Improved Isotopic Analysis for Ni, Cu, and Zn and its Application to Natural Water Samples

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Nickel (Ni), Copper (Cu), and Zinc (Zn) in the ocean are essential micronutrients or toxicants to marine communities. Although various studies on these metals have been conducted, understanding their behaviour in the surface ocean is still unmatured. These metals are supplied from land to the surface ocean through river and atmosphere. Isotope ratios of Ni, Cu, and Zn are useful to identify the sources of the metals, to estimate relative importance of the sources, and to track the biogeochemical cycles of the metals in the ocean.

We have improved the method for determining isotope ratios of Ni, Cu, and Zn in natural water samples using NOBIAS Chelate PA1 chelating resin and AG MP-1 anion exchange resin. The NOBIAS Chelate PA1 extraction collects the three metals and removes interfering major elements in samples. We found that hydrofluoric acid solution is effective to elute iron and manganese with retaining the three metals on the resin. Following anion exchange separates Ni, Cu, and Zn from each other. For the anion exchange, hydrochloric acid solution was conventionally used as the mobile phase [1,2]. We used acetic acid solution in addition to hydrochloric acid solution [3] and enabled to remove interfering elements from Cu effectively and to reduce largely the processing time and the total volume of the mobile phase.

This method was applied to natural water samples including rain, snow, rime, and river water collected from western Japan. The isotope ratios of Ni, Cu, and Zn in rain samples collected from an urban site and a mountainous site were obviously different from those in lithogenic materials, which implies that these samples were significantly contaminated by anthropogenic sources regardless of the sampling sites.

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[2] Marechal, et al (1999) *Chemical Geology* **156**, 251-273.
[3] Yang, S.-C. et al (2018) *Analytical and Bioanalytical Chemistry* **411**, 765-776.