Triethylamine-assisted Mg(OH)$_2$ coprecipitation/preconcentration for determination of trace metals and rare earth elements in seawater by inductively coupled plasma mass spectrometry (ICP-MS)

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HIGHLIGHTS

- Triethylamine is used first time for Mg(OH)$_2$ coprecipitation of trace elements in seawater.
- Quantitative coprecipitation of weakly scavenged Cd, Co, Cu, Ni, V, Se, Sb and Zn was achieved.
- Sequential coprecipitation affords total removal of Ca, Na and K matrices.
- Collision reaction interface (CRI) technology with H$_2$ gas afforded accurate determination of Cr and Fe in seawater.
- Determinations are carried out with external standards without matrix-matching or method of standard additions.

GRAPHICAL ABSTRACT
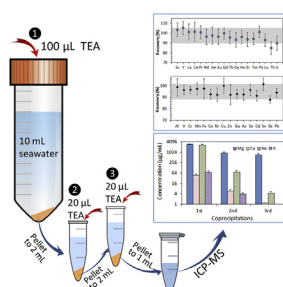
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ABSTRACT

In this paper, we report an improved magnesium hydroxide, Mg(OH)$_2$, coprecipitation method for the determination of 16 trace elements (Al, V, Cr, Mn, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Sb, Sn and Pb) and 18 rare earth elements (REEs), including Sc, Y, U and Th in seawater and estuarine water samples. The procedure involves coprecipitation of the trace elements and REEs on Mg(OH)$_2$ upon addition of a small volume of triethylamine (TEA) followed by analysis of the dissolved pellet solutions by inductively coupled plasma mass spectrometry (ICP-MS). Three-step sequential coprecipitation was carried out on 10 mL aliquots of seawater to eliminate the matrix ions and to preconcentrate the analytes of interest into a 1 mL final volume. Spike recoveries varied from 85% (Th) to 105% (Y). Calcium (Ca), sodium (Na) and potassium (K) matrices were virtually eliminated from the analysis solutions. Collision reaction interface (CRI) technology utilizing H$_2$ and He gases was employed to determine its effectiveness in removing the spectral interferences originating from the residual Mg matrix, TEA and plasma gases. H$_2$ was more effective than He in reducing spectral interferences from TEA and plasma gases. Limits of detection (LODs) ranged from 0.01 ng L^{-1} (Ho) to 72 ng L^{-1} (Al). The method was validated by using certified seawater (CASS-4) and estuarine water (SLEW-3) reference materials. Precision for five (n = 5) replicate measurements were between 1.2% (Pr) and 18% (Lu). Fe, Pb, Sn, and Zn impurities in TEA were significant in comparison to the levels in CASS-4 and SLEW-3, while relatively high background signals

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impacted determinations of low levels of Sc and Th. The effects of these hurdles on precision and accuracy were alleviated by measuring these elements in spiked CASS-4 and SLEW-3.

1. Introduction

Elemental impurities, including rare earth elements (REEs) in seawater originate from a variety of natural and anthropogenic processes. Accurately determining the concentrations of these elements in seawater has become of increasing interest because they play important roles in oceanic production as well as provide important information about geochemical cycling of metals, anthropogenic inputs and coastal pollution [1,2]. For instance, cadmium, cobalt, copper, iron, manganese, nickel, and zinc are micronutrients for phytoplankton and other marine microorganisms [1–3]. Lead is often utilized as an indicator of anthropogenic inputs and coastal pollution [4] while aluminum and scandium are tracers of oceanographic processes [5,6]. REEs have also long been used as tracers of oceanic mixing and surface water complexation [7–10]. In recent years, they are released to aquatic environments as a result of increasing use in industrial and medical applications as catalyst and magnetic resonance imaging (MRI) contrast agents [7–11]. Today, REEs are also realized as indicators of coastal pollution due to increasing discharges to coastal and estuarine waters [7–11].

Despite instrumental advancements, accurate determination of trace elements in seawater remains a challenge. This is mostly because of very low elemental concentrations ranging from parts per trillion (ppt) to low parts per billion (ppb) in a highly saline water (ca. 3.5% salt). Among various instrumental approaches, inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique offering excellent sensitivity, multielement detection capability and the ability to perform isotopic ratio analysis. ICP-MS has also been the most relied technique of the international trace metal measurement research program (GEOTRACES) which was initiated for fast and accurate determination a suite of trace metals (e.g., Al, Cd, Cu, Fe, Mn, Pb and Zn) in the oceanic waters to improve understanding of the processes involved in oceanic trace element cycles and their effects on the changing environmental conditions [12,13]. Nevertheless, direct determinations from seawater by ICP-MS are often hampered by spectral and non-spectral interferences. In addition to sample introduction challenges and reduced sensitivity due to heavy salt matrix, salt-based and Ar-based polyatomic interferences interfere with isotopes in the mid-mass (m/z) range [14,15]. Seawater matrix could also cause spectral interferences on REEs, such as $^{135}Ba^{16}O^+$ and $^{137}Ba^{16}O^+$ on $^{151}Eu^+$ and $^{153}Eu^+$, and $^{138}BaH^+$ on $^{139}La^+$, and $^{138}Ba^{16}OH^+$ on $^{155}Gd^+$. Though several groups reported direct determination of trace elements from seawater by high resolution magnetic sector instruments (HR-ICP-MS) [16,17], separation procedures are preferred, even with HR-ICP-MS determinations, to eliminate the salt matrix prior to analysis to avoid problems from exposure of the instrument to salt matrices [18,19].

Coprecipitation methods have been attractive means for eliminating the salt matrix and preconcentrating the trace elements in seawater [20–32]. Coprecipitation as metal hydroxides has also added advantage for ICP-MS since acid dissolution yields metals ions in slightly acidic solution [20–32]. Various coprecipitation methods have been reported utilizing solutions of lanthanum, La(III) [20], gallium, Ga(III) [21,22], yttrium, Y(III) [23] and iron, Fe(III) [24–26] and Mg(II) [27–32] for scavenging the trace metal ions in seawater onto insoluble $La(OH)_3$, $Ga(OH)_3$, $Y(OH)_3$, $Fe(OH)_3$, $Mg(OH)_2$ respectively. Among these approaches, $Mg(OH)_2$ coprecipitation has been popular for ultra-trace analysis as it uses Mg(II) available in seawater. The first published report of $Mg(OH)_2$ precipitation was based on the precipitation of $Ga(OH)_3$ in the presence of Mg(II) using sodium hydroxide (NaOH) at pH 9 resulting in coprecipitation of Al, Co, Cr, Fe, La, Mn, Ni, Ti, V, Zn, Y and Pb for determination by atomic emission spectroscopy (ICP-AES) [22]. Since then, $Mg(OH)_2$ coprecipitation has been studied for ICP-MS determination with various modifications without adding any additional coprecipitation agent. Elements, including Fe, Cr, Mn and Pb [27–32] were quantitatively coprecipitated from seawater.

Ammonium hydroxide (NH_4OH) has been the preferred reagent in recent studies concerning $Mg(OH)_2$ coprecipitation for ICP-MS applications as it is commercially available as high-purity reagent. Secondly, it is a weak base and thus precipitation could be achieved with little to no adjustment of solution pH. The major limitation of NH_4OH-induced $Mg(OH)_2$ coprecipitation, however, is that it only scavenges metals ions (e.g., Fe, Cr, Mn and Pb, and REEs) whose hydroxides are insoluble in water. Published literature indicates that attempts have also been made to coprecipitate Cd, Co, Cu and Zn, but the results are somewhat sporadic [28,31,32]. While Co and Zn were scavenged partially in some studies [31,32], Cd and Cu could not be precipitated with $Mg(OH)_2$ [28]. This is due to the fact that formation of hydroxides of these elements is very sensitive to pH of the medium. In slight excess of NH_4OH, these elements form soluble ammonia complexes (e.g., $Cu(NH_3)_4^{2+}$ and $Cd(NH_3)_4^{2+}$) and tend to stay in solution. In their conclusion statement, Ardini et al. [31] indicated the need for coprecipitation of Cu, Cd, Co and proposed several approaches of coprecipitation. Yet, no significant improvement has occurred over the last decade. Within this context, $Mg(OH)_2$ coprecipitation deserves implementation of new tactics to overcome its known limitations to be a large-scale multielement coprecipitation method in seawater analysis.

In this paper, we described a $Mg(OH)_2$ coprecipitation using triethylamine (TEA), an aprotic base, for scavenging the trace metals and REEs from seawater. Simultaneous coprecipitations were performed with NH_4OH and TEA to verify the relative strengths and deficiencies of the procedures with pre-cleaned real seawater samples. The coprecipitation with TEA afforded quantitative scavenging of a large suite of trace elements including those that form ammonia complexes (e.g., Cd, Cu, Co, Ni, and Zn). Experimental conditions were optimized for removal of seawater matrix via sequential coprecipitations. The CRI was optimized using H_2 and He gases. The performances of the cell gases were examined for eliminating the spectral interferences associated with residual TEA and Mg matrix, and plasma argon. To the best of our knowledge, this is first report demonstrating the analytical merits of TEA as a unique reagent for improving the scope of $Mg(OH)_2$ coprecipitation in seawater analysis by ICP-MS.

2. Experimental

2.1. Reagents and materials

Ultra-pure deionized water (18.2 MΩ cm resistivity) obtained by dual system cleaning was used throughout. Tap water was first