Simple estimation method for concentration of polythionate ions in Yugama, a crater lake of Kusatsu-Shirane volcano

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Introduction

The Kusatsu-Shirane volcano is an active volcano in Japan. It has three crater lakes at its summit. Yugama, the largest one of the three is an active crater lake. The water of Yugama contains aqueous sulfur oxyanions like polythionate ions. The concentration of polythionate ions in Yugama is a good indicator of the volcanic activity of the volcano since it fluctuates with the flux of SO_2 and H_2S supplied into the lake water from the subaqueous fumaroles.[1)] The precise determination method of polythionate ions is, however, bothersome because of their instability in aqueous circumstances, and requires the high technique of skilled analysts and some dedicated equipment. In this context, we have proposed a simple estimation method for contents of polythionate ions, which can be manipulated even by not-so-skilled analysts. The method was based on the concentration difference between SO_4^{2-} measured by ion chromatography and total SO_4^{2-} (*T*-SO_4^{2-}) measured by the gravimetric analysis preceded by oxidation of sulfur species.[2)] In this study, we examined a simpler and easier determination method of *T*-SO_4^{2-} using inductively coupled plasma atomic emission spectrometry (ICP-AES) instead of the conventional gravimetric method.

Experimental

Yugama water samples collected at a fixed sampling point (U-1) located at the southwestern shore of Yugama in 2016 were subjected to this study. We measured *T*-SO_4^{2-} concentration of a Yugama water sample repeatedly by the gravimetric method and the ICP-AES and examined the validity of the analytical data. The detailed analytical procedures are as follows:

・Gravimetric method. The sample was first boiled to remove dissolved H_2S, and bromine water was then added for oxidation of all dissolved sulfur oxyanions to SO_4^{2-}. Next, an adequate amount of barium chloride solution was added to the resultant solution to precipitate SO_4^{2-} as barium sulfate. We determined the *T*-SO_4^{2-} concentration from the weight of the precipitated barium sulfate based on the conventional procedure of the gravimetric analysis.

・ICP-AES. The sample was adequately diluted after boiled, and its sulfur concentration was measured by the ICP-AES (SEIKO SPS3520UV-DD). The spectrometer used was equipped with a vacuum chamber for the detection and measurement of sulfur emission lines in the vacuum-ultraviolet region. The concentration of *T*-SO_4^{2-} was obtained from the measured sulfur concentration.

Results and discussion

The concentration of *T*-SO_4^{2-} in the Yugama water sample obtained by the gravimetric analysis and the ICP-AES are 5,349±34 mg/L (±: the 95 % confidence limit with n=3) and 5,260±82 mg/L (95 % confidence limit with n=5), respectively. The two analytical results were equal to each other within the experimental uncertainty, with the value by the ICP-AES showing a slightly larger error. Other than these measurements, the independent ICP-AES determination procedure for *T*-SO_4^{2-} was repeated three times and yielded 5,301±82 mg/L (95 % confidence limits, n=3). This value is also equal to the above mentioned values within the experimental uncertainty. In addition, the average *T*-SO_4^{2-} concentration in eight Yugama water samples collected between April and July in 2016 were determined by the two analytical methods. The determined values by the two methods agreed well with each other. All those

results revealed that the *T*-SO_4^{2-} concentration was able to be determined more easily by the ICP-AES than by the gravimetric analysis, enabling the estimation of the concentration of polythionate ions in a rather short time.

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