

# Uncertainty in Determination of Sulfate in Crater Lake Water by Ion Chromatography

\*CHEN YIFAN<sup>1</sup>, Yoshikazu Kikawada<sup>2</sup>

1. Graduate School of Science and Technology, Sophia University, 2. Faculty of Science and Technology, Sophia University

Kusatsu-Shirane Volcano, located in Gunma Prefecture, is an active volcano, which has an active crater lake called Yugama. Many researchers are paying attention to changes in the chemical composition of Yugama water to evaluate the volcanic activity of the volcano.

By observing the chemical composition of active crater lakes like Yugama, indicators such as  $\text{SO}_4^{2-}/\text{Cl}^-$  mole ratio can be measured to evaluate the volcanic activity<sup>[1]</sup>. Additionally, the  $\text{SO}_4^{2-}/\text{Cl}^-$  mole ratio of volcanic hot spring changes with activation of volcanic activity and may reflect the state of volcanic activity<sup>[2,3]</sup>. Thus, the  $\text{SO}_4^{2-}/\text{Cl}^-$  mole ratio of geothermal fluids is the key indicator for monitoring volcanic activity. Needless to say, to determine the  $\text{SO}_4^{2-}/\text{Cl}^-$  mole ratio correctly, accurate and precise analytical methods of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  are required.

Ion Chromatography (IC) is a common method used for quantitative analysis of anions. However, the IC's analytical accuracy may be significantly reduced depending on the sample's characteristics. In this study, we will discuss the difficulties in determination of anions, especially sulfate, in geothermal fluids by using IC. The IC analysis for anions in the Yugama sample in our laboratory gave confusing results. The higher the dilution ratio of the sample when it is measured, the higher the determined concentration of  $\text{SO}_4^{2-}$  is presented in the IC analysis. On the other hand, IC has no such abnormality in the  $\text{Cl}^-$  determination.

The water samples of Yugama have several characteristics. Firstly, it shows high acidity with a pH value of around 1. Secondly, it is high salinity the water samples containing thousands of mg/L  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  and hundreds of mg/L Al, Ca and Fe. There are polythionate ( $\text{S}_n\text{O}_6^{2-}$ ) besides  $\text{SO}_4^{2-}$  as dissolved sulfur species in Yugama water<sup>[4]</sup>.

Considering the characteristics of Yugama water, we conducted laboratory experiments to clarify the factors that affect the results of  $\text{SO}_4^{2-}$  determination by IC. We prepared a series of  $\text{Cl}^-$ - $\text{SO}_4^{2-}$  solutions simulated the Yugama water. Then, by changing the several parameters in the solutions, such as  $\text{Al}^{3+}$  and other metal cations concentration and pH, investigate the factors that affect the determined  $\text{SO}_4^{2-}$  concentration by IC. The IC system used in this study is Metrohm 883 Basic IC plus (Metrosep A Supp 4-250/4.0 column, electrical conductivity detector) with 1.8 mM  $\text{Na}_2\text{CO}_3$ -1.7 mM  $\text{NaHCO}_3$  eluent.

Based on the experimental results, it was suggested that the high concentration of  $\text{Al}^{3+}$  and low pH in the analytical sample interfere with the measurement results of  $\text{SO}_4^{2-}$  by IC depending on the analytical conditions. When applying IC to the determination of anions in some crater lake water and hot spring water with high salinity, it is needed that the appropriate verification of analytical accuracy in advance.

Y. Taran, E. Kalacheva, Acid sulfate-chloride volcanic waters; Formation and potential for monitoring of volcanic activity, *Journal of Volcanology and Geothermal Research*, Volume 405, 107036, ISSN 0377-0273, 2020. Takafumi Furukawa, Akira Ueda. Tamagawa hyper-acidic hot spring and phreatic eruptions at Mt. Akita-Yakeyama: Part 1. The isotopic and chemical characteristics of the hot spring water. *Journal of Volcanology and Geothermal Research*, Volume 412, 2021. Akira Ueda, Toshiaki Tanaka, Minoru Kusakabe, Takafumi Furukawa. Tamagawa hyper-acidic hot spring and phreatic eruptions at Mt. Akita-Yakeyama Volcano: Part 2. Secular variations of  $\text{SO}_4/\text{Cl}$  ratios and their relationship to the phreatic eruptions. *Journal of Volcanology and Geothermal Research*, Volume 414, 2021. Bokuichiro Takano. Correlation of Volcanic Activity with Sulfur Oxyanion Speciation in a Crater Lake. *Science*, Vol.235, 4796, p1633-1635, 1987.

Keywords: hydrothermal fluids, Ion Chromatography, sulfur species, crater lake