



# Automated on-line flow-injection ICP-MS determination of trace metals (Mn, Fe, Co, Ni, Cu and Zn) in open ocean seawater: Application to the GEOTRACES program



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## ARTICLE INFO

### Article history:

Received 31 December 2012

Received in revised form 7 June 2013

Accepted 8 June 2013

Available online 15 June 2013

### Keywords:

Trace metals

Seawater

ICP-MS

Flow injection

Isotope dilution

Automation

Chelating resin

GEOTRACES

## ABSTRACT

Large programs in chemical oceanography currently require the determination of multiple trace elements in hundreds to thousands of open ocean seawater samples. For example, the international GEOTRACES program would benefit greatly from rapid, precise, automated, multi-element analytical methods for multiple trace metals in seawater. An automated, on-line extraction, flow-injection ICP-MS method is presented here for simultaneous determination of Mn, Fe, Co, Ni, Cu and Zn in open ocean seawater samples. A fully automated commercially available system buffers the pH of the samples on-line and extracts the metals of interest from 9 mL of seawater onto a chelation resin column, which is then eluted (1.6 M HNO<sub>3</sub>) directly into a magnetic sector ICP-MS. The resulting transient peaks elute in 45 μL (~30 s) yielding a preconcentration factor of ~200, and the total analysis cycle requires 8.75 min per sample. Elemental concentrations are calculated from integrated peak areas using a combination of isotope dilution and matrix-matched standard curves. Procedural blanks determined at periodic intervals (every 10 samples) throughout each sample run are used for blank correction and for calculating detection limits (range 0.3 to 16 pmol kg<sup>-1</sup> seawater for these elements). Replicate analyses of a Ross Sea in-house consistency standard and four GEOTRACES reference seawater materials (Atlantic and Pacific, surface and deep water) are used to demonstrate precision of 1–3% (RSD) and very good agreement with reference consensus values for all elements except Co. Determined Co concentrations are ~40% lower than consensus values, consistent with the presence of strong Co ligands in seawater, and the absence of a UV-oxidation step in this method. As illustrated by oceanographically consistent profiles at the GEOTRACES Atlantic and Pacific baseline stations, this method provides highly precise measurement of trace metals over the full range of concentrations occurring in the global ocean. Moreover, the full methodology, including flow-injection hardware and control software, is readily transferable to other users.

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## 1. Introduction

Trace metals play important roles in ocean biogeochemistry by acting as critical micronutrients for primary producers (Sunda, 2012). For instance, iron availability limits primary productivity and controls phytoplankton species assemblage over substantial portions of the ocean (Boyd et al., 2007), modulating the biological uptake of CO<sub>2</sub> in the ocean. Trace metal distributions in the oceanic water column reflect the interaction of biogeochemical processes and the physical dynamics of the ocean, and can act as tracers of major chemical input pathways to the world's oceans. The incorporation of metals into sinking particulate matter results in their deposition to deep ocean sediments and other depositional archives, where they can act as paleoceanographic proxies

to reveal aspects of the chemical, biological, and physical structure of the past ocean (Lea, 2006). For some trace metals, inputs to the ocean are being influenced by human activities such as mining, fossil fuel combustion and coastal industries. As well, climate warming and land-use practices are affecting the deposition of terrigenous dust to ocean, an important source of metals to open ocean surface waters (Baker and Croot, 2010; Wozniak et al., 2013).

A key goal of the international GEOTRACES program is to infer and quantify biogeochemical processes from comprehensive measurements of the distributions of trace elements and their isotopes through all of the major ocean basins (SCOR Working Group, 2007; [geotraces.org](http://geotraces.org)). The technology required to sample open ocean water for trace element analysis, without contamination, has evolved from the specialized province of a few practitioners to nearly routine use of commercially available oceanographic equipment (Measures et al., 2008; Sohrin and Bruland, 2011; Cutter and Bruland, 2012; Planquette and Sherrell, 2012; Fitzsimmons and Boyle, 2012) or custom-built sampling systems

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(de Baar et al., 2008). Large programs such as GEOTRACES, as well as sample-intensive trace metal studies using similar sampling methods (Sedwick et al., 2008; Lannuzel et al., 2011; Noble et al., 2012; Yager et al., 2012), can thus generate many hundreds or thousands of carefully-collected seawater samples requiring the analysis of multiple trace elements. While methods developed over the past ~35 years have produced a relatively large data base of oceanic concentrations for some elements (e.g. > 13,000 measurements of dissolved Fe; Tagliabue et al., 2012), the current large sampling programs have created an increasing need for new methods that are accurate, precise, efficient, and capable of determining multiple elements in a single analytical run.

The analysis of seawater for trace metals requires that elements present typically at  $\text{pmol kg}^{-1}$  to  $\text{nmol kg}^{-1}$  concentrations be determined in a matrix dominated by the major seawater ions at high  $\text{mmol kg}^{-1}$  concentrations. Recent methodological developments have been reviewed in the context of the ongoing GEOTRACES program (Sohrin and Bruland, 2011). Typically, analytical methods involve separation of the trace metals from the major ions and dissolved organic matter, and preconcentration of the metals to increase the signal to blank ratio, determined in part by instrumental detection limits. Methods published over the last three decades have employed solvent extraction (Bruland et al., 1979), solid phase extraction (De Jong et al., 2008; Milne et al., 2010; Lee et al., 2011; Biller and Bruland, 2012), co-precipitation with insoluble metal complexes (Boyle and Edmond, 1977) or seawater  $\text{Mg}(\text{OH})_2$  (Wu and Boyle, 1997; Saito and Schneider, 2006; Wu, 2007), and electrochemical titration (e.g. Croot, 2011). Instrumental detection has most commonly employed graphite furnace atomic absorption spectrometry (GFAAS) or inductively coupled plasma mass spectrometry (ICP-MS), although some methods employ chemiluminescence or spectrophotometric colorimetry, in addition to voltammetry (Buffle and Tercier-Waeber, 2005). Some separation and preconcentration techniques are very labor intensive or require relatively large seawater samples (100's of mL), making them impractical for use on large sample sets, either because of sample size requirements or more often because of the person-hour cost of a skilled analyst. At least two methods have avoided the complications of elemental extraction and preconcentration by analyzing seawater by direct injection ICP-MS (Field et al., 1999; 2007) but the detection limits of these methods, as well as some of the preconcentration methods (e.g. Ho et al., 2010) are insufficient to determine all of the key trace metals of interest at concentrations occurring in the open ocean.

Many of the recent advances in seawater trace metal analysis have employed solid phase extraction, either in batch mode (Lee et al., 2011) or via chelating columns (Milne et al., 2010; Biller and Bruland, 2012), using several types of chelating resin. The column methods are amenable to flow-injection techniques (Lohan et al., 2005; Milne et al., 2010; Biller and Bruland, 2012) which aid efficiency and reproducibility, particularly if they are automated (Yang et al., 2009; Ho et al., 2010; Hathorne et al., 2012) and incorporate on-line detection (Yang et al., 2009; Hathorne et al., 2012). Appropriate and careful standardization is crucial to method accuracy and precision, and matrix matching can be a significant issue for achieving demonstrably excellent accuracy in methods that employ external standard calibration. Hence, some methods use isotope dilution standardization, which can provide excellent accuracy and reproducibility, and obviates matrix matching of external standards (Milne et al., 2010; Lee et al., 2011). The demonstrated quality of long term precision is particularly important to the generation of large coherent data sets, and to the comparison of results among participating laboratories. The more recent published methods represent important advances, but require unremitting attention of a full-time expert operator (Lohan et al., 2005; Saito and Schneider, 2006; Milne et al., 2010; Biller and Bruland, 2012), or alternatively have been applied only to a single element or a limited range of elements (Yang et al., 2009; Lee et al., 2011; Hathorne et al., 2012).

Here we describe a new method that combines the positive attributes of several of the existing methods, achieving simultaneous

and automated determination of the biogeochemically relevant elements Mn, Fe, Co, Ni, Cu, and Zn in seawater. The method employs flow-injection with syringe pumps, isotope dilution standardization (Mn and Co by matrix-matched standard curves), and on-line ICP-MS detection. We demonstrate the utility and performance of the method through the analysis of standard seawater materials established during the GEOTRACES program, and of full depth vertical profiles in the North Atlantic and North Pacific oceans, using samples collected during the intercalibration cruises of the US GEOTRACES program.

## 2. Experimental

### 2.1. Reagents and materials

All solutions used to prepare reagents were of the highest purity available. Ultrapure concentrated nitric acid ( $\text{HNO}_3$ ), concentrated hydrochloric acid (HCl), glacial acetic acid, ammonium hydroxide (20–22%) (Baseline, Seastar Chemicals, Sydney, BC, Canada or Optima, Fisher Scientific, Waltham, MA, USA) and deionized water (Milli-Q Advantage A10, Millipore, Billerica, MA, USA; hereafter referred to as "MQ") were used to prepare all solutions as follows. The acetic acid–ammonium acetate buffer, a 0.5 M acetic acid and 0.6 M ammonium hydroxide solution, used for the on-line pH adjustment of the samples, was prepared in 2 L batches and adjusted to  $\text{pH } 8.30 \pm 0.05$  with ammonium hydroxide. The 1.6 M  $\text{HNO}_3$  elution acid was prepared by 10-fold dilution of concentrated  $\text{HNO}_3$  with MQ water, and was spiked with  $1.0 \mu\text{g L}^{-1}$  In, Ba and U to allow ICP-MS tuning on this matrix prior to each analytical run. An autosampler and column rinse solution of 0.012 M HCl in MQ water was prepared in a 4 L bottle and made fresh for each run of analyses. A solution of the same composition was used as the carrier solution driven by the syringe pumps to move sample and buffer through the flow injection system.

To ensure low blanks, required for the determination of trace metals in open ocean seawater, all surfaces that come in contact with the solutions used in the analysis were cleaned using well established trace metal protocols. All reagents, standards, samples, and blanks were prepared in acid cleaned low density polyethylene (LDPE) or Teflon fluorinated ethylene propylene (FEP) bottles. Bottles were cleaned by filling with ~1.2 M HCl, Trace Metal Grade (TMG; Fisher), sealing lids tightly, and heating in an oven at  $60^\circ\text{C}$  in double zip lock bags for at least 12 h. The bottles were then inverted during cooling and were subsequently rinsed thoroughly three times with MQ water. The system was cleaned initially by running 70% isopropyl alcohol, 2.9 M hydrofluoric acid, 6.0 M HCl and 8.0 M  $\text{HNO}_3$  through all tubing excluding the syringes. The following solutions were passed through the columns at a flow rate of  $1 \text{ mL min}^{-1}$  to clean the resin prior to use: (1) 10% (v/v) methanol in 1.6 M  $\text{HNO}_3$ , 50 mL, (2) 0.012 M HCl-acidified seawater, (3) 6.0 M TMG HCl, 250 mL, (4) MQ water, 200 mL and (5) 1.6 M  $\text{HNO}_3$ , 125 mL. The buffer column was cleaned by eluting with 1.6 M  $\text{HNO}_3$  every 15–20 days of analysis.

High and low enriched isotope primary spike mixtures ( $^{57}\text{Fe}$ ,  $^{62}\text{Ni}$ ,  $^{65}\text{Cu}$ ,  $^{68}\text{Zn}$ ) were prepared from individual enriched isotope solutions (Oak Ridge National Laboratory) in 0.08 M  $\text{HNO}_3$  and the mixtures calibrated by ICP-MS against commercial ICP-MS standards (high purity standards,  $10 \mu\text{g mL}^{-1}$ ) using reverse isotope dilution (ID). The working high and low spike mixtures were prepared by 10-fold dilution of the primary spike mixtures in 0.024 M HCl. The relative concentrations in the high and low primary spike mixtures were determined for optimal spiking ratios at (1) the mean metal concentrations expected for the seawater sample set to be analyzed, and (2) for blanks and very low Zn concentrations found in some near-surface waters (Sargent et al., 2002, pp. 30–32). Elemental concentrations of the working high and low spike solutions (Table 1) were set to allow conveniently small yet precise and accurate spike additions to seawater samples.

The stock solution used for generating the matrix-matched standard curves and added to samples as a check of method accuracy (see

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