

An improved method for rapid preconcentration and determination of bioactive trace metals in seawater using solid phase extraction and high resolution inductively coupled plasma mass spectrometry

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Abstract

Investigating how bioactive trace metals influence the cycling of macro-nutrients and carbon in oceanic and neritic environments is hindered by the labor-intensive and slow metal preconcentration methods currently available. We describe here a solid phase extraction method that rapidly preconcentrates a suite of bioactive trace metals from seawater. The ligand bis(2-hydroxyethyl) dithiocarbamate (HEDC) is added to seawater samples and forms neutrally-charged, but polar (water soluble) metal–ligand complexes with Fe, Co, Ni, Cu, Zn and Cd. These neutral complexes can be recovered onto polystyrene-based C-18 resin columns for subsequent elution with acidic methanol. Metals are recovered quantitatively between sample pH 5–8.5. Sample flow rates of $> 10 \text{ ml min}^{-1}$ can be used, making it logistically possible to extract the larger sample volumes necessary for determining open ocean metal concentrations on conventional analytical instruments. Moreover, the method is well suited for developing flow extraction instrumentation for autonomous shipboard and in situ metal extractions and determinations. Here, we combine rapid seawater extractions with the measurement of bioactive metal concentrations by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). The low instrumental blank and high sensitivity and precision of HR-ICP-MS analyses combine to yield detection limits of $\leq 5 \text{ pM}$ for the bioactive metals of interest. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: bioactive trace metals; seawater; solid phase extraction

1. Introduction

Increasing recognition of the importance of trace metal effects on marine primary production (Martin et al., 1994; Coale et al., 1996) and algal species composition (Brand et al., 1983; Bruland et al.,

1991; Sunda and Huntsman, 1995) has driven a greater demand for accurate, precise metal determinations at the very low concentrations found in seawater. The workhorse preconcentration method for trace metal analyses over the last two decades has been solvent extraction (Danielsson et al., 1978; Bruland et al., 1979). In this approach, trace metals are chelated by synthetic organic ligands added to the sample and the resultant hydrophobic metal–

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ligand complexes concentrated into a water immiscible organic solvent (e.g., chloroform, MIBK, freon) before being analyzed, typically by graphite furnace atomic absorption. However, these techniques are labor-intensive and thus preclude sampling on the small temporal and spatial scales needed to assess the effects of physical, chemical and biological processes on metal interactions with the biota. There is a need to develop a quick, easy, quantitative multi-element preconcentration technique for bioactive metal cations (e.g., Fe, Co, Ni, Cu, Zn and Cd) to replace solvent extraction methods, particularly given the growing use of inductively coupled plasma mass spectrometry (ICP-MS) as a rapid multi-element instrumental detection system. The new extraction method must be applied easily to a range of sample volumes yet also be clean and precise enough to permit accurate trace metal determinations at picomolar levels in seawater.

Solid phase extraction offers a major advantage over standard solvent extraction methods in that it is readily amenable to automation. There are two broad types of solid phase extraction. In one, seawater is passed slowly over a resin containing immobilized chelating ligands (i.e., chelating ion exchange) while in the other, chelating ligands are added to the sample and the resultant metal–organic complexes sorbed to a resin. The problem with immobilized ligand approaches is that sample flow rates typically must be very low ($< 1\text{--}2\text{ ml min}^{-1}$) to ensure quantitative metal recoveries; ligand exchange reactions can be very slow for certain trace metals (e.g., Fe, Co, Ni). Much higher sample flow rates can be used if the complexing ligand is added to the sample for equilibration before passage through the extraction column; sorption kinetics of neutral metal–organic ligand complexes generally are much faster than metal complexation kinetics. Ligands traditionally used in solvent preconcentration methods, however, form neutral lipophilic metal complexes that not only partition readily into organic solvents but also tend to sorb to the walls of bottles and tubing, preventing complete metal recoveries on the analytical column.

King and Fritz (1985) presented a novel approach to overcome this sorption problem which was then modified by van Geen and Boyle (1990) for the automated extraction of coastal seawaters. In this

method, the widely used diethyldithiocarbamate (DDC) ligand is replaced with bis(2-hydroxyethyl) dithiocarbamate (HEDC). Substitution of the two ethylene groups of DDC with ethanol imparts greater polarity (thus water solubility) to the neutral, lipophilic metal ligand complexes; metal–ligand complexes $[Me(HEDC)_n^0]$ still sorb onto a C-18 hydrophobic resin but not onto bottle or tubing walls (Fig. 1). Although a clear improvement over more labor intensive solvent extractions, the method described by van Geen and Boyle is slow (flow rates of $\sim 10\text{ ml h}^{-1}$) and restricted to high sample pH for complete recoveries of Cd, Zn and Fe. The slow flow rates make the method logistically unsuitable for the determination of bioactive metals in open ocean seawaters because larger sample volumes need to be preconcentrated to acquire adequate sensitivity for most analytical instruments. In addition, the high

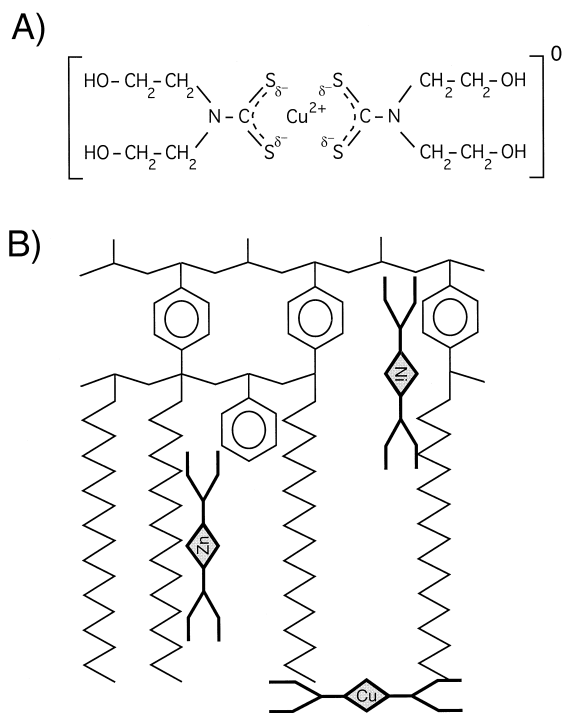


Fig. 1. (A) Schematic of a 2:1 HEDC copper complex. The hydroxyl groups impart enough polarity to the neutral, lipophilic metal ligand complexes to render them water soluble, minimizing sorption to bottle and tubing walls. (B) Schematic of HEDC–metal complex sorption to the polystyrene-based C-18 resin. The non-charged complexes will readily sorb to C-18 components as well as any of the exposed divinyl-benzene backbone of the resin.

pH requirement can cause operational problems in flow extraction methods due to the precipitation of insoluble Mg salts upon in-line mixing of high pH reagents with acidic seawater samples (Wells, unpublished). Limited precipitation of these salts also can result in incomplete metal recoveries on the column (e.g., Wu and Boyle, 1997).

We present here an HEDC solid phase extraction method which overcomes these limitations. The method operates at high sample flow rates (≥ 10 ml min^{-1}) and provides quantitative metal recoveries between pH 5–8.5. Low reagent blanks combined with high precision of replicate analyses yields extremely low analytical detection limits. This method is well suited for developing autonomous and ship-board flow extraction instrumentation for metal determinations.

2. Experimental

2.1. Reagents

The polystyrene-based hydrophobic C-18 resin (BPR-80, 20–50 μm) was kindly supplied by Benson Polymeric (Sparks). This resin was first identified by van Geen and Boyle (1990) to have lower metal blanks than other polystyrene-based resins. Commercially available silica-based C-18 resins are unsuitable for low level Fe and Zn determinations because the silica support is a significant source of contamination for these metals, particularly at near-neutral pH (Wells, unpublished). Sep-Pak light[®] polyethylene columns (Millipore) were disassembled, the silica-based C-18 resin discarded, and column components cleaned overnight in warm 6 N HCl. After rinsing with deionized water (Milli-Q), the 0.3 ml columns were slurry packed with the polystyrene-based C-18 resin from Benson. The newly packed resin columns were cleaned with repeated passes of 1 N HNO_3 methanolic solution to reduce column blanks for trace metals of interest. Blanks were improved further by conducting three separate blank runs before using the columns to process samples or procedural blanks (see below).

HEDC was synthesized from reagent grade chemicals according to the method of King and Fritz (1985). Sodium hydroxide (40.0 g; 1 mol) and di-

ethanolamine (105.1 g; 1 mol) were dissolved in 400 ml of methanol in a 1 l round bottom flask. The solution was cooled to below 10°C in an ice bath and the head space purged with N_2 while 114 g (1.5 mol) of carbon disulfide was added dropwise. After 2 h, the methanol was removed in a rotary evaporator at a bath temperature of 35°C. The resultant viscous liquid was crystallized by addition of 400 ml of 2-propanol accompanied by vigorous mixing. The yellow precipitate was filtered and dried under vacuum at room temperature. The yield of sodium (2-hydroxyethyl)dithiocarbamate was ~ 150 g (0.88 mol); a quantity sufficient for thousands of metal extractions. These crystals have been stored in a freezer for 5 years without any noticeable decrease in complexation capacity.

A 0.35 M HEDC stock was prepared in deionized (Milli-Q) water, buffered to pH 8.5 (see below), and purified by three sequential passes through pre-cleaned C-18 columns. Contaminant metals bound by HEDC as $\text{Me}(\text{HEDC})_n^0$ complexes are sorbed to the resin while the hydrophilic free ligand (HEDC^-) passes through the column. Aliquots of the purified ligand stock were transferred to acid-cleaned polyethylene bottles and frozen until use. We found noticeable decreases in metal recoveries 2–3 days after thawing the HEDC solution, so a fresh sub-stock was used each day.

A maleic acid/ammonium hydroxide buffer was chosen for this study because it provided greater buffering capacity in the pH range 4.5–9 than ammonium acetate (Pai et al., 1990). A 500 ml buffer stock (0.5 M) was prepared and adjusted to pH 8.5 with ammonium hydroxide. The buffer was cleaned three sequential times by adding 2 ml of purified HEDC and processing through pre-cleaned C-18 columns.

Column elutions were done with 3 ml of 1 N HNO_3 in methanol. Both the acid (Fisher Trace Metal Grade) and methanol (HPLC Grade) were purified separately by sub-boiling distillation in an all-quartz still and stored in acid-cleaned Teflon[®] (acid) and polyethylene (methanol) bottles until use. Ammonium hydroxide used for pH adjustments was purified by passive vapor phase equilibration; an open container of concentrated reagent was placed inside a sealed plastic bucket overnight alongside an open Teflon[®] bottle containing deionized water.

2.2. Seawater collection

Seawater samples used to verify the method were obtained from surface waters of Narragansett Bay, RI and from the California Current. Narragansett Bay samples were collected by peristaltic pump using Teflon® sample tubing attached to a boom, so that the intake could be submerged to 1 m depth 3 m from the gunwale of the fiberglass boat. Surface waters from the California Current were collected using Teflon® tubing attached to a towed fish boomed out from the vessel and pumped with an all-Teflon® double diaphragm pump. In both cases, sample seawaters were filtered (0.2 µm) using acid-cleaned inline polypropylene capsule filters (MSI) attached downstream of the pump. Seawaters were collected in acid-washed fluorinated polyethylene bottles (Nagene®) and were acidified to pH < 2 with 6 N quartz-distilled (Q) HCl.

All sample processing was done in a class 100 HEPA (High Efficiency Particle) filtered air bench situated in a clean room maintained at positive pressure by inputs of HEPA filtered air. All plasticware (Teflon®, polyethylene) and tubing (Teflon®, C-FLEX®) was cleaned rigorously by extended soaking in trace metal clean acids at an elevated temperature. Column eluates were exposed briefly to ambient air conditions at the time of analysis.

2.3. Procedure

Sub-samples (60 ml) were transferred into 60 ml Teflon® bottles and 0.2 ml of HEDC stock added (final sample concentration = 1.2×10^{-3} M), followed by 1 ml of buffer and enough NH₄OH or HCl to achieve the desired pH. The sample was then pumped through the C-18 resin by peristaltic pump at flow rates up to 10 ml min⁻¹ using the simple apparatus shown in Fig. 2. Afterwards the column was rinsed to remove salt with ~ 2 ml of deionized water buffered to the extraction pH and eluted with 3 ml of 1 N HNO₃ methanolic solution. The column eluates were warmed and slowly taken to dryness. High temperature drying was observed to decrease metal recoveries, presumably due to volatilization of metal–ligand complexes. The dried extracts were then reconstituted in 1 ml of 0.1 N HNO₃. Procedural blanks were quantified by processing deionized

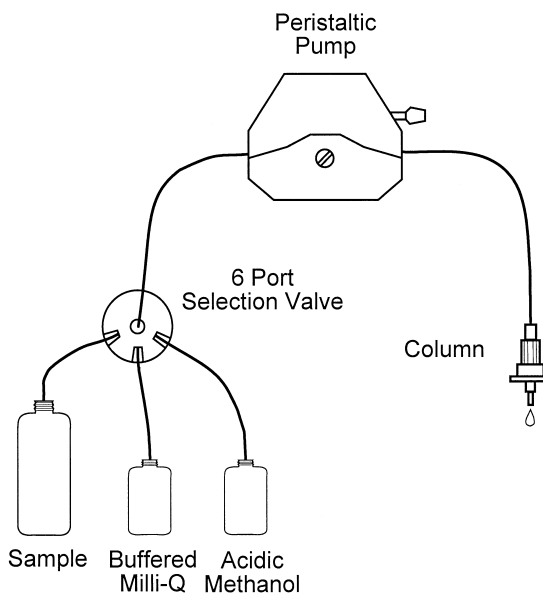


Fig. 2. Configuration of the extraction apparatus used here. This simple apparatus can easily be adapted to process four or more columns simultaneously. Teflon tubing was used throughout except for a short length of C-FLEX® tubing in the pump assembly.

water (Milli-Q) having the same acid additions as did the seawater samples.

The pH dependency of metal recoveries were determined using spike additions of ⁵⁹Fe, ⁶⁵Zn, ⁵⁷Co, and ¹⁰⁹Cd to California Current waters. Absolute metal additions with these radiotracer spikes were insignificant (< 2 pM). Isotope activities in column extracts were quantified simultaneously by gamma counting using an intrinsic germanium detector. Recoveries were calculated from counts obtained from three comparator solutions (identical in volume and geometry to sample extracts) containing the same spike addition as the samples.

To field test the method, Narragansett Bay coastal seawater was extracted with both the HEDC column method and the standard solvent extraction technique using pyrrolidinedithiocarbamate/diethylenedithiocarbamate (PDC/DDC) (Bruland et al., 1979) and the recoveries of Fe, Cu, Zn, and Co compared. Sample waters ranged in salinity from 24.6–30.5 and total dissolved metal concentrations varied by two orders of magnitude (~ < 1–100 nM). Details on sampling sites and metal determinations by solvent extractions are presented in Wells et al. (submitted).

2.4. Dissolved metal determinations

Metal concentrations in solvent extracts were determined on either a Perkin Elmer 5000 or a Perkin Elmer 4100ZL graphite furnace AA spectrometer using Zeeman background correction. Solid phase extracts were analyzed on a Finnigan MAT ELEMENT magnetic sector (high resolution) ICP-MS. Conventional quadrupole ICP-MS instruments have unit mass resolution, and thus significant corrections must be applied for polyatomic interferences when determining low level transition metal concentrations. In contrast, the magnetic sector ICP-MS used here in medium resolution ($R = 4000$) completely resolves trace metal isotopes from their polyatomic interferences, making determinations of low level metal concentrations straightforward (Fig. 3). In addition, the high sensitivity (> 10 MHz ppm^{-1} in (115) at $R = 4000$) and low instrument background (dark noise < 0.2 cps) allows accurate determinations of low level trace metal concentrations (Feldmann et al., 1994; Gießmann and Greb, 1994).

For the determinations reported here, sample extracts were pumped into a CETAC[®] microconcentric nebulizer (MCN-100) at a flow rate of $60 \mu\text{l min}^{-1}$ while the instrument scanned the mass concentrations of the dominant natural isotopes of Fe (56), Co (59), Ni (58), Cu (63) and Zn (64); Cd (111) was

Table 1

Procedural blanks for 1 ml extracts of 100 ml of deionized water at pH 8.5 ($n = 15$)

Metal	Procedural blanks		Detection limits	
	$\mu\text{g l}^{-1}$	s.d.	ng l^{-1}	pM
Fe	0.23	0.05	0.30	5.4
Co	0.022	0.004	0.02	0.3
Ni	0.06	0.03	0.18	3.1
Cu	0.06	0.03	0.18	2.8
Zn	1.51	0.06	0.36	5.5
Cd	0.19	0.04	0.24	2.1

Detection limits shown are calculated by taking $3 \times$ the standard deviation of the blank and adjusting the value to a 500 ml sample volume. Detection limits therefore will be proportionately higher with smaller sample volumes.

selected for analysis over Cd (114) to better minimize potential interferences. Each sample peak was scanned for 0.01 s, moving from low mass to high mass, and the run repeated 20 times. Concentrations were determined by comparison to linear standard curves generated from analysis of multi-element standards prepared in 0.1 N HNO_3 . The sample values reported here are the mean of these 20 measurements, normalized to an internal standard (20 ppb In) in the 0.1 N HNO_3 used to reconstitute the dried column extracts. This internal standard, measured on each run, corrects for minor changes in instrument sensitivity during the analyses. Internal

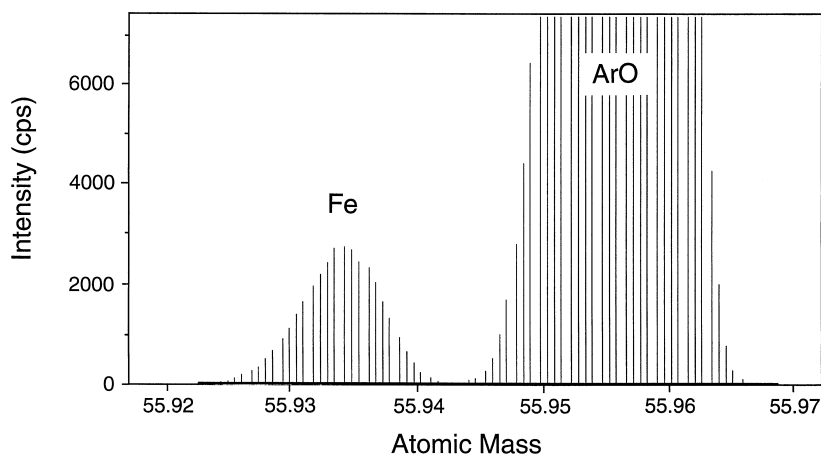


Fig. 3. Example spectrum of 3 ppb Fe solution employing the instrument conditions used for the analyses presented here. The resolution of the instrument is more than sufficient to clearly separate the Fe mass peak from the ArO mass peak which overshadows low level Fe analyses by conventional quadrupole ICP-MS. Similar or greater mass separations are achieved for other transition metals. Note that with background counts of less than 1 cps, the instrument also provides very high sensitivity (~ 10 ppt for Fe).

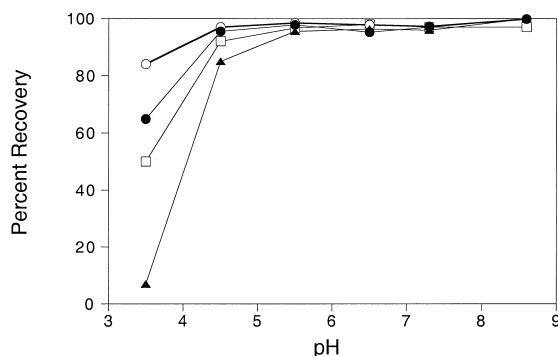


Fig. 4. The pH dependence for HEDC recoveries of ⁵⁹Fe (●), ⁶⁵Zn (▲), ⁵⁷Co (○) and ¹⁰⁹Cd (□) from seawater.

standard counts in samples tended to be slightly lower than in standards (< 10%), likely due to residual sea salt in the reconstituted sample extracts. Variations in the In counts among samples run on a given day were minimal (RSD = < 2.5%). The total analysis time per sample was ~ 3 min, leaving ~ 800 μ l of sample extract for future replicate determinations if instrumental precisions (typically < 5% based on RSD of the 20 measurements in the data acquisition scheme) were unacceptably high.

3. Results

Procedural blanks for the HEDC method are shown in Table 1. The good precision of replicate extractions yields extremely low detection limits for these bioactive metals when working with larger

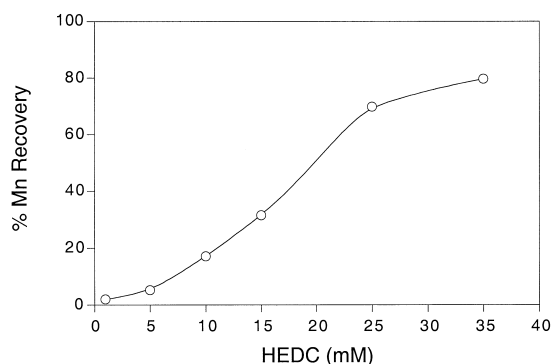


Fig. 5. The effect of increasing concentrations of HEDC on ⁵⁴Mn recovery from seawater.

(500 ml) sample volumes (< 6 pM; defined as 3 \times s.d. of replicate blanks).

We initially had difficulty in obtaining the quantitative metal recoveries achieved by van Geen and Boyle (1990) with this ligand. We subsequently found that quantitative recoveries could be attained in our scaled-up system only by thoroughly equilibrating the acid-cleaned resin to the extraction pH before processing the sample. Rinsing columns with buffered (4 mM maleic acid) deionized water until the pH of the column outflow matched that of the inflow was not sufficient; \geq 3 min of resin contact time with the buffer solution was necessary. With this added step, quantitative recoveries (95–103%) of Fe, Zn, Co and Cd were obtained at extraction pH

Table 2

Intercomparison of Fe, Zn, Cu, and Co concentrations in seven Narragansett Bay surface water samples as determined by standard solvent extraction (pH 4.5) with analysis by GFAA and HEDC column extraction (pH 8.0) and ICP-MS analysis

Metal	Solvent extracted (nM)	Column extracted (nM)	Difference (nM)
Fe	1.5	1.2	0.3
	1.9	0.7	1.2
	3.6	3.0	0.6
	5.3	5.4	0.1
	18	18	0
	18	16	2
Zn	98	101	3
	15	–	–
	15	16	1
	16	17	1
	21	21	0
	23	24	1
Cu	66	68	2
	70	72	2
	7.4	7.9	0.5
	11	12	1
	12	13	1
	15	15	0
Co	16	16	0
	24	24	0
	27	28	1
	1.2	1.1	0.1
	1.2	1.2	0
	1.2	1.2	0
	1.3	1.6	0.3
	2.5	2.4	0.1
	2.6	2.5	0.1
	2.6	2.7	0.1

between ~ 5 to ≥ 8.5 but decreased at $\text{pH} \leq 4.5$ in the order $\text{Zn} > \text{Cd} > \text{Fe} > \text{Co}$ (Fig. 4).

Diethyldithiocarbamate forms comparatively weak complexes with Mn in seawater, so if Mn determinations are desired samples normally are split for separate analyses (Landing and Bruland, 1987). However, Statham (1985) found the solvent extraction recovery of Mn using a 1:1 mix of diethyldithiocarbamate and pyrrolidinedithiocarbamate improved significantly at high ligand concentrations. We increased HEDC concentrations up to 35 mM in a separate set of experiments and achieved Mn recoveries of up to 80% at pH 6.5 (Fig. 5).

To better evaluate the performance of the modified HEDC method, we analyzed coastal seawater samples from Narragansett Bay using both HEDC/solid phase extraction and a standard PDC/DDC solvent extraction method. For the HEDC/solid phase method, 60 ml of seawater was extracted at pH 8.5 while solvent extractions were performed on 250 ml samples at pH 4.3. Extraction efficiencies of 100% were used for calculating concentrations from both methods. The mean concentrations of replicate Fe, Zn, Cu and Co determinations using the two methods are grouped in Table 2. The results demonstrate a 1:1 relationship between the methods across the range of metal concentrations typical for coastal waters.

4. Discussion

Neutral, water soluble HEDC–metal complexes are quantitatively retained on a hydrophobic column at high sample flow rates ($\geq 10 \text{ ml min}^{-1}$). The primary restriction for sample flow rates here is the small bead size of the resin used; the increased backpressure associated with higher flow rates shortened pump-tubing lifetimes considerably. We have found that substituting larger bead-size polymeric C-18 resins provides quantitative metal recoveries at sample flow rates of at least 40 ml min^{-1} (data not shown). Thus, the solid phase extraction is readily suited for preconcentrating large (250–500 ml) sample volumes needed for determining very low metal concentrations. Much smaller sample volumes are appropriate for nearshore waters where metal concentrations are higher.

We found the resin columns could be re-used several times without suffering higher blanks if the eluted columns were polished after sample elution with a second acidic methanol flush. However, on occasions we did observe a small degree of metal carryover if samples having high metal concentrations ($> 20 \text{ nM}$) were processed before samples having low metal concentrations ($< 1 \text{ nM}$). We therefore recommend additional polishing steps be taken when samples of widely varying metal concentrations are being processed.

Combining this rapid preconcentration method with high-resolution ICP-MS offers a quick, straightforward analytical method for multi-element trace metal determinations in both nearshore and offshore seawaters. Even in the case of conventional analytical determinations by GFAA, the speed of the metal extraction greatly reduces the time needed for sample analyses compared to other column or solvent extraction methods. The high sensitivity and very low background of the Finnigan ELEMENT makes it possible in most cases to use smaller sample volumes than extracted here. The ability to scale down sample sizes depends upon the metal concentrations, the magnitude of the procedural blanks, and the overall analytical precision. Although pre-cleaning of buffer and ligand stocks is easily accomplished using the same apparatus as for sample processing, several passes over the column will not entirely remove the last vestiges of Fe and Zn contamination from the buffer reagent (which accounts for $> 70\%$ of the procedural blank). But even so, the blank is small enough that the high precision of low level determinations (Table 1) is more important with regard to estimating method detection limits (defined as $3 \times$ the s.d. of replicate analyses). The excellent precision of replicate HEDC extractions is presumably attributable in part to the fewer sample transfer steps than needed for solvent extractions. Combining the high precision with larger sample volumes yields extremely low analytical detection limits (Table 1).

Our results show a significantly reduced pH dependency for metal recoveries than reported by van Geen and Boyle (1990). They found Cu and Ni were recovered fully at pH 5 but that pH 8.4 was needed to ensure quantitative recovery of Zn and Cd. Our findings show that recoveries of Fe, Co, Zn and Cd are quantitative across a wide range of pH (~ 5 – 8.5).

We believe this difference lies in prolonged pH equilibration of the resin matrix prior to sample processing (vs. only buffering the interstitial volume of the resin). Unlike silica-based resins, polystyrene is porous so that protons will migrate into the bead matrix during acid-cleaning. Although residual acid is rinsed quickly from the interstitial regions of the resin beads (as indicated by changes in the column outflow pH), continued diffusion of protons from the bead matrix could lower the pH at the bead surface and cause dissociation of the sorbed metal ligand complexes.

This effect would have not been significant at the very slow flow rates used by van Geen and Boyle ($\sim 10 \text{ ml h}^{-1}$, van Geen and Boyle, 1990), where pH equilibration of the bead matrix with the buffered seawater would have been complete before a significant portion of the sample had been processed. Nonetheless, this effect might explain why their recoveries of Cd and Zn were incomplete below pH 8.4 (i.e., longer matrix pH equilibration time due to smaller proton diffusion gradients). Similarly, the smaller buffering capacity of freshwater solutions could explain the 10–15% lower Zn recoveries they observed in freshwater samples (van Geen and Boyle, 1990) (e.g., Fig. 4).

Mn recoveries were marginal, even at HEDC concentrations up to 35 mM. In contrast, Statham (1985) reported quantitative recovery of Mn by solvent extraction at pH 5–9 with 10 mM PDC/DDC. It is unclear whether the lower recoveries here result from a lower affinity of HEDC for Mn or a lower partition coefficient of the Mn (HEDC)₂⁰ complex for the C-18 resin, or both. Regardless, the comparatively high blanks at these elevated HEDC concentrations are unacceptable for low level determinations of Fe and Zn. In addition, reliable Mn determinations using the HEDC method would require a yield tracer. Without resorting to the logistical difficulties surrounding use of radioactive ⁵⁴Mn, the choice of a suitable tracer element is not straightforward. We therefore view the HEDC method as inappropriate for Mn determinations and currently are working on developing an alternate approach.

This method was developed to obtain total dissolved ($< 0.2 \mu\text{m}$) metal concentrations. We utilize an acidification step (to pH ~ 1.7) for two reasons: (1) to dissociate any organic chelates of bioactive

metals, and (2) to solubilize any colloidal inorganic metal forms present. HEDC then is added just prior to buffering the sample to the extraction pH (ideally pH 5–6). The vast excess of HEDC (1.2 mM) over natural chelator concentrations (nM) assures preferential coordination of Me-HEDC complexes upon pH adjustment. In the case of acidified samples, a lower extraction pH is preferable because less base/buffer is needed and thus lower blanks can be achieved. We do not recommend applying the method to non-acidified seawater samples because complexation of dissolved metals by HEDC may occur to a lower extent due to competition with natural metal chelates and inorganic colloidal forms.

The simplicity, speed and reusable column features of this rapid HEDC/solid-phase extraction method opens the way towards developing practical autonomous multi-metal samplers. We have developed a compact manually-operated extraction unit based on this method for shipboard use so that samples can be processed shortly after collection. We are investigating the minimum period of sample acidification needed to obtain quantitative results for all metals. Currently the system comprises two columns run simultaneously for replicate sample extractions, but it could easily be expanded to increase the number of parallel columns. Combined with rapid, multi-element determination by high-resolution ICP-MS, this solid phase preconcentration method decreases sample processing times by an order of magnitude and greatly facilitates studies of short term metal–biota interactions. We intend to automate this procedure in the near future. Because HEDC degrades in solution at room temperature within a couple of days, we are investigating other more robust ligands that will enable the development of an autonomous in situ, low level multi-metal extraction device.

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