	0.871	64.2	2495	1381
	May 20, 2012	16.1	1.12	30.6	18.6	100	19.4	77.9	157	0.969	83.7	2777	1459
	July 2, 2014	26.3	1.26	25.9	14.5	83.6	13.8	68.9	124	0.760	67.3	2575	1362
	November 3, 2015	17.5	0.98	37.0	20.6	105	24.4	83.0	186	1.16	85.1	3947	1817
	November 12, 2015	18.4	0.93	37.1	20.7	107	25.2	82.1	192	1.19	88.2	4111	1825
	November 14, 2016	12.3	0.92	46.0	25.4	129	31.6	98.6	249	1.49	88.9	4976	2204
	October 24, 2021	18.7	1.09	48.5	32.4	155	30.6	126	249	1.35	87.3	4131	1251
	September 6, 2022	26.9	1.06	39.7	20.3	131	27.1	100	219	1.15	75.6	3892	1183

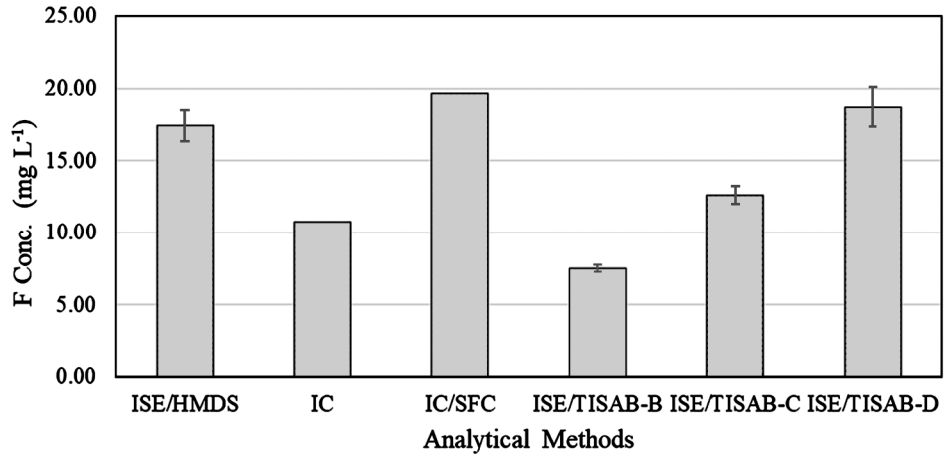

Fig. 3　Determined values of fluoride ions in Yugama water samples collected on July 13, 2015, using the ISE/HMDS, IC, IC/SFC, ISE/TISAB-B, ISE/TISAB-C and ISE/TISAB-D methods. The error bars represent 95% confidence limits.

methods using distillation as pretreatment. In contrast, the determination values of the ISE/TISAB-B and ISE/TISAB-C methods were lower than those of the methods with distillation, and the values were different depending on the type of TISAB used. The analytical results above indicate that directly determining fluoride ions in Yugama water by ISE is not impossible, but selecting the TISAB with appropriate composition is essential.

Figure 4 shows the quantitative values obtained by applying the ISE/HMDS, ISE/TISAB-B, ISE/TISAB-C, and ISE/TISAB-D methods to three Yugama samples collected at different times. The determination values obtained by the ISE/HMDS and ISE/TISAB-D methods were agreed upon within the analytical uncertainty for all samples. On the other hand, the determination values by the ISE/TISAB-B and ISE/TISAB-C methods were clearly lower than those by the ISE/HMDS method. Furthermore, although the concentration of fluoride ions in the 2014 water sample was more than 25% lower than those in the 2015 and 2016 samples, the determination values of the ISE/TISAB-B method did not reflect such differences in concentration, and all

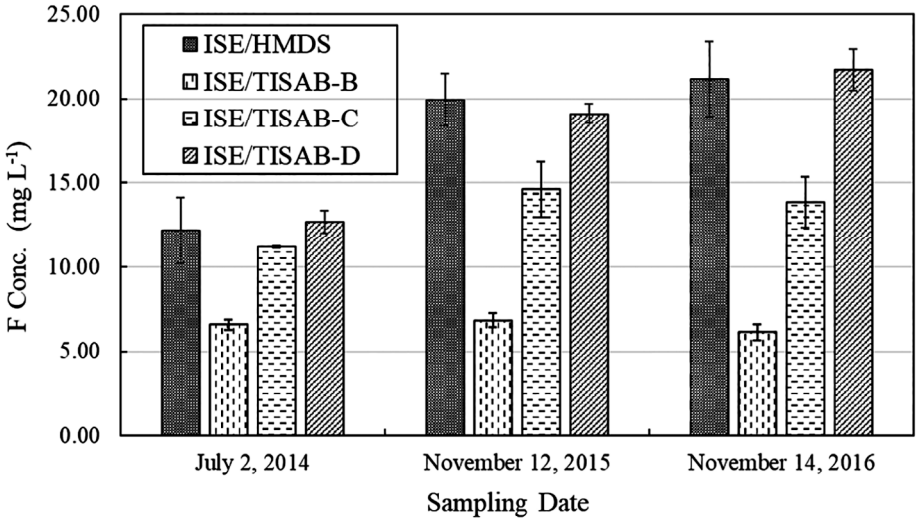

Fig. 4　Comparison of analytical results for fluoride ion determined by applying ISE/HMDS, ISE/TISAB-B, ISE/TISAB-C and ISE/TISAB-D methods to Yugama water samples collected on July 2, 2014, November 12, 2015 and November 14, 2016. The error bars represent 95% confidence limits.

Table 3　The results of spike and recovery tests using ISE/TISAB-C and ISE/TISAB-D methods for Yugama water collected on October 24, 2021.

Analytical Methods	Spike (mg L^{-1})	Measured F Conc. (mg L^{-1})	Recovery (mg L^{-1})	Recovery (%)
ISE/TISAB-D	0	17.71	0	-
	4.00	21.79	4.08	101.9
	8.00	25.77	8.06	100.7
	12.00	29.45	11.74	97.8
	16.00	32.70	14.98	93.6
ISE/TISAB-C	0	14.19	0	-
	4.00	15.70	1.51	37.8
	8.00	17.66	3.46	43.3
	12.00	19.12	4.93	41.1
	16.00	20.94	6.74	42.2

samples had almost equal determination values of 6 to 7 mg/L. In other words, the results of the ISE/TISAB-B method are considered to be completely meaningless.

Table 3 and Fig. 5 show the results of the spike and recovery tests with the ISE/TISAB-C and ISE/TISAB-D methods. The recovery of the ISE/TISAB-C method was 38–43%, while that of the ISE/TISAB-D method was 94–102%. Thus, the ISE/TISAB-D method can reliably determine fluoride ion concentrations in Yugama water.

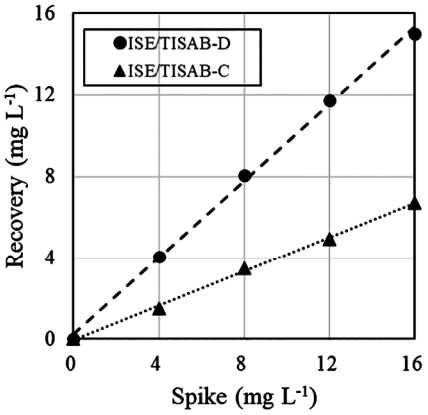

Fig. 5　Results of the spike and recovery test using ISE/TISAB-C and ISE/TISAB-D methods for Yugama water samples collected on October 24, 2021. The plots were made from the data in Table 2.

3.2　Applicability of ISE/TISAB-D method

From the above experimental results, it can be concluded that TISAB-D is the only TISAB applicable for directly determining fluoride ions in Yugama water among the TISABs tested in this study. TISAB-D is equivalent to TISAB-IV in ASTM D1179 "Standard Test Methods for Fluoride Ion in Water" (ASTM, 2021). The components acting as metal ion masking agents (complexing agents) in TISAB-B, TISAB-C, and TISAB-D are citric acid, CyDTA/citric acid, and THAM/tartaric acid, respectively. In the ISE measurement conditions in this study, all of the TISABs supposedly contain an excess of complexing agents in comparison with the concentrations of dissolved components with high affinity for fluoride ions, such as aluminum and iron ions, in Yugama water, but the differences in their complexing abilities may cause the differences in applicability.

The THAM in TISAB-D forms very stable complexes with aluminum ions (Gil *et al.*, 1997) and is considered to be very effective for Yugama water samples with high concentrations of aluminum ions. Although CyDTA in TISAB-C also has a higher complexing ability with aluminum and iron ions (JSAC, 2021), the amount of CyDTA might be insufficient for the concentration of coexisting metal ions in Yugama water samples under the experimental conditions used in this study. Moreover, citric acid, which is the complexing agent in TISAB-B, also forms stable complexes with aluminum ions. However, its complexing ability with aluminum is lower than CyDTA's and comparable to fluoride ions (JSAC, 2021). Therefore, the masking effect was insufficient despite the sufficient concentration of complexing agents compared to the metal ions in the samples in the case of the ISE/TISAB-B and ISE/TISAB-C methods. In the direct determination of fluoride ions in sample water containing metal ions by ISE, it is essential to include an appropriate complexing agent at an appropriate concentration, and it is crucial to select an appropriate TISAB composition that matches the physicochemical properties of the sample water.

Table 1, Fig. 3 and Fig. 4 show the determination values of the ISE/HMDS and ISE/TISAB-D methods agreed within an analytical uncertainty. Based on errors in Fig. 3, Fig. 4 and Coefficient of Variation (CV%) presented in Table 1, the ISE/TISAB-D method exhibits the comparable precision and repeatability as the ISE/HMDS method. Figure 4 show the ISE/HMDS method occasionally exhibited slightly higher errors than the ISE/TISAB-D method (e.g., the

results of November 22, 2015 and November 14, 2016), this may be due to the recovery error in the distillation process being reflected in the analytical error. The ISE direct determination with appropriate TISAB may save the laborious distillation process and improve the precision of the analysis. The ISE direct determination method is simple and quick because it does not require complicated distillation as a pretreatment step, and it is possible to obtain determination values for many samples quickly.

3.3 Time-series data on fluoride ion concentrations in Yugama water

The ISE/TISAB-D method was shown to be a reliable fluoride ion determination method applicable to Yugama samples. It was used to determine the fluoride concentrations in Yugama water from 2002 to 2024. Table 4 and Fig. 6 show the variation in fluoride and chloride ion concentrations over 13 years. As can be seen in the figure, the fluoride ion concentration shows almost the same fluctuation behavior as that of chloride ion, which is also a halogen. However, the fluoride ion concentration showed a distinct increase from 2007 to 2008 and from 2013 to 2016, which was much larger than the increase of chloride ion concentration during the same period. The variation of the F/Cl concentration ratio shows that the ratios were high from 2007 to 2008 and from 2013 to 2016 (Fig. 6). The fluoride and chloride ions originate from HF and HCl in the volcanic fluid that degassed from the magma, and both of them are soluble in liquid phase. Compared to HCl, higher volatilization temperatures are required for HF, and HF is more easily removed from the fluid due to the reaction with rock (Yoshida 1990). When volcanic activity becomes more active, higher temperature fluids supply the hydrothermal system, leading to an increase in the F/Cl ratio. The increase in the F/Cl concentration ratio observed during these periods coincides with a temporary increase in seismic activity in July and November 2007 and the subsequent appearance of new fumaroles on the north inner wall of Yugama in 2008 (JMA, 2008 ; 2009), and with the earthquake swarm with crustal deformation from March to August 2014 (JMA, 2015), respectively, suggesting a shallow supply of volcanic fluids. In general, supplied volcanic fluids are subject to significant dilution by meteoric water near the surface, so even in the case of an active crater lake such as Yugama, fluctuations in the concentration of halide ions do not necessarily directly reflect fluctuations in the supply flux of volcanic fluids, and an increase in concentration may not necessarily indicate an increase in volcanic activity. On the other hand, an increase in the F/Cl ratio is thought to reflect the rise in the temperature of deep fluids, suggesting increasing volcanic activity. Thus, the combination of changes in chloride and fluoride ion concentrations is expected to lead to a better understanding of the transition of volcanic activity. The appropriate ISE direct determination method can easily and quickly obtain determination values of fluoride ions in hydrothermal water samples. It will be a great help in the geochemical evaluation of volcanic hydrothermal activity.

Table 4　The time-series data of fluoride, chloride concentration and F/Cl molar ratio in Yugama water between 2002 and 2024.

Sampling Date	F Conc. (mg L^{-1})	Cl Conc. (mg L^{-1})	F/Cl Molar Ratio	Sampling Date	F Conc. (mg L^{-1})	Cl Conc. (mg L^{-1})	F/Cl Molar Ratio
July 29, 2002	10.7	2241	0.00892	November 3, 2015	20.5	3947	0.00969
August 2, 2003	11.7	2588	0.00841	November 22, 2015	20.8	4111	0.00945
May 25, 2004	12.0	2849	0.00784	April 25, 2016	19.7	4576	0.00802
August 1, 2004	11.9	2804	0.00793	May 16, 2016	19.5	4583	0.00793
June 5, 2005	11.2	2672	0.00785	May 31, 2016	21.9	4644	0.00882
July 29, 2005	10.7	2699	0.00737	June 14, 2016	21.5	4849	0.00827
May 21, 2006	10.2	2595	0.00731	July 4, 2016	21.5	4828	0.00831
July 31, 2006	9.05	2455	0.00687	August 3, 2016	21.6	4867	0.00828
September 22, 2006	9.24	2495	0.00691	August 17, 2016	21.3	5074	0.00782
May 28, 2007	13.0	2557	0.00951	September 5, 2016	20.2	4746	0.00794
August 1, 2007	13.7	2590	0.00990	October 3, 2016	18.9	4694	0.00750
July 26, 2008	11.1	2383	0.00866	October 31, 2016	19.3	4897	0.00734
October 30, 2008	11.4	2429	0.00873	November 13, 2016	19.2	4995	0.00716
May 23, 2009	10.9	2579	0.00792	November 14, 2016	19.0	4976	0.00711
May 23, 2010	11.3	2734	0.00771	April 23, 2017	19.6	4332	0.00845
August 2, 2010	10.9	2625	0.00774	May 14, 2017	19.1	4322	0.00827
May 15, 2011	11.7	2786	0.00781	June 12, 2017	18.9	4491	0.00784
July 31, 2011	10.7	2665	0.00750	July 3, 2017	18.6	4339	0.00799
October 8, 2011	9.59	2340	0.00764	August 10, 2017	17.1	4036	0.00789
May 20, 2012	10.4	2777	0.00697	September 5, 2017	17.6	4166	0.00788
August 26, 2012	8.90	2369	0.00701	June 3, 2018	16.8	4095	0.00767
May 12, 2013	9.24	2569	0.00671	June 25, 2018	17.0	4033	0.00786
August 1, 2013	12.4	2625	0.00878	July 31, 2018	17.3	4098	0.00789
September 8, 2013	13.3	2715	0.00911	August 21, 2018	17.6	4295	0.00764
November 2, 2013	12.5	2669	0.00874	October 14, 2018	19.9	4187	0.00885
May 25, 2014	12.1	2755	0.00817	October 29, 2018	19.6	4165	0.00880
June 24, 2014	12.0	2483	0.00902	November 12, 2018	19.9	4239	0.00874
July 2, 2014	11.6	2575	0.00844	April 4, 2019	20.1	4287	0.00874
August 4, 2014	12.8	3074	0.00778	June 19, 2019	18.1	4020	0.00838
September 3, 2014	13.0	2795	0.00869	August 5, 2019	18.6	4044	0.00857
September 19, 2014	13.9	2928	0.00887	October 28, 2019	16.9	3766	0.00837
September 29, 2014	14.4	3037	0.00887	August 31, 2020	18.2	3860	0.00878
October 21, 2014	12.9	3072	0.00783	October 5, 2020	19.0	3897	0.00912
November 10, 2014	17.1	3314	0.00962	October 26, 2020	19.1	3906	0.00914
May 11, 2015	17.8	3765	0.00881	May 26, 2021	19.2	4186	0.00858
June 1, 2015	18.2	3764	0.00903	July 11, 2021	19.1	4050	0.00882
June 22, 2015	18.0	3867	0.00866	October 24, 2021	19.5	4131	0.00883
July 13, 2015	18.2	3993	0.00851	June 13, 2022	18.2	3779	0.00897
August 4, 2015	19.4	4335	0.00836	September 6, 2022	18.8	3892	0.00903
September 3, 2015	20.4	4118	0.00924	September 8, 2023	20.2	4263	0.00884
October 5, 2015	20.1	4304	0.00871	June 3, 2024	19.9	3982	0.00930
October 20, 2015	19.4	4312	0.00838				

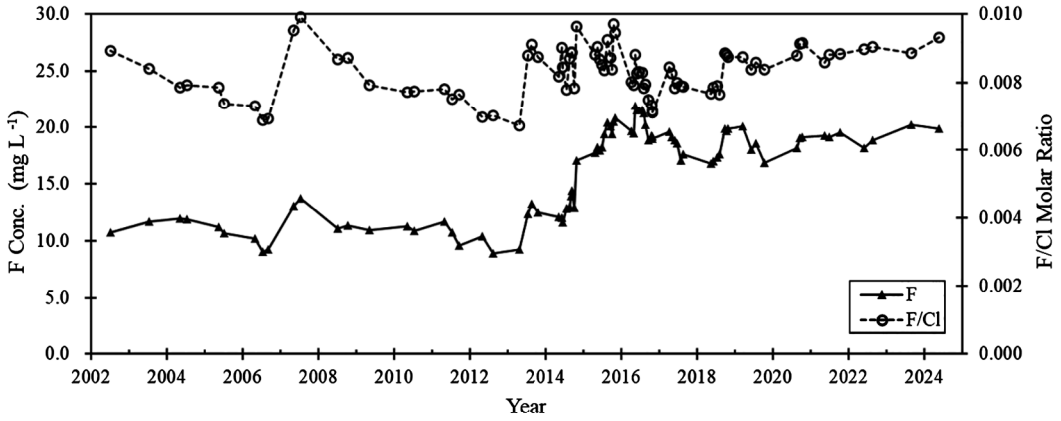

Fig. 6　The time-series data of fluoride concentration and F/Cl molar ratio in Yugama water between 2002 and 2024. The plots were made from the data in Table 4.

4. Conclusion

The total fluoride ion concentration in Yugama, an active crater lake of Kusatsu-Shirane volcano, which contains high concentrations of aluminum and other metal ions with high complexing ability with fluoride ions, could be accurately determined directly by ISE with the TISAB containing THAM as a metal complexing agent without any pretreatment such as distillation.

It is considered that this method can be applied to fluoride ion determination in lake water of various active crater lakes with compositions similar to those of Yugama. When applying this method to other samples, the levels of metal ion concentrations should be noticed, and appropriate dilution could be performed before analysis. Additionally, we recommend that the reliability of this method for a new sample can be verified by comparing the analysis results of other methods. The fluoride ion concentration is a vital indicator component in geochemical volcanic activity monitoring, and we hope that this method will be applied to monitoring many volcanic hydrothermal fluids and crater lake waters to clarify how fluoride ion concentrations vary.

Acknowledgments

We thank the local Kusatsu Town government for their support in sampling and field observations. We thank Dr. Kenji Nogami for instructing us on the HMDS distillation method.

References

Aiuppa, A., Federico, C., Paonita, A., Pecoraino, G. and Valenza, M. (2002) : S, Cl and F degassing as an indicator of volcanic dynamics : The 2001 eruption of Mount Etna. *Geophys. Res. Lett.*, **29**, 54-1-54-4.

Aiuppa, A., Federico, C., Giudice, G., Gurrieri, S., Paonita, A. and Valenza, M. (2004) : Plume chemistry provides insights into mechanisms of sulfur and halogen degassing in basaltic volcanoes. *Earth. Planet. Sci. Lett.*, **222**, 469-483.

ATSM (2021) : Standard Test Methods for Fluoride Ion in Water. ASTM D1179-16(2021)e1.

Buck, R.P. and Cosofret, V.V. (1993) : Recommended procedures for calibration of ion-selective electrodes. *Pure Appl. Chem.*, **65**, 1849-1853.

Corbillón, M.S., Carril, M.P., Madariaga, J.M. and Uriarte, I. (1995) : Fast determination of total fluoride by direct potentiometry in samples of aluminium fluoride and cryolite. *Analyst*, **120**, 2227-2231.

Deng, Y., Nordstrom, D.K. and McCleskey, R.B. (2011) : Fluoride geochemistry of thermal waters in Yellowstone National Park : I. Aqueous fluoride speciation. *Geochim. Cosmochim. Acta*, **75**, 4476-4489.

Frant, M. and Ross, J.W. (1968) : Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies. *Anal. Chem.*, **40**, 1169-1171.

Gil, R., Corbillón, M.S., Olazabal, M.A. and Madariaga, J.M. (1997) : Potentiometric study of the protonation equilibrium of Tris(Hydroxymethyl) aminomethane in aqueous sodium perchlorate solutions at 25℃ : construction of a thermodynamic model. *Talanta*, **44**, 891-896.

Hirabayashi, J. (1982) : Geochemistry of Sakurajima Volcano. *Bull. Volcanol. Soc. Jpn.*, **27**, 293-309. (in Japanese with English abstract)

Hoskins, W.M. and Ferris, C.A. (1936) : A method of analysis for fluoride : Application to determination of spray residue on food products. *Ind. Eng. Chem. Anal. Ed.*, **8**, 6-9.

JMA (2008) : Volcanic activity of Kusatsu-Shirane volcano in 2007. Japan Meteorological Agency. (in Japanese)

JMA (2009) : Volcanic activity of Kusatsu-Shirane volcano in 2008. Japan Meteorological Agency. (in Japanese)

JMA (2015) : Volcanic activity of Kusatsu-Shirane volcano in 2014. Japan Meteorological Agency. (in Japanese)

JSAC (2021) : "Stability constant" in "Analytical Chemistry Databook 6th Edition". The Japan Society of Analytical Chemistry (Ed.), Maruzen, Tokyo, Japan. pp. 32-53. (in Japanese)

Ministry of the Environment (2014) : Standard Methods of Analysis for Mineral Springs, Japan Revised in 2014 (Kosen Bunsekiho Shishin). (in Japanese)

Nogami, K. and Onizawa, S. (2020) : Fluorine and Chlorine Contents of Volcanic Ash from the 2004 Eruption of Asama Volcano, Japan. *Bull. Volcanol. Soc. Jpn.*, **65**, 1-12.

Ohba, T., Hirabayashi, J. and Nogami, K. (2000) : D/H and $^{18}O/^{16}O$ ratios of water in the crater lake at Kusatsu-Shirane volcano, Japan. *J. Volcanol. Geotherm. Res.*, **97**, 329-346.

Ohba, T., Hirabayashi, J. and Nogami, K. (2008) : Temporal changes in the chemistry of lake water within Yugama Crater, Kusatsu-Shirane Volcano, Japan: Implications for the evolution of the magmatic hydrothermal system. *J. Volcanol. Geotherm. Res.*, **178**, 131-144.

Ossaka, J., Ossaka, T., Hirabayashi, J., Oi, T., Ohba, T., Nogami, K., Kikawada, Y., Yamano, M., Yui, M. and Fukuhara, H. (1997) : Volcanic activity of Kusatsu-Shirane volcano, Gunma, and secular change in water quality of crater lake Yugama. *Chikyukagaku (Geochemistry)*, **31**, 119-128. (in Japanese with English abstract)

Peters, M.A. and Ladd, D.M. (1971) : Determination of fluoride in oxides with the fluoride-ion activity electrode. *Talanta*, **18**, 655-664.

Petrenko, D.B., Marchenko, D.Yu. and Vasil'ev, N.V. (2021) : Zirconium gallocyanin MS complex as

a highly selective reagent for the spectophotometric determination of fluoride. *Microchem. J.*, **164**, 106081.

Pickering, W.F. (1986) : The effect of hydrolysed aluminum species in fluoride ion determinations. *Talanta*, **33**, 661–664.

Smith, O.D. and Parks, T.D. (1955) : Volumetric Determination of Fluorine Involving Distillation from Sulfuric Acid Solution. *Anal. Chem.*, **27**, 998–1000.

Takano, B. (2001) : Geoscience of Active Crater Lakes. *J. Balneol. Soc. Jpn.*, **50**, 161–182. (in Japanese with English abstract)

Taran, Y. and Kalacheva, E. (2020) : Acid sulfate-chloride volcanic waters ; Formation and potential for monitoring of volcanic activity. *J. Volcanol. Geotherm. Res.*, **405**, 107036.

Taves, D.R. (1968) : Separation of fluoride by rapid diffusion using hexamethyldisiloxane. *Talanta*, **15**, 969–974.

Tsuchiya, K., Imagawa, T., Yamaya, K. and Yoshida, M. (1985) : Separation of microamounts of fluoride coexisting with large amounts of aluminium and silica by improved trimethylsilylating distillation. *Anal. Chim. Acta*, **176**, 151–159.

Wessel, P., Luis, J.F., Scharroo, R., Wobbe, F., Smith, W.H.F. and Tian, D. (2019) : The Generic Mapping Tools Version 6. *Geochem. Geophys. Geosyst.*, **20**, 5556–5564.

Willard, H.H. and Winter, O.B. (1933) : Volumetric method for determination of fluorine. *Ind. Eng. Chem. Anal. Ed.*, **5**, 7–10.

Yaguchi, M., Ohba, T. and Terada, A. (2021) : Groundwater Interacting at Depth With Hot Plastic Magma Triggers Phreatic Eruptions at Yugama Crater Lake of Kusatsu-Shirane Volcano (Japan). *Front. Earth Sci.*, **9**, 741742.

Yoshida, M. (1990) : Fractionation of fluorine and chlorine through the volcanic process. *Geochemistry of gaseous elements and compounds* (Durrance, E.M., Galimov, E.M., Hinkle, M.E., Reimer, G.M., Sugisaki, R. and Augustithis, S.S. eds.), 163–184. Theophrastus Publications, S.A.

Yoshida, M., Makihara, Y. and Katsura, T. (1978) : Separation of fluorine by microdiffusion method aided by hexamethyldisiloxane. *J. Chem. Soc. Jpn.*, **1978**, 1375–1379. (in Japanese with English abstract)

この論文に関連する学会発表：

陳怡帆，木川田喜一（2022 年 10 月 17 日）：火山性熱水におけるフッ化物イオン濃度簡易定量法の検討．日本火山学会 2022 年度秋季大会．