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Automated preconcentration of Fe, Zn, Cu, Ni, Cd, Pb, Co, and Mn in seawater with analysis using high-resolution sector field inductively-coupled plasma mass spectrometry

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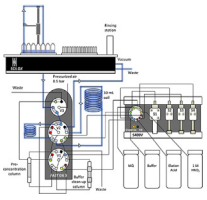
HIGHLIGHTS

- A rapid automated analytical method for simultaneous analysis of multiple trace metals in small volumes of seawater.
- Isotope dilution is utilized for concentration quantification, eliminating sensitivity to variation in recovery.
- Automated sample loading and elution volumes allow precise quantification via standard addition for monoisotopic elements.
- High accuracy was confirmed by analysis of reference seawaters SAFe S, D1 and D2.
- Improved recoveries for most tested trace metals using a WAKO resin in comparison to a NOBIAS Chelate-PA1 resin.

GRAPHICAL ABSTRACT



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ABSTRACT

A rapid, automated, high-throughput analytical method capable of simultaneous analysis of multiple elements at trace and ultratrace levels is required to investigate the biogeochemical cycle of trace metals in the ocean. Here we present an analytical approach which uses a commercially available automated preconcentration device (Sea*FAST*) with accurate volume loading and in-line pH buffering of the sample prior to loading onto a chelating resin (WAKO) and subsequent simultaneous analysis of iron (Fe), zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb), cobalt (Co) and manganese (Mn) by high-resolution inductively-coupled plasma mass spectrometry (HR-ICP-MS). Quantification of sample concentration was undertaken using isotope dilution for Fe, Zn, Cu, Ni, Cd and Pb, and standard addition for Co and Mn. The chelating resin is shown to have a high affinity for all analyzed elements, with recoveries between 83 and 100% for all elements, except Mn (60%) and Ni (48%), and showed higher recoveries for Ni, Cd, Pb, Co and Mn in direct comparison to an alternative resin (NOBIAS Chelate-PA1). The reduced recoveries for Ni and Mn using the WAKO resin did not affect the quantification accuracy. A relatively constant retention efficiency on the resin over a broad pH range (pH 5–8) was observed for the trace metals, except for Mn. Mn quantification using standard addition required accurate sample pH

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adjustment with optimal recoveries at pH 7.5 ± 0.3. UV digestion was necessary to increase recovery of Co and Cu in seawater by 15.6% and 11.4%, respectively, and achieved full break-down of spiked Co-containing vitamin B_{12} complexes. Low blank levels and detection limits could be achieved (e.g., 0.029 nmol L^{-1} for Fe and 0.028 nmol L^{-1} for Zn) with the use of high purity reagents. Precision and accuracy were assessed using SAFe S, D1, and D2 reference seawaters, and results were in good agreement with available consensus values. The presented method is ideal for high throughput simultaneous analysis of trace elements in coastal and oceanic seawaters. We present a successful application of the analytical method to samples collected in June 2014 in the Northeast Atlantic Ocean.

1. Introduction

A number of trace metals are essential micronutrients for phytoplankton growth and play important roles in ocean biogeochemical cycles [1,2]. In particular iron (Fe) has been identified as a micronutrient that directly limits phytoplankton growth in high nitrate low chlorophyll regions, which constitute ~30% of the oceans surface [1], and also controlling di-nitrogen fixation in oligotrophic gyres [3]. Other trace metals such as cobalt (Co), zinc (Zn), cadmium (Cd), manganese (Mn) and copper (Cu) may also be (co-)limiting for phytoplankton growth and/or influence phytoplankton community composition [2,4,5]. Major sources of trace metals to the ocean include continental shelf sediments, mineral dust, river discharge, submarine hydrothermal activity, and glacial melt waters [6]. Trace metal distributions are modulated by advection and diffusion, biological uptake, solubility, scavenging, organic ligand complexation and remineralization [6]. In addition, some trace metals can be used as tracers for source inputs (e.g. Mn for lateral transport from continental margins; [7,8], and Pb for anthropogenic inputs [9,10]).

Due to the complexity of these processes, and a paucity of data, our understanding of the distributions and dynamics of trace metals in the ocean remains limited. In response, the international GEOTRACES program was launched to sample and measure trace metal distributions throughout all of the major ocean basins in order to resolve controls on sources, sinks, and oceanic cycling of trace elements [11]. These sampling campaigns generate large numbers of seawater samples (often >1000) that require reliable, high throughput analytical methods to determine the concentrations of a range of trace metals.

Trace metals occur typically at very low concentrations in seawater, ranging from a few pmol L^{-1} to nmol L^{-1} which are challenging to measure. In addition, alkali and alkaline earth elements are present at relatively high concentrations of up to several hundred mmol L^{-1}, and may cause challenges during ICP-MS analysis as a result of salt precipitation in parts of the instrument and isobaric interferences with the analyte of interest. Consequently, for most seawater samples preconcentration of the analytes and removal of the salt matrix is required prior to analysis. A range of preconcentration and extraction methods have been developed, including organic solvent extraction [12,13], co-precipitation with magnesium hydroxide [14,15], and solid phase extraction using chelating resins in columns or as a batch extraction onto suspended resin beads [16–20].

A variety of resins have been developed with different functional groups that retain trace metals over a wide range of pH conditions, with recovery using diluted acids. For example, Toyopearl AF-Chelate-650 M with iminodiacetic acid (IDA) functional groups has been used in conjunction with ICP-MS detection for determination of seawater Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb [17]. A nitrilotriacetic acid (NTA)-type Superflow resin has been employed with a single batch extraction and ICPMS detection for Fe, Pb, Cd and Cu [20]. NOBIAS Chelate-PA1, containing ethylenediaminetriacetic acid and IDA functional groups on a hydrophilic methacrylate resin, has been applied for the analysis of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb with ICP-MS detection [16,19].

Here we present a new method for simultaneous, accurate, and precise determination of dissolved Cd, Pb, Fe, Cu, Ni, Zn, Co and Mn in seawaters using a commercially available automated preconcentration device with subsequent analysis by ICP-MS. We applied a resin with immobilized carboxymethylated pentaethylenehexamine (CM-PEHA) functional groups (WAKO; Kagaya et al., 2009). Sample quantification was undertaken using isotope dilution for all elements apart from the monoisotopic elements, Co and Mn. Accuracy and precision were examined using standard reference seawater and resin performance was extensively tested over pH ranges between 1.9 and 8.1 to assess whether this newly tested resin can achieve constant recoveries over a wider pH range than previously studied resins. Resin performance was also directly compared to an alternative resin (NOBIAS Chelate-PA1) using the same preconcentration set-up.

2. Experimental

2.1. Reagents for sample pre-concentration

All reagents were prepared in de-ionized water (>18.2 MΩ cm; Milli-Q, Millipore). Nitric acid (SpA, Romil) was purified by single distillation in a sub-boiling perfluoroalkoxy-polymere (PFA) distillation unit (DST-1000, Savillex). Glacial acetic acid and ammonium hydroxide (20–22%) were of the highest purity (Optima, Fisher Scientific). Ammonium acetate (NH_4Ac) buffer (1.5 M) was prepared in de-ionized water using 140 mL ammonium hydroxide solution and 90 mL acetic acid for 1 L buffer, and adjusted to pH 8.5 ± 0.05 using ammonium hydroxide or acetic acid. 1 M nitric acid was prepared using subboiled distilled nitric acid (d-HNO_3) diluted with de-ionized water. For preparation of the elution acid, 1 M d-HNO_3 was spiked with 250 ng L^{-1} indium (In) for drift correction during ICP-MS analysis. All reagents were stored in cleaned polypropylene (PP) containers provided by Elemental Scientific Inc. (ESI). All containers and sample bottles were cleaned by soaking in 2% Decon for 1 day, 1.2 M HCl (reagent grade) for 5 days, 1.5 M HNO_3 (reagent grade) for 5 days and a final rinse with de-ionized water and in between the soaking steps. The buffer and diluted acid were prepared inside a fume hood within a clean laboratory (ISO 5). Further reagent handling was carried out in an ISO 3 laminar flow bench with a HEPA filter unit.

2.2. Spike solutions

Quantification of samples and reference seawater was performed for Fe, Zn, Cu, Ni, Cd and Pb using isotope dilution, and for