

Methodological development for accurate Ni isotope measurement and its application in bivalve mollusks for environmental biomonitoring

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Bivalve mollusks are cosmopolitan organisms living on coastal shores widely used in environmental biomonitoring and as model species to understand bioaccumulation in marine invertebrates. This study developed a chromatographic purification method of diverse environmental matrices for Ni, Cu, and Zn from a single sample and evaluated Ni isotopes' utility for a biomonitoring study with bivalve mollusks from the French coasts. The three-step column separation method used different types of resins (anion exchange, cation exchange, and chelating resins) to remove matrix elements and recover target elements efficiently. In the first purification step, approximately 98% of matrix elements were removed in diluted HF and HCl solutions. In the second purification step, Ni, Cu, and Zn were sequentially separated from matrix elements with diluted HCl. Ammonium acetate and ammonia solutions were used for matrix removal in the third purification step with Chelex-100, and then Ni was purified in 2M HNO₃ with ~99% recovery. Isotope compositions were determined by MC-ICP-MS with different sample introduction systems (dry and wet plasmas). Analyzed Ni isotope values of various geological and biological reference materials were consistent with previous literatures within the analytical uncertainty. To assess its applicability in biomonitoring, we applied this method to mussels (*Mytilus edulis*) and oysters (*Crassostrea gigas*) from the Gironde Estuary and Vilaine Bay, France. The samples were acquired from the French "Mussel Watch Program". Overall, the $\delta^{60}\text{Ni}$ values in mussels are more positive than those of the oysters from the same sampling site. This difference can be attributed to various physiological mechanisms that handle these trace metals in their bodies. The $\delta^{60}\text{Ni}$ values in the oysters from the Gironde Estuary ranged from -0.06‰ to +0.48‰, showing a clear trend of increased Ni concentrations over the last 40 years, accompanied by lighter Ni isotopic compositions. Our findings suggest that Ni stable isotopes in marine bivalves may function as an effective biomonitoring tool for evaluating bioavailability, bioaccumulation processes, and anthropogenic influences of Ni on marine ecosystems. This work extends the utilization of isotope systems in bivalve mollusk in monitoring frameworks to improve the accuracy of distinguishing anthropic effects and deconvolving them of biogeochemical processes.