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TITLE: Determination of rare earth elements after pre-concentration using NOBIAS-chelate PA-1®resin: Method development and application in the San Francisco Bay plume

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ABSTRACT:

The resin NOBIAS-chelate PA-1® was used to develop an off-line pre-concentration and extraction method for rare earth elements (REEs) in seawater prior to quantification using magnetic sector, high resolution, inductively coupled plasma mass spectrometry (HR ICP-MS). The method employed an off-line manifold that is inexpensive, easy to set-up, and allows simultaneous processing of several samples. The method has low blanks and detection limits, which were in the range of 0.01 pmol kg? 1 to 0.82 pmol kg? 1, and yields quantitative recovery for all REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) precluding the need to use isotope dilution. The HR ICP-MS allows an integrated, time-averaged signal of the eluent sample, reducing the HR ICP-MS instrument time relative to an in-line extraction procedure. The applicability of the method was demonstrated in a test of the hypothesis that some REEs are being mobilized by anthropogenic activities and are elevated in San Francisco Bay (SFB) and its discharge plume into coastal waters off Central California. This was done by normalizing REE data from the SFB to those of the GEOTRACES Surface Coastal (GSC) reference sample, collected in the Santa Barbara Basin off Southern California. The normalized REE pattern indicated a substantial Gd anomaly of up to 30-fold higher than GSC in the industrial southern reach of the SFB (Lower South Bay), and to a lesser extent in the plume, indicative of anthropogenic Gd inputs, associated with the medical use of Gd-based contrasting agents in magnetic resonance imagery, from the surrounding metropolitan area. Smaller anomalies for Lu and Yb were also observed in the Lower South Bay and plume, which were tentatively attributed to industrial inputs. However, because of the relatively restricted industrial uses of these elements this hypothesis requires further investigation. Ce and Eu anomalies were observed in the northern reaches of the Bay and appeared to be associated with natural redox mediated behavior of these REEs.

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