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Examination of precipitation chemistry and improvements in precision using the $Mg(OH)_2$ preconcentration inductively coupled plasma mass spectrometry (ICP-MS) method for high-throughput analysis of open-ocean Fe and Mn in seawater

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Abstract

The chemistry of magnesium precipitation preconcentration of Fe, Mn, and Co from seawater was investigated, and this analytical technique was adapted for use with the Element-2 inductively coupled plasma mass spectrometer (E2 ICP-MS). Experiments revealed that the scavenging efficiency of Mn using the precipitation protocol described here was ∼95% and similar to that previously observed with Fe. In contrast, the scavenging efficiency of Co was three-fold lower than that of Fe and Mn, resulting in poor recovery. An increase in sample size to 13 mL led to several desired effects: (1) an increase in the Fe and Mn signals allowing a final dilution of samples to 0.5 mL and the use of an autosampler, (2) an increase in precision to ∼1–2.5% R.S.D., and (3) an increase in signal relative to the blank. Experiments suggest metal concentration from seawater occurs during the formation of $Mg(OH)_2$ precipitate, whereas P was scavenged by adsorption onto the $Mg(OH)_2$ particles. Example vertical profiles are shown for dissolved Fe and Mn from the Equatorial Pacific.

Keywords: ICP-MS; Iron; Manganese; Cobalt; Magnesium co-precipitation; Seawater; $Mg(OH)_2$

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1. Introduction

In recent decades the importance of trace elements, in particular iron, in controlling primary productivity of the oceans has become clear. The primary productivity in major regions of the oceans is predicted to be directly limited by iron or indirectly by iron limitation of the cyanobacterial nitrogen fixers [1]. However, geographical coverage of iron and other trace metals is quite sparse compared to major nutrients [2,3]. The difficulty in analytical methods and the potential for inadvertent contamination by metal-laden dust particles has limited the number of high-quality data sets, with studies often consisting of only a few vertical profiles or transects. Early reliable measurements of iron and other trace elements utilized the APDC solvent extraction method for pre-concentration coupled to atomic absorption spectrometry [4–6] or preconcentration with Chelex-100 and atomic adsorption analysis [7,8]. These methods, while having a high precision and accuracy, require large liter-scale sample volumes and are relatively labor intensive in both sample collection and analysis. More recently, electrochemical, flow-injection analysis with spectrophotometric detection, chemiluminescence, and inductively coupled plasma mass spectrometry (ICP-MS) methodologies have become available [9–16]. Electrochemical analyses have the advantage of being able to also characterize the natural organic ligands that bind iron and other metals in seawater [17–20]; however, these methods tend to be labor intensive, can require long deposition times to achieve good sensitivity with some elements (e.g. Zn and Cd), and can typically only analyze one or two elements at a time. For total dissolved metals, flow injection analysis with spectrophotometric detection and ICP-MS methods offer the potential for adaptation for high-throughput analysis of iron and other trace elements.

The ICP-MS methods currently utilize three approaches: (1) direct injection of small volumes of seawater for coastal

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seawater samples with high trace metal concentrations [21], (2) preconcentration using metal affinity resins [22–24], and (3) preconcentration using magnesium hydroxide ($Mg(OH)_2$) precipitation [14,15,25]. The latter two approaches have the sensitivity needed for open ocean samples, but both methods require detailed studies of the preconcentration chemistries involved to avoid artifacts or problems with accuracy. Recently, further examination of and improvements in the affinity resin chemistry (#2 above) have showed excellent precision and sensitivity for Fe and Cu, and pointed out complications with Fe(II) affinity and the need for H_2O_2 additions to oxidize Fe(II) [22]. The other low level ICP-MS method, the $Mg(OH)_2$ preconcentration technique (#3 above) is a straightforward technique that involves the addition of a base, such as ammonia, resulting in the precipitation of magnesium, which already present in the samples as a major constituent of seawater. The protocol for the method is straightforward: a known volume of seawater sample is spiked with an isotopic spike (e.g. ^{57}Fe), $Mg(OH)_2$ is precipitated by the addition of base (ammonia), centrifuged to remove the seawater supernatant, and finally redissolved in a small volume of dilute nitric acid for analysis on the ICP-MS. Because the precipitating components are part of the sample matrix (natural Mg in seawater), only a few reagents used in small quantities are required, thus avoiding the need for complex reagent cleanup protocols. Given that both of these low-level ICP-MS techniques may become the ideal methods for future large scale international ocean trace metal measurement programs (i.e. the proposed GEOTRACES [26]), improving our understanding of the chemistry behind them is imperative.

The Mg precipitation preconcentration technique has been used in various analytical formats over the years. Early inductively coupled plasma/atomic emission spectrometry (ICP-AES) approaches of this technique utilized the addition of gallium hydroxide to scavenge trace elements from seawater through the co-precipitation with $Mg(OH)_2$ [27]. This method relied on large 1 L sample volumes and filtration of the precipitant. The Mg precipitation preconcentration technique has also been applied to measuring low level oceanic dissolved phosphorus [28]. Most recently, this preconcentration technique has been coupled to ICP-MS analysis, allowing the use of isotope dilution methods for quantification of trace metals at small sample sizes [14,15]. This technique has also begun to be applied to the low level (oceanic) analysis of elements that do not lend themselves to the use of isotope dilution due to the lack of multiple stable isotopes (e.g. Mn [29]).

These recent developments suggest that Mg precipitation method has the promise of becoming a high-sensitivity and high-throughput technique capable of analyzing multiple elements at extremely scarce open ocean seawater abundances. However, the extension of this technique to multiple elements for simultaneous analysis requires a careful study of the chemistry involved in the pre-concentration step to ensure accuracy and maximize precision. There are methodological details and assumptions that are important in the application of this method, particularly for elements where there is only a single stable isotope and isotope dilution cannot be utilized. These have been discussed to some extent in previous studies [14,15,29], and in this manuscript we perform some detailed experiments examining the nature of the Mg precipitation and the resultant implications for these assumptions. We describe four assumptions here: first, the addition of the ^{57}Fe spike is important in acting as an internal standard for $Mg(OH)_2$ recovery during decanting steps, thereby correcting for small losses of the precipitate during decanting [29]. While this correction is already taken into account as part of the isotope dilution calculations, the correction is also important in its application to elements with only a single stable isotope where isotope dilution cannot be used. Second, the matrix effects associated with the $Mg(OH)_2$-rich solutions can also be corrected for using an iron isotopic spike [29] and/or indium as an internal standard. Third, the scavenging efficiency, which is basically the effectiveness of the $Mg(OH)_2$ in removing the trace element(s) of interest from the seawater, needs to be quantified on an element-by-element basis if isotope dilution cannot be used. Previous examinations of iron preconcentration have shown a scavenging efficiency of greater than 90% after single precipitations [15]. Fourth, the influence of the quantity of $Mg(OH)_2$ precipitate and the time allowed for the precipitation reaction on recoveries may have an influence on the scavenging efficiencies and matrix effects [15]. In this study, we present laboratory experiments that provide a detailed examination of the Mg precipitation chemistry, focusing on the influence of precipitation time, sequential precipitations, the use of previously precipitated seawater, and exposure of fresh seawater to precipitates on the precision, accuracy, and element-specific recovery. These results are then discussed within the context of the assumptions (listed above) involved in methodology and associated quantification calculations. In addition, an improvement in precision achieved with some minor adjustments is described. Finally, the ICP-MS performance with a desolvator and with X-sample and skimmer cones is described.

2. Materials and methods

2.1. Cleaning of plasticware

Oceanic samples have the lowest aqueous concentrations of trace elements found in nature. Significant precautions were taken at every step to avoid contamination from a wide variety of sources. All plasticware used in this study was rinsed with Milli-Q water, leached with 10% HCl (Baker Instra-analyzed grade) for one week or 48 h at 60 °C, rinsed three times with dilute ultraclean HCl (Seastar) at pH 2. Sample tubes were also rinsed with sample seawater prior to use. All cleaning and labwork was conducted in a filtered air cleanroom environment that exceeded Class-100 cleanroom specifications.

2.2. Sample collection and preservation

Uncontamined seawater was collected using 10 L Teflon coated Go-Flo bottles (General Oceanics) that had been washed with Citranox detergent initially and acid leached. Go-Flo bottles were attached to a non-metallic Kevlar line and a non-metallic metering block. Samples were dispensed from the bottle within a shipboard fabricated cleanroom with HEPA