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MULTIELEMENT SOLID PHASE PRECONCENTRATION USING A CHELATING RESIN OF STYRENE DIVINYLBENZENE COPOLYMER AND APPLICATION TO ANALYSIS OF SEAWATER AND FISH OTOLITHS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICPMS)

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Abstract

A new chelating resin has been synthesized by immobilizing 4-(2-thiazolylazo) resorcinol (TAR) onto styrene divinylbenzene copolymer and examined for on-line solid phase extraction/preconcentration of Cd, Co, Cu, Ni, Pb and Zn in seawater and fish otoliths for determination by inductively plasma mass spectrometry (ICP-MS). A volume of 5.0 mL sample solution was loaded onto the mini column of TAR immobilized resin at 2.0 mL min⁻¹ via a sequential injection system. The optimum pH for multielement preconcentration was around pH 5.5. Recoveries were better than 96% in artificial seawater. Elution was achieved with 1.0 mL of 0.75 mol L⁻¹ HNO₃. The resin possesses large sorption capacity ranging from 82.0 µmol g⁻¹ for Pb to 319 µmol g⁻¹ for Cu. The detection limits (3s) varied between 0.0016 µg L⁻¹ (Cd) and to 0.015 µg L⁻¹ (Zn) for preconcentration of 5.0 mL blank solutions (pH 5.5). Relative standard deviation (RSD) for three replicate runs was between 0.3% (Cd) and 6% (Zn) at 1.0 µg L⁻¹ level. The procedure was validated by analysis of Nearshore Seawater certified reference material (CASS-4), and then successfully applied to the determination of the trace elements in fish otoliths (CRM 22) and in coastal seawater and estuarine water samples.

Keywords

Solid phase extraction; TAR immobilized Chromosorb 106; seawater; fish otolith; ICP-MS

INTRODUCTION

Trace elements in seawater and fish otoliths possess important roles on global biogeochemical cycles, and oceanic ecosystem and fisheries dynamics (Lane and Morel 2007; Norisuye et al. 2007; Bruland, Donut and Hutchins 2009; Milne et al. 2010). Cobalt

(Co), copper (Cu), nickel (Ni), and zinc (Zn) are essential for the growth and sustainability of marine phytoplankton. Cadmium (Cd) is a toxic heavy metal, but recent studies show that Cd also plays important role through Cd-species anhydrase and is required by certain diatoms (Lane et al. 2007; Norisuye et al. 2007). Lead (Pb) is important tracer of natural or anthropogenic inputs through aerosol deposition and/or lateral transport from continental margins (Ho et al. 2010; Milne et al. 2010). Likewise, trace elements in fish otoliths are biological tracers of physico-chemical conditions of fish habitats and thus provide useful information in fisheries to elucidate life histories, nursery habitats, mixing rates and population dynamics of the fish species (Thresher 1999; Campana and Thorrold 2001; Arslan and Secor 2005; Campana et al. 2007; Gao et al. 2010). Otoliths are made up of CaCO_3 in the aragonite polymorph and contain trace elements that are derived from the water. Therefore, the elemental concentrations in otoliths are often as low as those in water (e.g., seawater).

Inductively coupled plasma mass spectrometry (ICP-MS) has been a powerful technique in trace element determinations in seawater owing to its multi-element detection capability and excellent sensitivity affording determinations at sub-parts per trillion levels. It has also been an indispensable tool in otolith microchemical analysis (Thresher 1999; Campana and Thorrold 2001; Arslan and Paulson 2002; Arslan and Secor 2005; Campana et al. 2007; Daniels and Arslan 2007; Gao et al. 2010). However, determination of trace elements, especially those in the mid-mass range, by traditional ICP-MS analysis is problematic due to the instrumental instability and spectral interferences caused by the salt matrices. The spectral interferences of matrix ions, and molecular ions of argon oxides and hydroxides, such as $^{40}\text{Ar}^{16}\text{O}^+$, $^{40}\text{Ar}^{16}\text{OH}^+$, $^{43}\text{Ca}^{16}\text{O}^+$, $^{44}\text{Ca}^{16}\text{O}^+$ and $^{23}\text{Na}^{40}\text{Ar}^+$, often preclude accurate determinations (Warnken et al. 2000; Arslan and Paulson 2002; Beck, Franks and Bruland 2002; Otero-Romani et al. 2005, 2009; Daniels and Arslan 2007; Biller and Bruland 2012). To overcome these hurdles, various approaches have been used for determination of trace elements in seawater and otoliths, which include solvent extraction (Batterham and Parry 1996; Yoshinaga, Morita and Edmonds 1999), cloud point extraction (Dasilva, Frescura and Curtius 2000), coprecipitation (Saito and Schneider 2006; Daniels and Arslan 2007), and solid phase extraction (SPE) (Warnken et al. 2000; Willie et al. 2001; Arslan and Paulson 2002; Beck et al. 2002; Camel 2003; Arslan and Secor 2005; Ho et al. 2010; Milne et al. 2010).

SPE approaches have been by far the most popular owing to their simplicity, high enrichment factors, and reduced risk of contamination. Polymeric supports possessing 8-hydroxyquinoline (8-HQ) (Wen and Shan 2002; Otero-Romani et al. 2005, 2011) and iminodiacetate (IDA) chelating groups (Warnken et al. 2000; Willie et al. 2001; Arslan and Paulson 2002; Gao et al. 2002; Jimenez, Velarte and Castillo 2002; Milne et al. 2010; Oliveira et al. 2011, Veguería et al. 2013) have been frequently used for preconcentration of trace elements from seawater and brines. In addition to 8-HQ and IDA, chitosan (Katarina et al. 2008), 1,5-bis(2-pyridyl)-3-sulphophenylmethylenethiocarbonohydrazide (PSTH) (Trujillo et al. 2012), 1-(2-thiazolylazo)-2-naphthol (TAN) (Zaporozhets et al. 1999; Yilmaz and Kartal 2012), succinic acid (Metilda et al. 2005), and 2,6-diacetylpyridine (Kara, Fisher and Hill 2006), Nobias-chelate PA1 chelating resin (Biller and Bruland 2012), ion imprinted polymer possessing 8-HQ (Otero-Romani et al. 2009) have been also utilized in

determination of trace elements from seawater. A comprehensive list of chelating agents utilized in SPE applications and their performances have been discussed in a review paper (Camel 2003).

Thiazolyazo reagents, such as 4-(2-thiazolyazo) resorcinol (TAR), form strong complexes with most transition elements and heavy metals and thus have been popular for preconcentration of trace metals (Karipcin et al. 2009; Karatepe et al. 2011). Recently, we have reported the synthesis of a novel chelating resin by coupling TAR via –N=N– group onto Chromosorb 106, a gas chromatographic resin of cross-linked styrene divinylbenzene and successfully utilized for determination of rare earth elements (REEs) in seawater samples at sub-ng mL⁻¹ levels (Zereen, Yilmaz and Arslan 2013). In this study, we examined the performance characteristics of the Chromosorb 106-TAR chelating resin as column packing for on-line solid phase extraction/preconcentration of trace transition elements and toxic heavy metals, including Cd, Co, Cu, Ni, Pb and Zn. The effects of various experimental variables, such as pH, acid eluent and its concentration, flow rates of sample and eluent, and capacity of the chelating resin were examined. The performance of the resin was verified with determination of the elements in seawater and fish otolith certified reference materials by ICP–MS.

EXPERIMENTAL

Reagents and materials

Double deionized water (18.2 MΩ cm) was produced by a Barnstead™ E–Pure system and a reverse–osmosis unit (SpectraPure). Multielement stock solutions of Al, As, Ba, Cd, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Sr, Tl and Zn were prepared from a 10 µg mL⁻¹ stock standard solution (SpexCertiPrep, Metuchen, NJ) in 0.75 mol L⁻¹ HNO₃ (Trace metal grade, Fisher Scientific). An ammonium acetate buffer solution (pH 9.0) was prepared with 182 mL of trace metal grade ammonium hydroxide (Fisher Scientific) and 112 mL of acetic acid (99.99+%, Sigma Aldrich) in 1.0 L deionized water. The pH of the experimental solutions was adjusted with this buffer solution to desired pH.

Artificial seawater was prepared from ultrapure reagents by dissolving 24.6 g NaCl (99.999%, Sigma Aldrich), 0.75 g KCl (99.995%, Alfa Aesar), 1.03 g CaCl₂ (99.99%, Sigma Aldrich), 3.06 g MgSO₄ (99.9%, Alfa Aesar), 2.18 g MgCl₂ (99.9%, Alfa Aesar) and 0.18 g NaHCO₃ (99%, Sigma Aldrich) in 1.0 L deionized water acidified to 0.015 mol L⁻¹ HNO₃. All other reagents, including 4-(2-thiazolyazo)resorcinol (TAR) (Alfa Aesar), sulfuric acid, hydrochloric acid, tin chloride (SnCl₂), sodium nitrite (NaNO₂) were reagent grade.

Chromosorb 106 resin (Supelco, Celite, CA, USA), gas chromatographic stationary phase of styrene divinylbenzene copolymer (180–250 µm in size) was used for synthesis of the chelating resin. The average surface area of the resin was 750 m² g⁻¹ with average pore diameter of 50 Å. The resin was cleaned with 0.5 mol L⁻¹ HCl, 0.5 mol L⁻¹ NaOH and finally with water, and air-dried prior to preparation of chelating resin with TAR.

Instrumentation

Measurements were performed by using a Varian 820MS inductively coupled plasma mass spectrometer (Varian, Australia). The instrument was equipped with a peltier-cooled double-pass glass spray chamber, an teflon Ari-mist nebulizer (SCP Science, Champlain NY), standard one-piece low flow ball-and-socket connection quartz torch, Ni sampler and skimmer cones and all-digital detector (DDEM, Model AF250, ETP Australia). Samples were introduced manually. The instrument was optimized daily for sensitivity, doubly charged ions (<1%) and oxides (<3%) with 5 $\mu\text{g L}^{-1}$ Ba, Mg, In, Ce, Pb solution. Signals for $^{138}\text{Ba}^+$, $^{25}\text{Mg}^+$, $^{115}\text{In}^+$, $^{140}\text{Ce}^+$, $^{208}\text{Pb}^+$ were monitored. Data collection was achieved by ICP-MS Expert software package (version 2.2 b126). The operating parameters of the instrument are summarized in Table 1. Two isotopes of the multi-isotopic elements, namely ^{63}Cu and ^{65}Cu for Cu, ^{66}Zn and ^{68}Zn for Zn, ^{60}Ni and ^{62}Ni for Ni, ^{111}Cd and ^{114}Cd for Cd, and ^{206}Pb and ^{208}Pb for Pb were monitored during the course of the method optimization and analysis of real samples. Germanium (^{72}Ge) and rhodium (^{103}Rh) were used as internal standard (IS) elements to correct for possible instrumental drift and sensitivity changes. ^{72}Ge was used for ^{59}Co , ^{60}Ni , ^{61}Ni , ^{63}Cu , ^{65}Cu , ^{66}Zn and ^{68}Zn while ^{103}Rh was assigned to ^{111}Cd , ^{114}Cd , ^{206}Pb and ^{208}Pb . The internal standard solution (5.0 $\mu\text{g L}^{-1}$ Ge and Rh in 0.15 mol L^{-1} HNO_3) was mixed on-line with the sample solution.

A Nexus, Model 870 FT-IR spectrometer equipped with a DTGS (Deuterated triglycine sulfate) infrared detector was used to record the FT-IR spectra of the intermediate products and functional groups chemically immobilized on the resin to verify the successful synthesis of Chromosorb 106 - TAR. Samples were prepared in potassium bromide pellets (Sigma Aldrich, IR grade). Spectra were collected using OPUS Version 4.2 software package in the range of 4000–400 cm^{-1} , at 10 scans and 4 cm^{-1} resolution. The pH of the solutions was measured by an Oakton pH 6 series microprocessor-based hand-held pH meter. The pH meter was daily calibrated before each measurement with pH 4 and 10 buffer solutions.

Solid phase extraction/preconcentration system

The column was made from 4.5-cm long teflon tubing (1.6 mm i.d.; 180 μL inner volume) which was packed with 40 mg of Chromosorb 106-TAR chelating resin. Both ends of the column were closed with glass wool to retain the resin. The column was cleaned by washing with 0.75 mol L^{-1} HNO_3 and deionized water before use. A FIALab-3200 (FIALab Instruments Inc., Bellevue, WA) sequential injection (SI) unit was used for automated solid phase extraction/preconcentration (Fig. 1). The unit was equipped with an 8-port multiposition selection valve (SV), a constant-speed peristaltic pump (PP), two 30,000-step syringe pumps (SP) (Cavro, Sunnyvale, USA) with a capacity of 5 mL for sample (SP_1) and 1 mL for eluent (SP_2). The central port (CP) on the SV was connected to the analytical column of the chelating resin. A manual valve (V_3) was placed on the sample line to direct the sample solution to the waste or to the column. Elution was made into 2-mL acid-cleaned centrifuge tubes (CT). The SI system was controlled by the FIALab software package (version 5.0) running on personal computer.

The operation of the FIA 3200 unit using the optimized SPE conditions is summarized in Table 2. In step 1, SP_1 aspirated 0.5 mL of sample solution at 6 mL min^{-1} and delivered to

waste through V₃ switched to port 1 (Step 2). In the meantime, column was washed with dilute buffer solution (pH 5.5) running through PP at 7 mL min⁻¹. In step 3, 5.0 mL of sample solution was aspirated at 6 mL min⁻¹ (V₁ at position 1) and loaded onto the column at 2 mL min⁻¹ (V₁ at position 3) (Step 4). At this step, PP was turned off. In step 5, SP₁ aspirated 3 mL of buffer solution and passed through to column to deliver the remaining sample solution in the line as well as to wash the column (Step 6). Elution was made with 1.0 mL of 0.75 mol L⁻¹ HNO₃ solution into the 2-mL acid cleaned centrifuge tube. After the column wash, SP₂ aspirated 1.0 mL of 0.75 mol L⁻¹ HNO₃ (Step 7, V₂ at port 1) at 6 mL min⁻¹ and then pumped through the column at 2 mL min⁻¹ (Step 8, V₂ at port 3).

Synthesis of Chromosorb 106–TAR chelating resin

TAR acts as terdentate ligand through the resorcinol OH, azo N and thiazolylazo N and hence forms colored, stable complexes with various bivalent transition metal ions (Karipcin et al. 2009; Karatepe et al. 2011). Chromosorb 106–TAR chelating resin was prepared according to the procedure as described previously (Zereen, Yilmaz and Arslan 2013). Procedural steps involving the synthesis and the proposed structure of the resin are shown in Fig. 2. Under continuous stirring, approximately 2 g of Chromosorb 106 resin was slowly added in a fume hood into a 250-mL round-bottom flask containing a mixture of 10 mL of concentrated HNO₃ and 25 mL of concentrated H₂SO₄. The mixture was heated at 60 °C for 1 h and then cooled in an ice bath and filtered. The nitrated resin was repeatedly washed with water to remove all free acid, and then added to reducing mixture of 16 g of SnCl₂, 20 mL of concentrated HCl and 20 mL of ethanol and refluxed at 90 °C for 24 h. The aminated resin was filtered off and then washed with water, 50 mL of 2 mol L⁻¹ NaOH and 50 mL of 2 mol L⁻¹ HCl, respectively. Excess HCl was washed off with water and the resin was transferred to a flask in ice–water bath. Onto the resin, 50 mL of 1.0 mol L⁻¹ HCl was added and allowed to react for about 3–4 h at room temperature, and then 50 mL of 1.0 mol L⁻¹ NaNO₂ were slowly added at 0–5 °C. The diazotized resin was quickly filtered, washed with ice–cold water and then added to a solution of TAR (1.0 g of TAR dissolved in 50 mL of 0.5 mol L⁻¹ NaOH) at 0–5 °C and reacted for 24 h. The resulting reddish–brown resin beads were filtered and then washed with 4 mol L⁻¹ HNO₃, acetone, and water, respectively, to remove the free TAR and impurities. The resin was dried at room temperature and stored in a desiccator until use.

Optimization of SPE conditions

The effect of solution pH was examined with 5.0 µg L⁻¹ multielement solutions within a pH range from pH 2 to 9. A volume of 5 mL multielement solution was loaded onto the column at 1.5 mL min⁻¹ and eluted with 1.0 mL of 0.75 mol L⁻¹ HNO₃. Following the optimization of the solution pH in deionized water, the retention performance was closely examined through recovery studies in artificial seawater across a pH range from pH 4 to 6. In this experiment, artificial seawater samples (5 mL) containing 5.0 µg L⁻¹ multielement spike were loaded onto the column and eluted with 0.75 mol L⁻¹ HNO₃. Then, the effect of HNO₃ concentration was examined with 0.075, 0.15, 0.3, 0.45 and 0.75 and 0.9 mol L⁻¹ to achieve quantitative elution of the retained elements. The volume of eluent acid was examined for 0.5, 1.0 and 2.0 mL of 0.75 mol L⁻¹ HNO₃ to determine the optimum volume.

The flow rates of sample solution and acid eluent were examined at the optimum pH conditions for $5.0 \mu\text{g L}^{-1}$ multielement solutions. To affect the analyte retention on the column, the flow rate of the sample solution was increased from 1.0 to 6.0 mL min^{-1} . Likewise, eluent flow rate was examined between 1.0 and 6.0 mL min^{-1} . The sorption capacity of the chelating resin was determined by batch method by equilibrating 50 mg of the resin in 20 mL, $50 \mu\text{g mL}^{-1}$ single element solution of Cd(II), Co(II), Cu(II), Ni(II), Pb(II) or Zn(II) at pH 5.5 on a oscillating shaker for 2 h. The concentration of metal ions remained in the solution were determined by ICP–MS.

Samples and preparation

Otolith and seawater certified reference samples were analyzed to verify the performance of the method. Fish otolith certified reference material (CRM No. 22) was purchased from the National Institute of Environmental Studies (NIES), Japan. The material was prepared from sagittal otoliths of emperor snapper (*Lutjanus sebae*). It is certified for Ba, Ca, K, Mg, Na and Sr along with indicative values for Cd, Cu, Pb and Zn. Otolith samples were prepared according to the procedures described elsewhere (Arslan and Paulson 2002; Kenduzler et al. 2012). Briefly, 50 mg sub-samples were digested in teflon tubes (4 mL) in concentrated HNO_3 . Each sample was first wetted with water and then dissolved slowly with dilute HNO_3 to avoid bubbling. Then, 1.0 mL of concentrated HNO_3 was added and the contents were heated to dryness at 120°C by using a 20-well digestion block (DigiPrepCube, SCP Science, Champlain, NY). At dryness, 1 mL water was added and reheated to dryness. At the end, the residue was dissolved in 2 mL of $0.015 \text{ mol L}^{-1} \text{HNO}_3$; pH was adjusted to pH 5.5 with pH 9.0 ammonium acetate solution and then diluted to 10 mL with water.

Nearshore seawater certified reference material (CASS–4) was obtained from the National Research Council of Canada (NRCC), which was certified for all the elements of interest in this study. The pH of the sub-samples from CASS–4 was adjusted to pH 5.5 with the ammonium acetate solution. Coastal seawater and estuarine water samples were also analyzed with the procedure. The seawater samples were collected at about 1 m depth from Galveston Bay, Galveston, TX. The estuarine water samples were collected from the Grand Bay Estuarine Research Reserve (NERR) in the northern Gulf of Mexico along the coast of Mississippi. The water samples were placed into acid-cleaned polypropylene bottles and acidified with $0.015 \text{ mol L}^{-1} \text{HNO}_3$ at the sampling site. At the laboratory, they were filtered through $0.45\text{-}\mu\text{m}$ membrane filters and stored in $0.015 \text{ mol L}^{-1} \text{HNO}_3$ until analysis. Sub-samples of these coastal water samples were prepared for analysis similarly to those of CASS–4.

RESULTS AND DISCUSSION

Synthesis of Chromosorb 106-TAR resin

The FT-IR spectra of pure TAR, Chromosorb 106, the intermediates and Chromosorb 106–TAR were recorded in KBr matrices. The absorption bands corresponding to the functional groups are listed in Table 3. Chromosorb 106 treated with $\text{HNO}_3/\text{H}_2\text{SO}_4$ exhibited two strong bands at 1528 and 1349 cm^{-1} of $-\text{NO}_2$ groups indicating the formation of Chromosorb 106– NO_2 . These bands disappeared upon reduction with SnCl_2 and a strong

band of -NH_2 group was observed at 1624 cm^{-1} , which confirmed the formation of aminated copolymer (e.g., Chromosorb 106- NH_2). The amine band disappeared in the FT-IR spectrum of Chromosorb 106-TAR that exhibited absorption bands at 1524 cm^{-1} associated with -N=N- group. Additional two bands peaks at 1612 and 3435 cm^{-1} were the characteristic vibrational bands of -C=N and -OH groups, respectively, indicating that TAR was chemically immobilized onto Chromosorb 106.

Effect of pH on the retention of trace elements

Prior to the investigation of Chromosorb-TAR chelating resin, attempts for multielement preconcentration were made by using the raw Chromosorb 106 resin. The sorption of the elements was very weak. The recoveries in deionized water (e.g., no salt matrix) ranged from 52% for Co to about 80% for Cu. Further, retention in general occurred at pH 8.8 to 9.5 which indicated the formation of insoluble hydroxides that were physically adsorbed on the column. In the presence of small amounts of salt matrix (ca. 0.1% seawater), all elements were swept from the column even at pH 9.0. These results confirmed that raw Chromosorb 106 did not contain any chelating functional groups. The FT-IR spectra of raw Chromosorb 106 (see Table 3) also supported the results that the absorption bands recorded for TAR and Chromosorb-TAR were absent in that of raw Chromosorb 106. As a result, the raw resin was not investigated any further and the method optimization was carried out for Chromosorb 106-TAR chelating resin.

The influence of the pH on the retention of the trace elements across a pH gradient from 2 to 9 is illustrated in Fig. 3. In the absence of matrix, all elements were retained within a broad pH range from pH 4 to 6 yielding recoveries better than 98% (Fig. 3A). However, real samples, such as seawater and otoliths contain substantial salt matrix which could alter the retention pattern (e.g., pH and recovery) of trace elements on the resin. Therefore, we further examined the retention pH between pH 4 and 6 in synthetic seawater medium. As can be seen from Fig. 3B, the retention shifted to higher pHs and occurred within a range between pH 5 and 6 (Fig. 3B), except that for Cd and Pb. Cadmium was retained between pH 5.5 and 6.0, whereas the optimum range for Pb was pH 4.0 and 5.5. At pH 6, the recoveries for Pb decreased down to 82% suggesting that the optimum pH for multielement preconcentration was at proximity of pH 5.5. Despite the changes in the retention pH, the results demonstrated that Chromosorb 106-TAR column possessed strong affinity to the elements of interest to afford extraction/preconcentration in seawater. Subsequent studies were carried out by adjusting pH of the solutions to pH 5.5.

Effect of eluent concentration and volume

Initial experiments indicated that elution of the trace elements could be achieved with both dilute solutions of hydrochloric acid (HCl) and nitric acid (HNO_3). The former is often preferred eluent for flame atomization determinations (FAAS) due to effective atomization of metal chlorides. Nitric acid, on the other hand, is the most suitable acid for ICP-MS determinations because of its simple mass spectra that is similar to that of air and water in argon plasma. Thus, we opted for dilute nitric acid and examined its concentration for quantitative stripping of the trace elements of interest from the column. As shown in Fig. 4, 1.0 mL of $0.15\text{ mol L}^{-1}\text{ HNO}_3$ was sufficient for elution of the Cd, Co, Ni, Pb and Zn, while

a minimum of $0.45 \text{ mol L}^{-1} \text{ HNO}_3$ was required to quantitatively strip Cu from the column ($\%R = 96 \pm 4$). Higher concentration of HNO_3 was also desired to avoid residual memory effects. Therefore, $0.75 \text{ mol L}^{-1} \text{ HNO}_3$ was chosen for elution. All elements were eluted from the column with 0.5 mL of $0.75 \text{ mol L}^{-1} \text{ HNO}_3$, except Cu that required 1.0 mL of $0.75 \text{ mol L}^{-1} \text{ HNO}_3$ for elution ($\%R = 98 \pm 3$). The recoveries for Cu did not change with larger volumes of acid (e.g., 2 mL) indicating 1.0 mL of $0.75 \text{ mol L}^{-1} \text{ HNO}_3$ was optimum for elution.

Effect of flow rates of sample and eluent solutions

The extent of interaction of metal ions with the chelating sites along the column is an important variable in multi-element preconcentration procedures since the kinetics of the chelation could vary substantially among the elements. The flow rate of the sample solution therefore plays a critical role in achieving quantitative recoveries of the elements in on-line SPE approaches. The flow rate of solutions was 1.5 mL min^{-1} during the optimization of load pH (e.g., Fig. 3B) that clearly shows that the metal ions were retained at around pH 5.5 as TAR-complexes in seawater matrix. The solution flow rate did not induce any noticeable differences in the retention of the elements when it was examined between 1.0 to 6.0 mL min^{-1} . The recoveries varied from 96% (Pb) to 101% (Ni). Yet, higher flow rates (e.g., above 4 mL min^{-1}) were not desirable due to increasing back-pressure on the column and syringe pump. Likewise, the flow rate of the eluent ($0.75 \text{ mol L}^{-1} \text{ HNO}_3$) did not affect the recoveries when it was increased from 1.0 to 6.0 mL min^{-1} . A flow rate of 2.0 mL min^{-1} appeared to be suitable for smooth operation of the SPE system.

Effect of column wash

Seawater is a highly saline medium with a number of dominant metal ions, such as Na ($>1\%$), Mg (ca. 1.3 mg mL^{-1}), Ca (ca. 0.4 mg mL^{-1}) and K (ca. 0.4 mg mL^{-1}) that could form molecular ions and thereby interfere with trace elements of interest in the mid-mass range (^{59}Co , ^{63}Cu and ^{60}Ni). Otolith solutions contain high levels of Ca that could also induce severe interferences unless the residual Ca is washed out effectively. In general, the retention of the matrix ions (Ca, Mg, Na and K) is determined by the load pH and sample volume. Preconcentration at slightly acidic pHs (e.g., 4.5 to 6) is advantageous since formation of hydroxide precipitates, and in due course the retention of alkali and alkaline earth elements on the column is avoided. Loading small volumes of saline solutions is also advantageous to rinse out the residual matrix ions from the column effectively. Nevertheless, the eluates from the column could contain significant levels of Ca, Mg, Na and K unless a column wash is performed (Zhu, Inagaki, and Chiba 2009). Washing with water was sufficient to eliminate the matrix ions from the analytical column of Toyopearl AF Chelate-650M (Arslan and Paulson, 2002; Veguería et al. 2013) and that of PSTH-cpg resin, (1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass) (Trujillo 2012). On the other hand, dilute ammonium acetate buffer solution provided better performance for Chelex 100 (Rahmi et al. 2007) and Nobias-chelate PA1 (Biller and Bruland 2012). Based on these reports, the efficiency of column wash for Chromosorb 106-TAR chelating resin was examined with deionized water and dilute ammonium acetate buffer solution for artificial seawater matrix. After loading artificial seawater (5 mL), the column was washed with either 2.0 mL deionized water or

diluted buffer solution (ammonium acetate, pH 5.5) (see Table 2). Then, matrix components remaining on the column were eluted with $0.75 \text{ mol L}^{-1} \text{ HNO}_3$ and analyzed by ICP-MS for Ca, Mg, Na and K levels as well as ^{63}Cu , ^{59}Co and ^{60}Ni isotopes to identify possible background signals (e.g., interferences) from $^{40}\text{Ar}^{23}\text{Na}^+$, $^{43}\text{Ca}^{16}\text{O}^+$ and $^{44}\text{Ca}^{16}\text{O}^+$, respectively. The results demonstrated that washing with buffer solution was more effective. The concentrations of Na ($<10 \text{ } \mu\text{g mL}^{-1}$) and K ($<2\text{--}3 \text{ } \mu\text{g mL}^{-1}$) were not significant in the analysis solutions. Calcium levels ranged from 12 to $18 \text{ } \mu\text{g mL}^{-1}$ and that for Mg were between 22 and $28 \text{ } \mu\text{g mL}^{-1}$. Further, the background signals for $^{63}\text{Cu}^+$, $^{59}\text{Co}^+$ and $^{60}\text{Ni}^+$ associated with $^{40}\text{Ar}^{23}\text{Na}^+$, $^{43}\text{Ca}^{16}\text{O}^+$ and $^{44}\text{Ca}^{16}\text{O}^+$, respectively, were significantly lower in indicating that a column wash with buffer solution was more conducive for removal of matrix ions and reducing the molecular ions interferences. This effect was attributed to efficient displacement of matrix ions by the NH_4^+ in the buffer solution. The volume of the wash-buffer solution was increased to 3.0 mL in analysis of real samples to successfully remove residual matrix ions prior to elution.

Column capacity and lifetime

The sorption capacity of the chelating resin was determined by batch method by equilibrating 50 mg of the resin in $50 \text{ } \mu\text{g mL}^{-1}$ (20 mL) solution of each metal ion for 2 h. The concentrations of the trace elements remained unsorted in solution were then determined by ICP-MS. The sorption capacities were 119, 162, 319, 211, 82.0, and $148 \text{ } \mu\text{mol g}^{-1}$ for Cd, Co, Cu, Ni, Pb and Zn, respectively. These capacities were comparable with those ($62\text{--}348 \text{ } \mu\text{mol g}^{-1}$) reported for Amberlite XAD-4 (another class of styrene divinyl benzene copolymer) functionalized with 2,6-diacetylpyridine (Kara, Fisher and Hill 2006) and those reported for the PSTH-cpg resin ($74.8\text{--}367 \text{ } \mu\text{mol g}^{-1}$) (Trujillo et al. 2012). The highest capacity was for Cu ($319 \text{ } \mu\text{mol g}^{-1}$) and that for Pb was the lowest ($82.0 \text{ } \mu\text{mol g}^{-1}$). Yet, these values suggest that the Chromosorb 106-TAR resin possesses large capacity for preconcentration of the elements from fish otoliths and natural water samples.

The resin appeared to be highly stable under heavy salt matrices and treatment with mineral acids. No significant changes were observed in the retention performance of the column nor did the pH range shift during repetitive loading and elution cycles. However, the sample loading speed deteriorated around 450–500 cycles because of the swelling of the resin occupying the entire free space inside column holder. This effect consequently restricted the smooth flow of the solution through column and increased back-pressure on the lines and syringe pump.

Figures of merit

Except mono-isotopic ^{59}Co , data for all elements were acquired by using multiple isotopes, including ^{63}Cu , ^{65}Cu , ^{66}Zn , ^{68}Zn , ^{60}Ni , ^{62}Ni , ^{111}Cd , ^{114}Cd , ^{206}Pb and ^{208}Pb to choose the most suitable isotopes for quantitative measurements. Molecular ions of $^{40}\text{Ar}^{23}\text{Na}^+$, $^{44}\text{Ca}^{16}\text{O}^+$ and $^{40}\text{Ar}^{26}\text{Mg}^+$ could induce interferences on $^{63}\text{Cu}^+$, $^{60}\text{Ni}^+$ and $^{66}\text{Zn}^+$ due to residual Na, Ca and Mg in the solution. Tin has an isobaric overlap from ^{114}Sn isotope on ^{114}Cd that could also lead to incorrectly high results if samples contain Sn or the chelating resin is contaminated with Sn used in synthesis. Under the optimum operating conditions, the effects of spectral interferences were not significant on

these isotopes. Thus, the results for the most abundant isotopes, namely ^{63}Cu , ^{60}Ni , ^{114}Cd and ^{208}Pb are reported for the respective elements. In case of Zn, ^{68}Zn isotope is assigned as primary isotope for Zn determinations by the instrument manufacturer, and hence is used to report the results for Zn in seawater and otolith samples.

Calibration was performed with external standards ranging from 0, 0.020, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, to $10\text{ }\mu\text{g L}^{-1}$. The standard solutions were preconcentrated using the optimum conditions as for the samples analyzed by ICP-MS. The calibration curves from the preconcentration of the aqueous standards were linear within the calibration range ($R^2 > 0.991$). Internal standard corrected signals ($\text{Analyte}_{\text{cps}}/\text{IS}_{\text{cps}}$) for six standard solutions that bracket the $\text{Analyte}_{\text{cps}}/\text{IS}_{\text{cps}}$ for samples were used for calculating the concentration of the trace elements. The limits of detection (LOD, 3s) were obtained from the preconcentration of 5 mL blank solutions ($n = 12$) at pH 5.5 into 1.0 mL of $0.75\text{ mol L}^{-1}\text{ HNO}_3$. The values were 0.0016, 0.0029, 0.012, 0.0064, 0.0021, 0.015 ng L^{-1} for ^{114}Cd , ^{59}Co , ^{63}Cu , ^{60}Ni , ^{208}Pb and ^{68}Zn , respectively. A comparison of the various performance characteristics of Chromosorb106-TAR resin is provided in Table 4 with other chelating resins reported for determination of transition elements in seawater samples by ICP-MS. Off-line preconcentration approaches are advantageous to reduce the cost ICP-MS analysis. Yet, the enrichment factors afforded by off-line approaches are limited by the large elution volumes that range from 0.5 to 4 mL as shown in Table 4. Large sample volumes could be used to achieve higher enrichment factors and better detection limits, but at the cost of reduced sampling rate. It is clear that the off-line preconcentration procedure using Chromosorb 106-TAR and utilizing FIA 3200 unit affords comparable sampling rate and detection limits with other resins for small sample volumes. It should be noted that the detection limits were influenced by the background and blanks signals of the individual elements, which were consistently higher for the ubiquitous Cu and Zn. Still, the detection limits for all the elements were sufficiently low for sample volume of 5 mL to achieve accurate determinations in otoliths and seawater samples despite a relatively small enrichment factor (ca. 5-fold). Relative standard deviation (RSD) for triplicate measurements (runs) of standard and artificial seawater solutions ranged between 0.3% for ^{114}Cd to 6% for ^{68}Zn at $1.0\text{ }\mu\text{g L}^{-1}$ level.

Analysis of seawater and fish otoliths

The performance of the preconcentration procedure was verified by analysis of Nearshore seawater certified reference material (CASS-4) and fish otolith certified reference material (CRM 22). Statistical analysis was performed with SYSTAT v13 statistics package. The results are summarized in Table 5 for CASS-4 and the coastal seawater and estuarine water samples. Recoveries ranged from 92% for ^{114}Cd to 115% for ^{208}Pb in CASS-4. The experimental values were not significantly different from the certified values within 95% confidence level ($p < 0.05$). No significant interferences were observed from the molecular ions of the residual matrix elements (e.g., Ca and Na) on $^{59}\text{Co}^+$, $^{60}\text{Ni}^+$ or $^{63}\text{Cu}^+$ indicating that the method would afford reliable determinations under saline solutions. The recoveries from the spiked samples ranged between 89 and 106%, and were consistent with the recoveries for CASS-4. In general, the concentrations of the elements in coastal seawater were higher, except that for Cd, compared with their levels in CASS-4, which was

indicative of leaching from the surface sediments. The concentrations of the elements in the estuarine water were substantially higher that could be caused by the constant supply of nutrient rich freshwater local rivers, creeks, and leaching from the surface and bottom sediments.

The elemental concentrations obtained for the fish otolith certified reference material (CRM 22) are summarized in Table 6. The results showed agreement with those reported elsewhere by solid phase preconcentration ICP-MS using Toyopearl AF-Chelate 650M (an iminodiacetate chelating resin) (Arslan and Paulson 2002) and solvent extraction isotope-dilution ICP-MS (Yoshinaga, Morita and Edmonds 1999). Calcium is the predominant matrix element in fish otolith CRM. The certified concentration of Ca is $38.8 \pm 0.5\%$ that would yield about $2,000 \mu\text{g mL}^{-1}$ Ca and sub- $\mu\text{g L}^{-1}$ (ppb) levels of trace elements in the otolith solutions (10 mL) from dissolution of 50 mg sub-samples. The most troublesome elements under the heavy Ca matrix are $^{59}\text{Co}^+$ and $^{60}\text{Ni}^+$ due to the interferences of $^{43}\text{Ca}^{16}\text{O}^+$ and $^{44}\text{Ca}^{16}\text{O}^+$, respectively. However, the results for $^{59}\text{Co}^+$ and $^{60}\text{Ni}^+$ isotopes were also highly consistent with the reported values indicating that the interferences from the calcium oxides were not significant. This result also verified the fact that washing with dilute buffer solution ensured effective cleaning of the residual Ca from the column even after loading elevated Ca solutions.

CONCLUSIONS

In this study, a new chelating copolymer of Chromosorb 106 was synthesized with TAR to develop a solid phase preconcentration method for multielement analysis of saline solutions. TAR was chemically attached to the styrene back-bone of Chromosorb 106 resin. The results demonstrated that Chromosorb 106-TAR possesses strong affinity and large sorption capacity to the trace elements allowing accurate determinations to be performed in seawater and fish otoliths by ICP-MS. Further, the resin is stable to treatments with mineral acids (e.g., $0.75 \text{ mol L}^{-1} \text{ HNO}_3$) and could be used for up to 500 load/elute cycles. The sequential injection system by means of syringe pumps provides the benefit of automation and precise control of the operation of the SPE system. The sealed column ensures an ultra-clean environment for chelating resin for determination of other trace elements by ICP-MS.

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Figure 1. Schematic diagram of solid phase preconcentration system utilized with FIA 3200 unit. SP₁ and SP₂ = Syringe pumps; PP = peristaltic pump; V₁ and V₂ = Three-way valve; V₃ = Two-way manual valve; S = Sample, B = Buffer (pH 5.5); E = Eluent (0.75 mol L⁻¹ HNO₃); CT = Collection tube; W = Waste; SV = 8-port selection valve; CP = Central port.

Figure 2.

Synthesis and proposed structure of the Chromosorb 106-TAR chelating resin.

Figure 3.

Elemental recoveries as a function of solution pH from preconcentration of $5.0 \mu\text{g mL}^{-1}$ multielement solution in deionized water (A) and in artificial seawater matrix (B). Elution was made with 1.0 mL of $0.75 \text{ mol L}^{-1} \text{HNO}_3$.

Figure 4.
Effect of HNO₃ concentration on the elution of the elements. Eluent volume is 1.0 mL.

Table 1

Operating parameters for Varian 820-MS ICP-MS instrument

RF Power (kW)	1.4
Plasma Ar flow (L min ⁻¹)	18
Auxiliary Ar flow (L min ⁻¹)	1.8
Nebulizer Ar flow (L min ⁻¹)	1.0
Sheath Ar flow (L min ⁻¹)	0.1
Sampling depth (mm)	6
Pump rate (mL min ⁻¹)	0.2
Stabilization time (s)	20
Spray chamber temperature (°C)	3
Scan mode	Peak hopping
Dwell time (ms)	20
Points/peak	1
Scans/peak	3
Scans/replicate	3

Table 2

Operation program of FIA 3200 sequential injection unit during solid phase extraction

Step	Syringe pumps		Volume (mL)	Flow rate (mL min ⁻¹)	Valve position			PP	Remark
	SP ₁	SP ₂			V ₁	V ₂	V ₃		
1	Aspirate	Off	0.5	6	1	-	1	On	Column wash/Line fill
2	Dispense	Off	0.5	6	3	-	1	On	Column wash/Line fill
3	Aspirate	Off	5	6	1	-	2	On	Column wash/Sample uptake
4	Dispense	Off	5	2	3	-	2	Off	Sample load
5	Aspirate	Off	3	6	2	-	2	Off	Buffer uptake
6	Dispense	Off	3	2	3	-	2	Off	Column wash
7	Off	Aspirate	1	6	-	1	-	Off	Eluent uptake
8	Off	Dispense	1	2	-	3	-	Off	Elution

Table 3
Infrared spectral data (cm^{-1}) of the intermediates and Chromosorb 106-TAR chelating resin

	$\nu\text{N-O}$	$\nu\text{N=N}$	$\nu\text{N-H}$	$\nu\text{C=N}$	$\nu\text{C-H}$ (aliphatic)	$\nu\text{C-H}$ (aromatic)	$\nu\text{O-H}$
TAR		1589		1630	2926	3120	3400
Chromosorb 106					2925	3020	
Chromosorb 106-NO ₂	1528, 1349				2929	3062	
Chromosorb-106-NH ₂			1624		2923	3019	
Chromosorb 106-TAR		1524		1612	2927	3032	3435

Comparison of analytical performances of cheating resins utilized for determination of trace elements in seawater by solid phase preconcentration and ICP-MS

Table 4

Sorbent (resin)	Analytes	Approach (Load pH)	Sample volume (mL)	Eluent	LOD ($\mu\text{g L}^{-1}$)	Sampling rate (min sample ⁻¹)	Reference
Chromosorb 106-TAR	Cd, Co, Cu, Ni, Pb and Zn	Off-line (pH 5.5)	5	1.0 mL, 0.75 M HNO ₃	0.0016 – 0.015	6.1	This work
Chelex 100	V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U	Off-line (pH 6.0)	50	0.5 mL, 2 M HNO ₃	0.0003 – 0.001	54	Rahmi et al. 2012
Ion imprinted polymer	Cu, Ni, Pb and Zn	Off-line (pH 8.5)	250	2.5 mL, 2 M HNO ₃	0.0022 – 0.009	85	Otero-Román et al. 2009
PSTH-cpg resin	Co, Cr, Ni, Cd, Mn, Zn, Cu Pb	On-line (pH 8.0)	2.1	0.75 M HNO ₃	0.002-0.260	6.9	Trujillo et al. 2012
Toyopearl AF Chelate-650 M	V, Mn, Co, Ni, Cu, Zn, Cd, Pb,	Off-line (pH 5.5 and pH 8.2)	4.0	2 mL, 1 M HNO ₃	0.01-0.08	5	Veguería et al. 2013
Toyopearl AF Chelate-650 M	Cd, Cu, Ni, Zn, and Mn	On-line (pH 5.6, pH 9 for Mn)	3.0	1.5 M HNO ₃	0.0014 – 0.086	7.2	Beck, Franks, and Bruland 2002
Nobias-chelate PA1	Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb	Off-line (pH 6.2)	40	4 mL, 1 M HNO ₃	0.0007 – 0.002	80	Billar and Bruland 2012

Table 5

Elemental concentrations ($\mu\text{g L}^{-1}$) and recoveries (R, %) for the trace elements from analysis of Nearshore seawater certified reference material (CASS-4, n=5), coastal seawater (n=4) and estuarine water (n=4) samples. Values are given as average $\pm$ standard deviation for given replicate analyses

Element	CASS-4			Coastal seawater			Estuarine water		
	Found	Certified	R (%)	Added	Found	R (%)	Added	Found	R (%)
^{114}Cd	0.024 ± 0.002	0.026 ± 0.003	92	0	0.020 ± 0.009	–	0	0.35 ± 0.01	–
^{59}Co	0.028 ± 0.005	0.026 ± 0.003	108	1	0.92 ± 0.02	90	1	1.33 ± 0.17	99
				2	1.85 ± 0.08	92	2	2.42 ± 0.72	104
^{63}Cu	0.589 ± 0.038	0.592 ± 0.055	99	0	0.33 ± 0.03	–	0	0.34 ± 0.08	–
				1	1.32 ± 0.07	99	1	1.38 ± 0.51	104
^{60}Ni	0.303 ± 0.025	0.314 ± 0.030	96	2	0.92 ± 0.06	–	0	44.6 ± 4.2	–
				1	1.89 ± 0.09	97	5	49.2 ± 3.8	92
^{208}Pb	0.011 ± 0.005	0.0098 ± 0.0036	115	2	2.72 ± 0.12	90	10	55.1 ± 1.8	105
				0	0.56 ± 0.03	–	0	2.89 ± 0.17	–
^{68}Zn	0.384 ± 0.069	0.381 ± 0.057	101	1	1.58 ± 0.02	102	5	8.16 ± 0.85	105
				2	2.55 ± 0.01	99	10	12.7 ± 1.8	98
				0	0.67 ± 0.16	–	0	2.43 ± 0.63	–
				1	1.72 ± 0.02	105	5	7.17 ± 0.02	95
				2	2.62 ± 0.12	98	10	12.6 ± 0.8	102
				0	1.35 ± 0.06	–	0	57.0 ± 4.7	–
				1	2.24 ± 0.14	89	5	62.3 ± 1.8	106
				2	3.32 ± 0.10	98	10	66.0 ± 4.6	90

Table 6

Elemental concentrations ($\mu\text{g g}^{-1}$) in fish otolith CRM (No: 22) determined by the solid phase preconcentration ICP-MS procedure. Values are given as average $\pm$ standard deviation for five replicate analyses (n = 5)

Element	Found	Information values		
		ID-ICP-MS ^a	SPE-ICPMS ^b	LLE-ID-ICPMS ^c
¹¹⁴ Cd	0.0031 $\pm$ 0.0005	0.028	0.029 $\pm$ 0.0002	0.028 $\pm$ 0.0002
⁵⁹ Co	0.0036 $\pm$ 0.0004		0.0032 $\pm$ 0.0007	-
⁶³ Cu	0.737 $\pm$ 0.021	0.74	0.756 $\pm$ 0.066	0.742 $\pm$ 0.007
⁶⁰ Ni	0.026 $\pm$ 0.003		0.022 $\pm$ 0.004	-
²⁰⁸ Pb	0.027 $\pm$ 0.007	0.023	0.026 $\pm$ 0.002	0.023 $\pm$ 0.003
⁶⁸ Zn	0.515 $\pm$ 0.062	0.47	0.526 $\pm$ 0.088	0.471 $\pm$ 0.002

^aYoshinaga, J., A. Nakama, M. Morita, and J.S. Edmonds. 2000. *Mar. Chem.* 69:91-97.

^bArslan, Z. and A. J. Paulson. 2002. *Anal. Bioanal. Chem.* 372: 776-785.

^cYoshinaga, J., M. Morita, and J. S. Edmonds. 1999. *J. Anal. At. Spectrom.* 14: 1589-1592.