An advanced method for preconcentration and determination of Zr, Hf, Nb, and Ta in seawater

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Zr, Hf, Nb, and Ta are known as high field strength elements (HFSE) being dissolved in seawater at very low concentrations (< 250 pmol/kg). Dissolved Zr paired with Hf and dissolved Nb paired with Ta have been proposed as tracers for water masses[1]. In the previous study, 8-hydroxyquinoline (8HQ) bonded covalently to a vinyl polymer resin (TSK-8HQ) was used for preconcentration of Zr, Hf, Nb, and Ta from seawater. However, the 8HQ group was gradually broken away from this resin during repetitive use.

We have developed a new method using NOBIAS Chelate-PA1 resin (Hitachi High-Technologies). This resin has both ethlenediaminetriacetic and iminodiacetic acid moieties that form stable complexes with trace metals at low pH and eliminate alkali and alkaline earth metals[2]. In addition, this resin is excellent in durability. To automate the preconcentration, we used this resin in a closed column attached to an off-line automated solid-phase extraction system (SPE-100, Hiranuma). First, diluted CH_3COOH-NH_3 buffer (0.01 M, pH4.0, 20 mL) was passed through the column for conditioning. A sample solution buffered with 0.01 M CH_3COOH-NH_3 to pH 4.0 was passed through the column, followed by 20 mL of the diluted CH_3COOH-NH_3 buffer to remove sea salts remaining in the column. Finally, the adsorbed metals were eluted by back flushing with 10 mL of 5 M HF-2 M HNO_3. The eluate was added with a small amount of H_2SO_4 and evaporated to near dryness using a closed evaporation system. The metals were re-dissolved in 5 mL of 0.5 M HNO_3 and determined using a high resolution ICP-MS Element 2 (Thermo Scientific) by a calibration curve method. We will report details of the method and analytical results of North Pacific seawater to compare with those by the previous method.

[1] Firdaus, M.L. *et al*. (2011) *Nat. Geosci*. **4**, 227–230. [2] Sohrin, Y. *et al*. (2008) *Anal. Chem*. **80**, 6267-6273.