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Solid phase extraction of rare earth elements in seawater and estuarine water with 4-(2-thiazolylazo) resorcinol immobilized Chromosorb 106 for determination by inductively coupled plasma mass spectrometry

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Abstract

A solid phase preconcentration method has been developed using new chelating resin prepared by immobilization of 4-(2-thiazolylazo) resorcinol (TAR) on Chromosorb 106. The method was optimized for determination of rare earth elements (REEs) in seawater and estuarine water samples by inductively coupled plasma mass spectrometry (ICP-MS). The effects of various experimental parameters, such as load pH, eluent concentration, sample and eluent flow rates were examined to find the optimum operating conditions. The REEs were quantitatively retained from saline solutions on a minicolumn Chromosorb 106-TAR resin at pH 5.0 and then eluted with 1.0 mL of 1% (v/v) HNO_3. The resin possesses large sorption capacity for REEs ranging from 81.1 μmol g^{-1} for Lu and 108 μmol g^{-1} for Nd. Detection limits (3s) varied between 0.06 ng L^{-1} for Pr to 0.31 for Ce for preconcentration of 5.0 mL blank solutions (pH 5.0). The relative standard deviation for triplicate measurements was less than 5% at 0.1 μg L^{-1} level. The method was validated by analysis Nearshore seawater certified reference material (CASS–4). The elemental results were comparable with the values reported in literature. The method was verified by analysis of spiked and unspiked coastal seawater and estuarine water samples.

Keywords

Rare earth elements; Chromosorb 106; 4-(2-thiazolylazo) resorcinol (TAR); solid phase preconcentration; seawater; ICP-MS

1. Introduction

Rare earth elements (REEs) have been widely used in environmental monitoring as indicators of geochemical and archeological studies [1, 2]. These elements also possess diverse nuclear, metallurgical, chemical, catalytic, electromagnetic, and optical properties. Applications/uses of the REEs have increased in last decade in technological gadgets (lasers, magnets, batteries, magnetic refrigeration) and medical diagnostics (reagents in magnetic resonance imaging), and continue to increase considering the futuristic applications concerning high-temperature superconductivity, safe storage and transport of hydrogen for a post-hydrocarbon economy [3]. As a result, they would be increasingly released to the environment, entering food chain as they are taken up by aquatic micro-organisms and scavengers. Although REEs are not considered as priority environmental contaminants

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unlike ubiquitous heavy metals (e.g., As, Cd, and Pb), they are known to induce adverse health effects and stimulate crystallization of urinary stones [4, 5]; and therefore, require sensitive methods for accurate monitoring in complex biological and environmental samples.

The concentrations of REEs in seawater and freshwater samples are usually at sub-parts per trillion range (sub-ng L^{-1}) levels. Determinations at such low levels can only be achieved by using highly sensitive techniques, such as ICP-MS that affords excellent sensitivity when coupled to analytical preconcentration procedures [6–12]. Salt matrix leads to spectral interferences and suppresses the sensitivity, and consequently precludes direct determination of REEs in seawater by ICP-MS. To overcome these difficulties various approaches, such as coprecipitation [13, 14], solvent extraction [15, 16], and solid phase extraction (SPE) [17–23] have been utilized to selectively isolate the REEs from the sample matrix prior to analysis. Among these techniques, SPE approaches have been highly attractive as they offer simplicity, high enrichment factors with small samples, and reduced risk of contamination.

The choice of the sorbent is important in the efficacy of the solid phase extraction procedures. In general, the sorbent material should possess high capacity, long lifetime and the ability to extract a suite of elements quantitatively within a wide pH range [24, 25]. In addition, the sorbent should not retain matrix elements, alkali and alkaline earth metals. Various chelating agents have been immobilized on polymeric supports to produce chelating sorbents for determination of REEs by SPE in natural water samples. These functional groups include 8-hydroxyquinoline (8-HQ) [26], iminodiacetate (IDA) [22, 27], hydroxamic acid [6], 2-amino-5-hydroxy benzoic acid [28], 2,6-diacetylpyridine [20] and fluorinated β-diketone [29]. Chemical immobilization offers the ability to customize the sorption medium with different functional groups to improve selectivity, sorption capacity and reusability [30]. An additional advantage of the use of chelating polymeric resins for ICP-MS determinations comes from the fact that retained elements could be quantitatively stripped from the column with dilute acid solutions.

Chromosorb series support materials are a class of porous, hydrophobic polymers of styrene divinylbenzene that are used as stationary phases in gas chromatography. The first paper describing the application of Chromosorb type resins for solid phase preconcentration was reported by Elci *et al.* [31] more than a decade ago for determination of Pb(II) in the form of dithiocarbamate (DDC) complexes. Since then various types of Chromosorb resins have been used in preconcentration of trace transition metal chelates from aqueous solutions for determination by AAS techniques [32–34]. In most applications, retained metal-chelates were eluted using a mixture of acidified organic solvents or pure organic solvents that are not suitable for ICP-MS applications as they deteriorate plasma stability and lead to carbon build-up throughout the interface. Conversely, Chromosorb series polymers possess styrene divinylbenzene back-bone and offer the ability to synthesize chelating polymers by chemical immobilization of chelating agents, such as 4-(2-thiazolylazo) resorcinol (TAR) that forms strong complexes with most transition elements over a wide pH range, [35–37]. Further, quantitative elution of the retained species could be achieved with dilute acids without using organic solvents affording a more conducive medium for accurate multi-element determination by ICP-MS.

In this study, we synthesized a new chelating resin through chemical immobilization of TAR onto Chromosorb 106 to develop a sensitive and robust on-line solid phase extraction procedure for determination of rare earth elements (REEs) (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) in seawater samples by ICP-MS. Various experimental parameters, such as pH, flow rates, eluent concentration, and sorption capacity were examined to affect the quantitative retention of the elements on a mini-column of TAR-immobilized

Chromosorb 106. The effect of salt matrix on the retention performance of the column was evaluated in artificial seawater samples. The procedure was verified with analysis of certified seawater reference material (CASS-4) and applied to the determination of the REEs coastal seawater and estuarine water samples by ICP-MS.

2. Experimental

2.1. Reagents and materials

Double deionized water (18.2 MΩ cm) was used for preparation of solutions. The deionized water was obtained from a Barnstead E-Pure system fed by a reverse-osmosis unit (SpectraPure). Single elements standard solutions (1000 μg mL^{-1}) of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were obtained from Spex Certiprep (Metuchen, NJ). A 100 μg L^{-1} (ppb) multielement stock solution was prepared for method development and calibration standards in 2% (v/v) HNO_3 (Trace metal grade, Fisher Scientific). Additional standards for spike applications were prepared from either 10 or 100 μg L^{-1} (ppb) single element solutions. An ammonium acetate buffer solution was prepared with 182 mL of trace metal grade ammonium hydroxide (Fisher Scientific) and 112 mL of acetic acid (99.99+%, Aldrich) in 1.0 L deionized water. The pH of the buffer solution was adjusted to pH 9.0 with ammonium hydroxide. The pH of the experimental solutions was adjusted by using the buffer solution to the desired pH.

An artificial seawater solution was prepared by dissolving 24.6 g NaCl (99.999%, Aldrich), 0.75 g KCl (99.995%, Alfa Aesar), 1.03 g $CaCl_2$ (99.99%, Aldrich), 3.06 g $MgSO_4$ (99.9%, Alfa Aesar), 2.18 g $MgCl_2$ (99.9%, Alfa Aesar) and 0.18 g $NaHCO_3$ (99%, Aldrich) in 1.0 L deionized water acidified to 0.1% (v/v) HNO_3. All other reagents used for synthesis of the chelating resin, including sulfuric acid, hydrochloric acid, tin chloride ($SnCl_2$), sodium nitrite ($NaNO_2$) were of reagent grade. Thiazolyazo reagent, 4-(2-thiazolylazo)resorcinol (TAR) was from Alfa Aesar.

Chromosorb 106 resin (Supelco, Celite, CA, USA), a cross-linked styrene divinylbenzene (S-DVB) polymer, was used for the synthesis of the chelating resin. The size of the resin varied between 180 and 250 μm with an average surface area of 750 m^2 g^{-1} and pore diameter of 50 Å. Raw Chromosorb 106 was cleaned from impurities before synthesis of the chelating resin by treating the beads first with water followed by 0.5 mol L^{-1} HCl, and 0.5 mol L^{-1} NaOH, respectively. In the end, cleaned resin was washed with copious amount of water to obtain a neutral solution. The beads were then dried at 105 °C in an oven.

2.2. Instrumentation

A Varian 820MS inductively coupled plasma mass spectrometer (Varian, Australia) was used for the determinations. 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 with 5 μg L^{-1} solution of ^{138}Ba, ^{25}Mg, ^{115}In, ^{140}Ce, ^{208}Pb for sensitivity, doubly charged ions (<1%) and oxides (<3%). 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. Rhodium (^{103}Rh) was used as internal standard (IS) element to correct for possible instrumental drift and sensitivity changes. The internal standard solution (5.0 μg L^{-1} Rh in 1% (v/v) HNO_3) was mixed on-line with the sample solution before nebulization.

Infrared (IR) spectra were taken by using a Nexus Model 870 FT-IR spectrometer equipped with a DTGS (Deuterated triglycine sulfate) infrared detector. 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 measurements were made with an Oakton pH 6 series microprocessor-based hand-held pH meter.

2.3. Solid phase preconcentration system

A FIAlab-3200 (FIAlab Instruments Inc., Bellevue, WA) sequential injection (SI) unit was used for automated solid phase extraction (Fig. 1). The unit was equipped with an 8-port 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. The column was made of teflon tubing of 180 μL inner volume (45 mm × 1.6 mm i.d.) which was packed with TAR-immobilized Chromosorb 106 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 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 V_3 switched to port 1 (Step 2). In the meantime, column was washed with dilute buffer solution (pH 5.0) running through PP at 7 mL min^{-1}. In step 3, 5.0 mL of sample solution was aspirated at 6 mL min^{-1} (V_1 at position 1) and loaded onto the column at 3 mL min^{-1} (V_1 at position 3) (Step 4). In step 5, SP_1 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 1% (v/v) HNO_3 solution. After the column wash, SP_2 aspirated 1.0 mL of 1% (v/v) HNO_3 (Step 7, V_2 at port 1) at 6 mL min^{-1} and then pumped through the column at 3 mL min^{-1} into acid cleaned centrifuge tube (Step 8, V_2 at port 3).

2.4. Preparation of Chromosorb 106-TAR chelating resin

The synthesis of Chromosorb 106-TAR resin was performed as described below. First, 2 g of cleaned Chromosorb 106 were added into mixture of 10 mL nitric acid and 25 mL sulfuric acid, and stirred in a water bath at 60 °C for 1 h. The mixture was cooled in an ice bath and filtered. The nitrated resin was isolated, washed with copious of water to eliminate the traces of acids, and then converted to amine-form by refluxing at 90 °C for 24 h in a mixture of 16 g of $SnCl_2$ 20 mL of concentrated HCl and 20 mL of ethanol. The aminated resin was filtered, washed with water and 2 mol L^{-1} NaOH to remove residual acid, and then suspended in 50 mL of 1.0 mol L^{-1} HCl in the bath (0–5 °C). For diazotization, 50 mL of 1.0 mol L^{-1} $NaNO_2$ solution was slowly added to the aminated suspension. The contents were stirred vigorously for about 1–2 h. For coupling with TAR the diazotized resin was quickly filtered, washed with ice-cold water and then resuspended in ice-cold water (0–5 °C). A solution of TAR (1.0 g of TAR dissolved in 50 mL of 2% (m/v) NaOH) was added dropwise to the suspension under vigorous stirring. The mixture was allowed stand for 24 h in refrigerator at 4 °C. The resulting reddish-brown resin beads were filtered and washed with 4 mol L^{-1} HNO_3, acetone, and water, respectively, to remove the impurities and free TAR. The resin was dried at room temperature and stored in a desiccator until use. The proposed structure of the chelating resin is shown in Fig. 2.

2.5. Preparation of the column

The column was made of 4.5 cm long teflon tubing (1.6 mm i.d.) as the resin holder which was packed with 40 mg of Chromosorb 106-TAR chelating resin. Both ends of the column were supported with glass wool to avoid the loss of the resin, and then tightened using

flangeless fittings (GlobalFia Inc., Fox Island, WA). For cleaning, the column was washed with 5% (v/v) nitric acid and deionized water, respectively.

2.6. Optimization of experimental conditions

To affect the retention of the REEs on the column, the load pH was varied from pH 2 to 9 for 0.5 μg L^{-1} multielement REEs solutions in deionized water. Solutions (5 mL) with appropriate pH were loaded onto the column at 1.5 mL min^{-1} and eluted with 2.0 mL of 2% (v/v) HNO_3. The optimum working pH window obtained from this initial study was closely examined under salt matrix with artificial seawater across a pH range from pH 4 to 6. In this experiment, artificial seawater samples (5 mL) containing 0.5 μg L^{-1} multielement spike were loaded onto the column and eluted with 2% (v/v) HNO_3 similarly. In the following studies, the concentration of HNO_3 solution was varied from 1 to 5% (v/v) to determine the optimum acid medium for elution of the elements from the column. Later, the flow rates of sample and eluent solutions were examined at the optimum pH conditions for 0.5 μg L^{-1} REEs solutions by increasing the flow rates for both from 1.0 to 6.0 mL min^{-1}.

2.7. Method validation

Samples of the Nearshore seawater certified reference material (CASS-4) obtained from National Research Council of Canada (NRCC) were analyzed to verify the performance of the method. The method was also applied to the analysis of coastal seawater and estuarine water samples. 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 to 0.1% (v/v) HNO_3 at the sampling site. At the laboratory, they were filtered through 0.45 μm membrane filters and stored in 0.1% (v/v) HNO_3 until analysis.

2.8. Calibration

Calibration was performed with external standard solutions within a range from 0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, to 1.0 μg L^{-1}. The calibration standards were preconcentrated using the optimum conditions as for the samples. After preconcentration, all samples were analyzed by ICP-MS for the elements of interest. The internal standard corrected signals (S_{REE}/S_{IS}) for five standard solutions that bracket that of samples were used for calculating the concentration of the REEs.

3. Results and discussion

3.1. Characterization of the chelating resin

The FT-IR spectra recorded in KBr matrices for Chromosorb 106, TAR and Chromosorb 106–TAR. FT-IR spectra of unfunctionalized Chromosorb 106 and TAR functionalized Chromosorb 106 showed distinct absorption bands. The latter possessed absorption peaks at 3435, 1702 and 1612 cm^{-1}. These peaks at 3435, 1702 and 1612 cm^{-1} were assigned to the characteristics vibrational bands of –O–H, –C=N– and –N=N– groups, respectively, (see Fig. 2), confirming successful synthesis of the Chromosorb 106-TAR resin.

3.2. Effect of pH on the retention of the elements

The pH of the sample solution is an important variable to achieve quantitative extraction of the elements as it mediates the surface charge of the sorbent and the extent of electrostatic interaction between the chelating functional groups and the analyte ion. The effect of the solution pH on the retention of the REEs on the chelating column of Chromosorb 106-TAR resin is illustrated in Fig. 3 in deionized water. The elements were retained within a pH

range from 3 to 7. The retention below pH 4 and above pH 6 was weak as indicated by the poor recoveries of the elements. In order to determine the performance of the column under salt matrix, the pH window between pH 4 and 6 was further examined in artificial seawater spiked with 0.5 μg L^{-1} with REEs. The results are shown in Fig. 4. Most elements, except Ce, Nd and Pr, showed quantitative retention (e.g. R> 95%) within a pH range from 4.5 to 5.5. The recoveries for Ce, Nd and Pr were 87, 91 and 92% at pH 4.5 that improved with higher pHs. The data indicated that the best operating pH under seawater matrix for these elements was around pH 5.5 that also provided the highest recoveries. However, the column retention tended to decline above pH 5.5. These results suggested that the optimum pH for the preconcentration of the REEs was pH 5.0 which was also advantageous for minimizing the sorption of residual matrix ions, such as Ba, Ca and Mg on the column compared with pH 5.5.

3.3. Effect of eluent concentration

The unfunctionalized Chromosorb 106 is highly hydrophobic, therefore, non-polar or slightly polar organic solvents are required for desorption of the chelated metal complexes from the column. On the other hand, the TAR functionalized Chromosorb 106 was more hydrophilic allowing elution to be achieved with acids. Dilute HNO_3 solutions with concentration from 1 to 5% (v/v) were examined for eluting the retained REEs from the column. All elements were eluted successfully by 1.0 mL of each HNO_3 solution. Mean recoveries for 1% (v/v) HNO_3 solutions ranged from 95% (Dy) to 101% (Eu and Lu), while that for 5% (v/v) HNO_3 were between 95% (Tb) and 101% (Tm and Yb). It is important to note that the use of high concentration of HNO_3 is not desirable, unless necessary, as it would deteriorate the lifetime of the column under repetitive elutions. Therefore, 1% (v/v) HNO_3 (1.0 mL) was chosen to recover the elements from the column throughout. This was also beneficial for rapid conditioning of the column for replicate measurements.

3.4. Effect of flow rates of sample and eluent solutions

In a multielement preconcentration system, the kinetics of retention and desorption could vary significantly among the elements. While the flow rate of the sample solution influences the retention of REEs ions on the cleating column, that of eluent determines the efficiency of desorption. No significant changes were detected in the recoveries when the flow rate of the REEs solution at pH 5.0 was increased from 1.0 to 6.0 mL min^{-1}, indicating that the sorption of the REEs ions by the Chromosorb 106-TAR occurred rapidly. The recoveries for all REEs were between 96% (Sm) and 101% (Tb). Even though recoveries were not affected, flow rates greater than 5.0 mL min^{-1} caused notable back-pressure on the sample syringe pump, therefore, the flow rate was adjusted to 3.0 mL min^{-1}. The optimum flow rate of the eluent (1% (v/v) HNO_3), was found to be 3.0 mL min^{-1} when varied similarly from 1 to 6 mL min^{-1} which was also the optimum for smooth operation of the syringe pump during collection of the eluate in the microcentrifuge tubes.

3.5. Column wash and lifetime

The REEs elements belong to the upper-mid range of mass spectrum and thus are relatively free from the interferences of argon plasma. Apart from monoisotopic ^{141}Pr, ^{159}Tb, ^{165}Ho and ^{169}Tm, they have multiple isotopes allowing a selection of suitable (interference-free isotope) to be used for determination. Furthermore, molecular ion interferences observed on REEs are in general caused by polyatomic oxides of another REE, such as $^{147}Sm^{16}O^+$ on ^{163}Dy, $^{160}Nd^{16}O^+$, $^{150}Sm^{16}O^+$ on ^{166}Er, $^{149}Sm^{16}O^+$ on ^{165}Ho, and $^{140}Ce^{35}Cl^+$ and $^{159}Tb^{16}O^+$ on ^{175}Lu. Nonetheless, several isotopes are prone to the interferences of molecular ions from the matrix elements in seawater, such as ^{153}Eu from $^{137}Ba^{16}O^+$, ^{172}Yb from $^{137}Ba^{35}Cl^+$, ^{157}Gd from $^{138}B^{19}F^+$. Therefore, the cleaning of the column after loading saline solutions (e.g., seawater) is an important step to avoid the spectral interferences and

minimize the introduction of the matrix elements (e.g., Ba, Ca, Mg, Sr, Cl) to ICP-MS. The efficiency of deionized water and buffer solution (pH 5.0) was examined after loading artificial seawater solution (5 mL). The background signals for ^{44}Ca, ^{25}Mg, ^{137}Ba, ^{138}Ba as well as some REEs, including ^{140}Ce, ^{153}Eu, ^{172}Yb, ^{157}Gd, were monitored in 1% (v/v) HNO_3 eluent solution. In general, cleaning the column with buffer solution provided lower background signals in comparison to that with deionized water. A volume of 3.0 mL of buffer solution was sufficient to effectively rinse out the matrix components adsorbed on the column.

The stability of column was monitored during the course of the method optimization studies. No significant variation was observed in the retention pH nor did the recoveries decrease to approximately 500 uses (loading/elution cycles). This performance was indicative of the high stability of the Chromosorb-TAR resin to repetitive washing and elution with acids. Further, the conditioning/regeneration of the column was readily achieved by washing with deionized water (Steps 1 through 3 in Table 2) prior to loading of the sample. It is however important to note that the resin expands inside the resin holder over the course of the extensive use (ca. 350–400 cycles), which consequently leads to notable increase in the back-pressure on the syringe pump and the teflon tubings due to the restriction in the flow rate of the solution.

3.6. Sorption capacity of Chromosorb 106-TAR resin

The capacity of is an important factor in determining the mass of the resin needed to achieve quantitative extraction/preconcentration of the elements from a given sample solution. The sorption capacity of Chromosorb 106-TAR resin was determined for each REE individually by batch approach. In a particular setting, 100 mg of the resin was equilibrated at pH 5.0 by shaking for 24 h in the excess REE solution (50 mL, 10 mg L^{-1}). The resin was then separated from the solution by filtration and concentration of the remaining metal ion in the solution was determined by ICP-MS. The amount of analyte element that could be sorbed by one gram of the resin was calculated according to the mass balance below,

$$q = \frac{(C_0 - C_e) \times V}{m}$$

where, q is the mass (mg) of the analyte sorbed per unit mass of Chromosorb 106-TAR resin (mg g^{-1}, dry-basis), C_0 and C_e are the initial and final concentrations of the analyte ion, respectively, in mg L^{-1} in the aqueous phase, and V and m are the volume of the aqueous phase in liter (L) and the dry mass of the Chromosorb 106-TAR resin used in gram (g). The calculated sorption capacities (q) were then converted units of μmol g^{-1}. The sorption capacities determined for Chromosorb 106-TAR are summarized in Table 3 along with those reported for different chelating sorbents. The values for Chromosorb 106-TAR were better than or comparable to the other resins, indicating that the resin possessed high sorption capacity for simultaneous preconcentration of REEs in natural water samples.

3.7. Analytical performance

The detection limits and sensitivity (slope of the calibration curve) of the method are summarized in Table 4. The calibration curves for all REEs were linear within the range from 0.01 to 1.0 μg L^{-1}. The detection limits were obtained from preconcentration of 5.0 mL of blank solution (pH 5.0) and calculated based on the analyte concentration equivalent to the signal (cps) for three times standard deviation (3s) of the blank solutions (n=12). Despite a small enrichment factor, *viz.* 5-fold, the detection limits ranged from as low as 0.06 ng L^{-1} for Pr to 0.31 for Ce ng L^{-1} and were sufficiently low for accurate

determination of REEs in seawater samples. The relative standard deviation (RSD) for triplicate measurements of standard solutions ranged from as low as 0.8% for Tb to 5% for Ho at 0.1 μg L^{-1} level.

3.8. Method validation and applications

The concentration of REEs in seawater sample is extremely low. Therefore, there is not a suitable reference material for testing the performances of new methods in determination of REEs. CASS-4 (Near-shore certified reference seawater) has been produced for analyses concerning the trace transition elements and heavy metals. Although the certified values for REEs in CASS-4 are not available, its homogeneity and chemical stability would still make CASS-4 a suitable surrogate CRM for evaluating the performance of the Chromosorb 106-TAR system. For preconcentration, the pH of 5.0 mL sub-samples of bottled CASS-4 were adjusted to pH 5.0 and loaded onto the column followed by elution with 1.0 mL of 1% (v/v) HNO_3. The results are summarized in Table 5. The values were comparable with the information values reported by other groups [16, 23, 26], indicating the that the present method was suitable for determination of REEs in seawater and similar natural water samples.

In the last stage of the study, the method was applied to the analysis of the coastal seawater (Galveston Bay, TX) and estuarine water samples from NERR. The results are summarized in Table 6. Determinations were also performed with spiked water samples to verify the results. The recoveries obtained for the elements from the spiked samples ranged between 92 and 105%. The concentrations of REEs in estuarine water were higher compared with their levels in coastal seawater, which could be attributed to contributions from the local freshwater rivers, creeks, and leaching from the surface and bottom sediments. The differences in geographic locations (e.g., land origin) could also contribute to the higher REEs levels in the estuarine water.

4. Conclusions

In this study, a robust and sensitive solid phase extraction procedure was developed using a chelating resin of TAR immobilized Chromosorb 106 for the determination of REEs in seawater and other natural water samples by ICP-MS. Chromosorb 106-TAR resin possesses large capacity and strong affinity for the retention of REEs under salt matrices and therefore is suitable for solid phase extraction of REEs in other saline samples, such as fish otoliths and biogenic minerals. The enrichment factors were typically 5-fold affording detection limits within a range of 0.06 and 0.31 ng L^{-1}. These detection limits are well below the REEs concentrations in seawater samples, which when salt matrix is removed provides significant sensitivity and interference-free determinations of REEs in seawater. Furthermore, the column shows little or no affinity to alkaline and alkaline earth elements at the optimum operating conditions. The retained matrix elements (e.g., Ba and Cl) could be readily removed by washing the column with buffer solution (pH 5.0) to eliminate the spectral interferences from oxides and chlorides on REEs.

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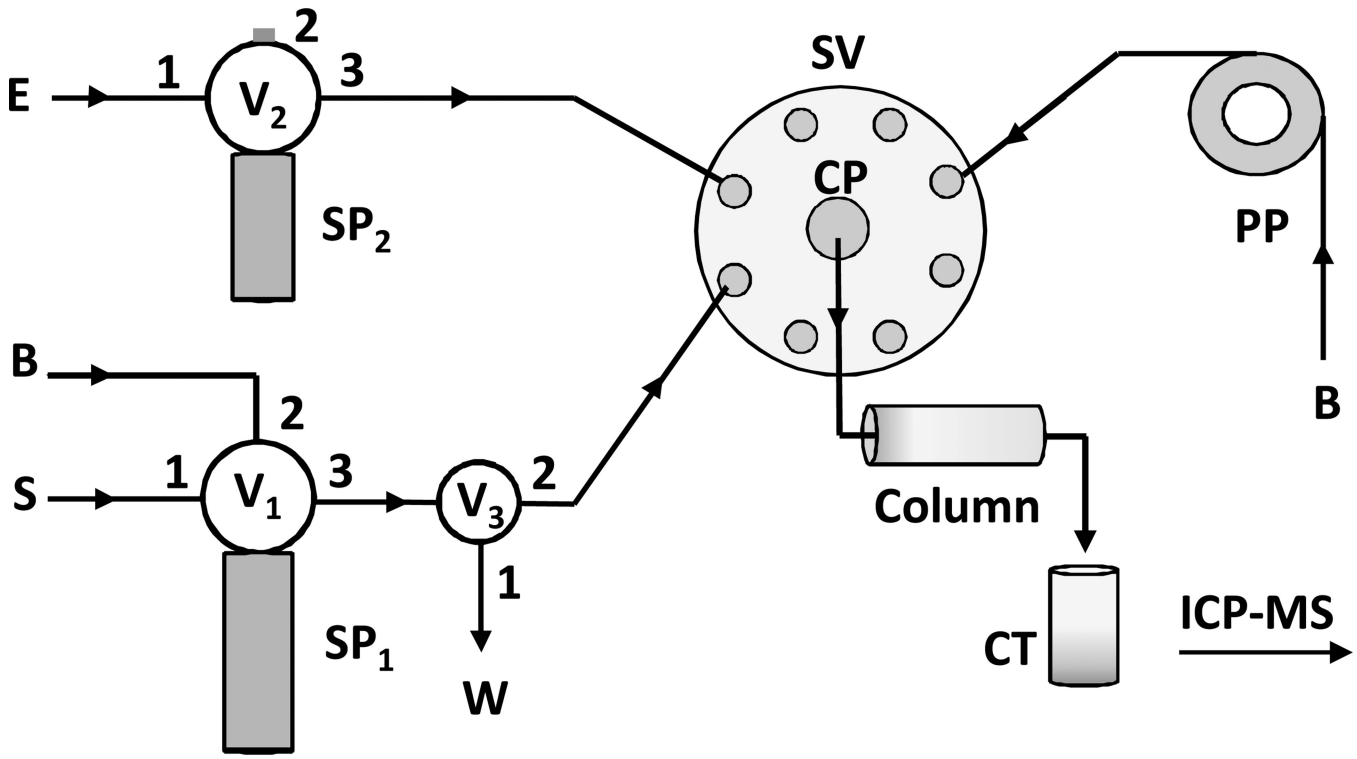

Fig. 1.

Schematic diagram of solid phase preconcentration system utilized with FIA 3200 unit. SP_1 and SP_2 = Syringe pumps; PP = peristaltic pump; V_1 and V_2 = Three-way valve; V_3 = Two-way manual valve; S = Sample, B = Buffer (pH 5.0); E = Eluent (1% v/v HNO_3); CT = Collection tube; W = Waste; SV = 8-port selection valve; CP = Central port.

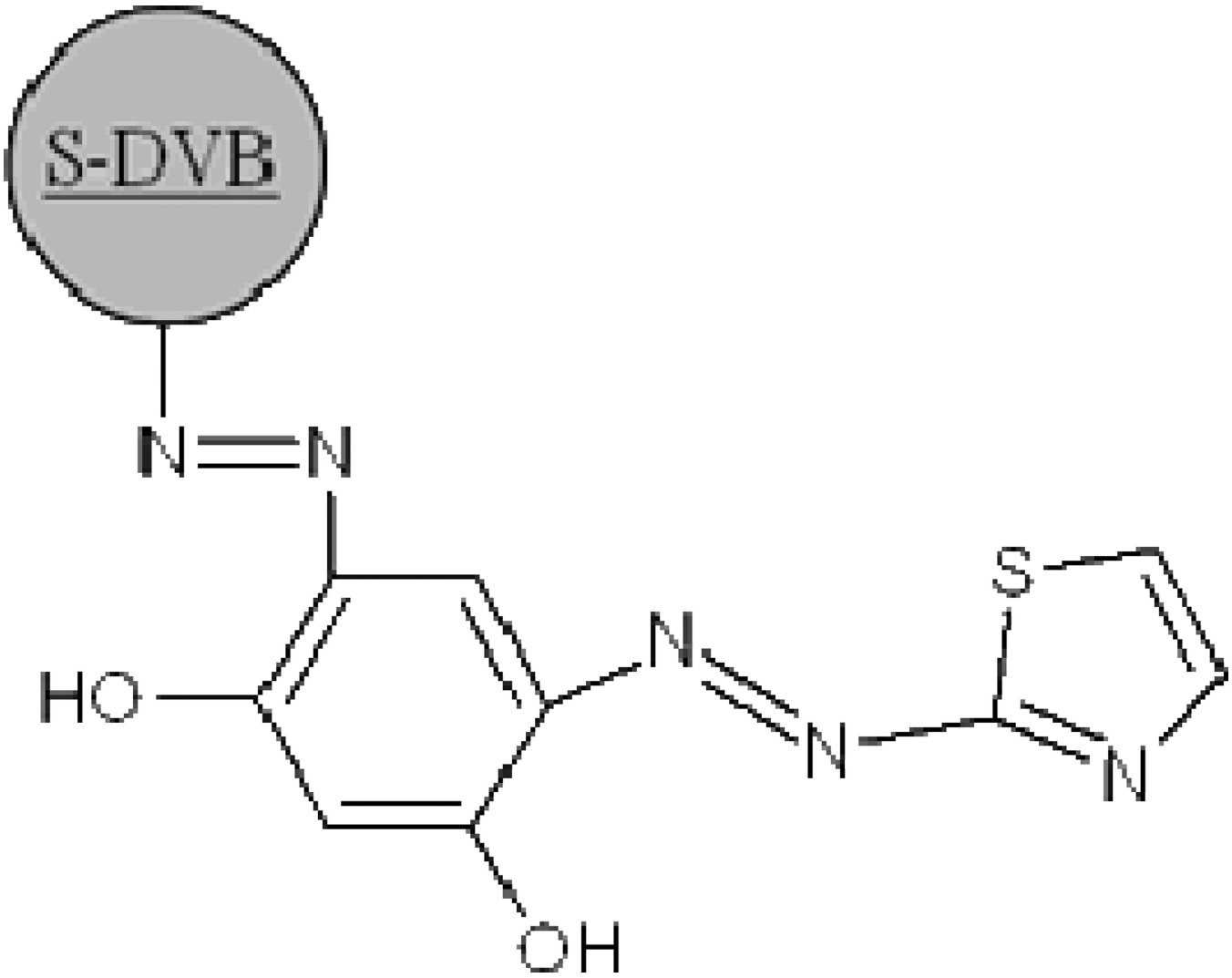

Fig. 2.
Proposed structure of the Chromosorb 106-TAR chelating resin.

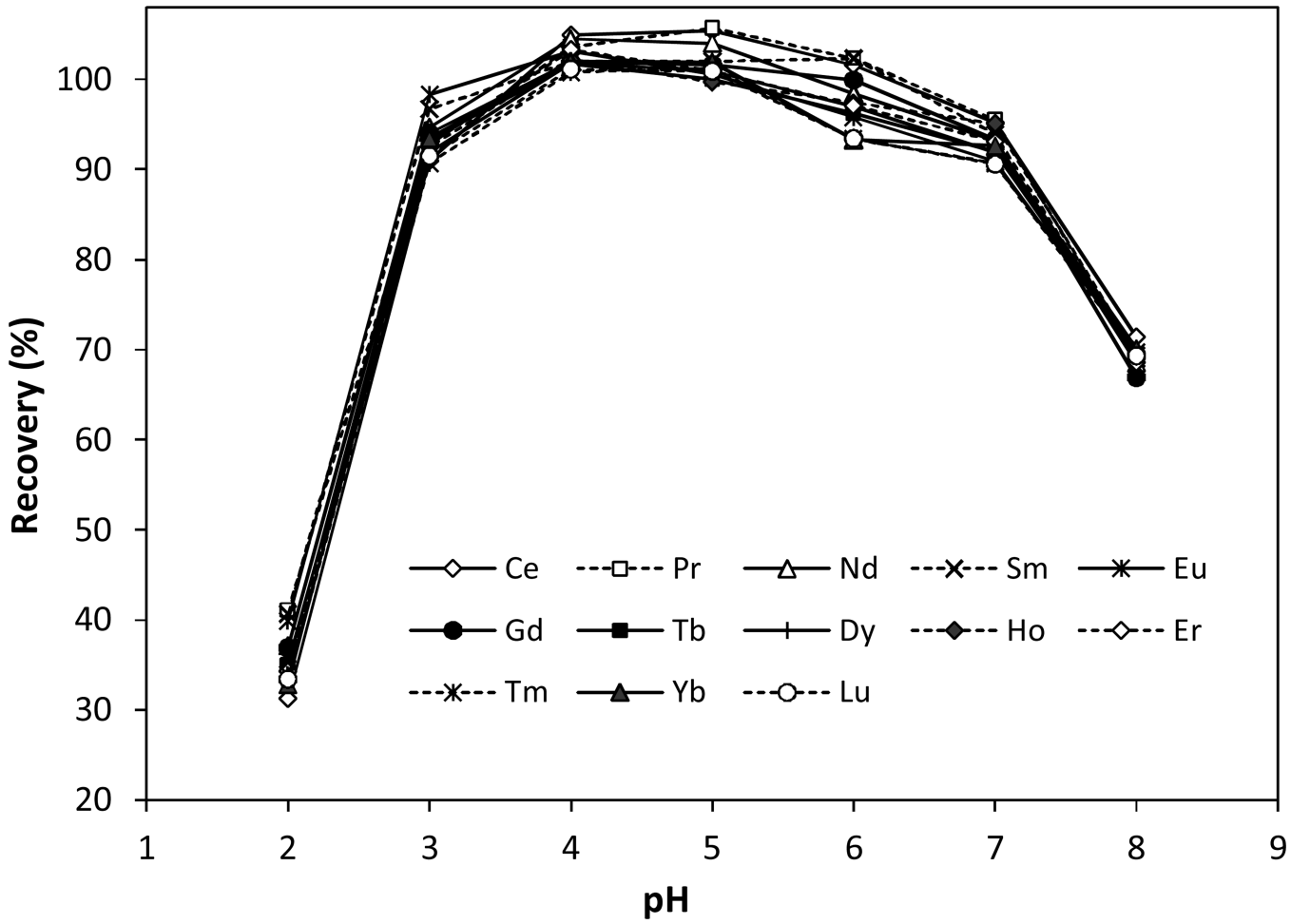

Fig. 3.
The effect of load pH on the retention of the REEs on the column in deionized water in the absence of matrix.

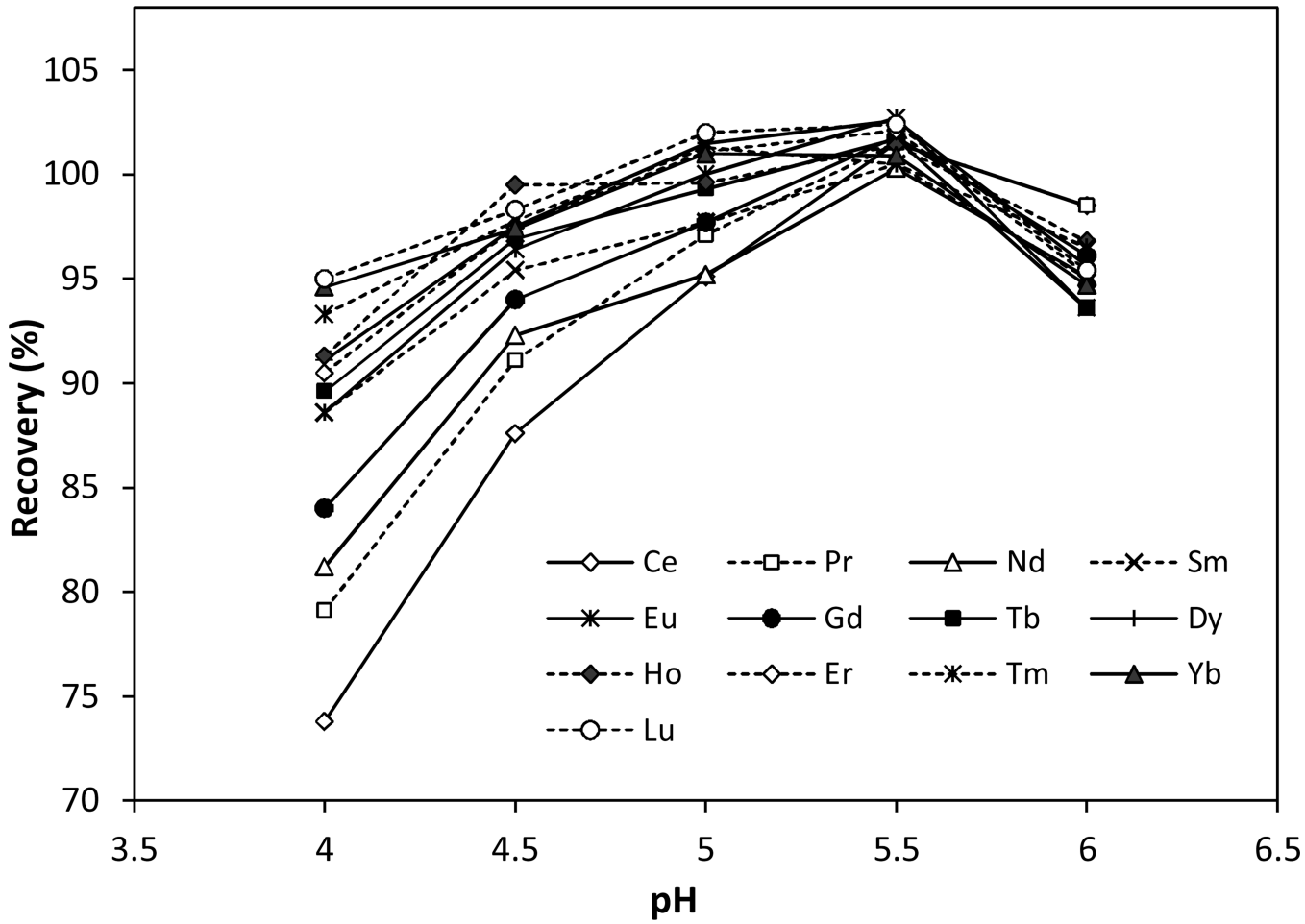

Fig. 4.
The retention profiles of the REEs in artificial seawater matrix as a function of load pH.

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 (rpm; mL min^{-1})	6; 0.2
Stabilization time (s)	20
Spray chamber temperature (°C)	3
Scan mode	Peak hopping
Dwell time (ms)	20
Monitored isotopes	^{140}Ce, ^{141}Pr, ^{146}Nd, ^{149}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu
Points/peak	1
Scans/peak	3
Scans/replicate	3

Table 2

Operation program of the FIA 3200 sequential injection unit for solid phase extraction

Step	SP_1	SP_2	Volume (mL)	Flow rate (mL min^{-1})	Valve position			PP	Remark
					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	3	3	-	2	Off	Sample load
5	Aspirate	Off	3	6	2	-	2	Off	Buffer uptake
6	Dispense	Off	3	3	3	-	2	Off	Column wash
7	Off	Aspirate	1	6	-	1	-	Off	Eluent uptake
8	Off	Dispense	1	3	-	3	-	Off	Elution

Table 3

Comparison of sorption of capacities (μmol g^{-1}) of various chelating resins for REEs with those for Chromosorb 106-TAR

Sorbent	Element													Ref.#
	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
2,6-Diacetylpyridine functionalized Amberlite XAD -4	124	126	123	117	53.4	136	108	113	58.6	106	-	79.2	47.3	20
Alkyl phosphinic acid resin	14.4	14.3	14.0	13.9	14.1	13.9	13.8	13.7	13.4	13.2	13.4	13.1	13.5	17
Poly(acrylaminophosphonicdithiocarbamate) fiber	216	219	220	217	215	202	202	194	190	181	183	183	17	21
Fluorinated β-diketone immobilized S-DVB	68	-	58	61	56	55	-	63	-	55	-	53	54	29
8-Quinolinole-immobilized fluorinated metal alkoxide glass	-	-	-	36	-	-	-	-	-	-	-	60	-	26
Poly(hydroxamic acid) resin	-	-	-	898	-	-	-	-	-	-	-	-	-	6
TAR immobilized Chromosorb 106	102	101	108	105	95.1	96.4	88.0	94.3	85.0	100	91.4	87.5	81.1	this work

Table 4

The detection limits (LOD, ng L^{-1}) and typical calibration curves for the REEs. The×and *y* stand for concentration (μg L^{-1}) and internal corrected signal (S_{REE}/S_{IS}), respectively

Element		LOD	Calibration equation	R^2
Ce	140	0.31	$y = 1.1482x + 0.0094$	0.9994
Pr	141	0.06	$y = 1.3918x + 0.0115$	0.9995
Nd	146	0.10	$y = 0.2459x + 0.0023$	0.9995
Sm	149	0.11	$y = 0.1911x + 0.0021$	0.9994
Eu	153	0.06	$y = 0.7255x + 0.0066$	0.9996
Gd	157	0.21	$y = 0.2352x + 0.0023$	0.9994
Tb	159	0.07	$y = 1.3465x + 0.0136$	0.9995
Dy	163	0.22	$y = 0.3243x + 0.0031$	0.9997
Ho	165	0.18	$y = 1.2947x + 0.0128$	0.9989
Er	166	0.19	$y = 0.431x + 0.004$	0.9994
Tm	169	0.07	$y = 1.2606x + 0.0111$	0.9995
Yb	172	0.14	$y = 0.2817x + 0.0026$	0.9996
Lu	175	0.08	$y = 1.1962x + 0.0122$	0.9995

Table 5

Comparison of REE concentrations (ng L^{-1}) reported for Nearshore seawater certified reference material (CASS-4) with those by this method (n = 5)

Element	Isotope	Found	Reported values		
			Ref. 16	Ref. 23	Ref. 26
Ce	140	5.47 ± 0.16	4.62 ± 0.94	6.1 ± 0.3	1.97 ± 0.20
Pr	141	1.28 ± 0.07	1.40 ± 0.09	1.42 ± 0.04	1.01 ± 0.06
Nd	146	4.93 ± 0.62	6.03 ± 0.54	5.5 ± 0.5	4.26 ± 1.13
Sm	149	5.46 ± 0.22	5.73 ± 0.24	5.5 ± 0.5	2.05 ± 0.26
Eu	153	0.28 ± 0.04	0.24 ± 0.01	0.19 ± 0.03	0.48 ± 0.11
Gd	157	1.21 ± 0.03	1.34 ± 0.07	1.4 ± 0.2	1.07 ± 0.40
Tb	159	0.26 ± 0.02	0.21 ± 0.01	0.17 ± 0.03	0.32 ± 0.01
Dy	163	1.41 ± 0.08	1.49 ± 0.07	1.5 ± 0.2	1.04 ± 0.29
Ho	165	0.46 ± 0.05	0.41 ± 0.04	0.35 ± 0.03	0.42 ± 0.10
Er	166	1.22 ± 0.11	1.38 ± 0.12	1.1 ± 0.1	0.82 ± 0.12
Tm	169	0.32 ± 0.04	0.22 ± 0.03	0.20 ± 0.05	0.37 ± 0.05
Yb	172	1.32 ± 0.11	1.43 ± 0.40	1.2 ± 0.2	1.08 ± 0.08
Lu	175	0.21 ± 0.08	0.25 ± 0.08	0.16 ± 0.03	0.40 ± 0.14

Table 6

Elemental concentrations (ng L^{-1}) and recoveries (R) for REEs from analysis of estuarine water and coastal seawater samples. Values are given as average ± standard deviation for given four replicate analyses

Element	Estuarine water				Coastal seawater			
	Found	Added	Total found	R (%)	Found	Added	Total found	R (%)
Ce	278 ± 21	200	471 ± 16	97	17.8 ± 0.3	20	38.8 ± 0.8	105
Pr	80.3 ± 1.2	100	183 ± 8.2	103	4.26 ± 0.22	10	14.1 ± 0.52	96
Nd	156 ± 5	100	248 ± 12	95	14.3 ± 0.6	10	23.4 ± 1.1	94
Sm	91.7 ± 2.5	100	185 ± 4	93	3.78 ± 0.14	10	13.9 ± 0.23	103
Eu	21.2 ± 1.3	20	41.7 ± 1.1	102	1.09 ± 0.03	2	3.01 ± 0.07	93
Gd	81.2 ± 3.9	100	176 ± 4	94	3.91 ± 0.21	10	13.6 ± 0.32	92
Tb	9.5 ± 0.4	20	30.0 ± 1.6	105	0.82 ± 0.01	2	2.76 ± 0.08	93
Dy	37.9 ± 1.5	40	78.3 ± 4.1	101	3.32 ± 0.11	10	13.1 ± 0.21	93
Ho	10.3 ± 0.4	20	29.6 ± 1.1	91	0.96 ± 0.06	2	2.91 ± 0.17	95
Er	20.1 ± 1.0	20	39.8 ± 1.3	98	2.82 ± 0.12	2	4.95 ± 0.16	105
Tm	4.61 ± 0.08	10	14.4 ± 0.14	95	0.72 ± 0.02	2	2.68 ± 0.04	94
Yb	18.7 ± 1.3	20	38.9 ± 0.9	101	2.08 ± 0.08	2	4.04 ± 0.05	98
Lu	4.32 ± 0.11	10	14.1 ± 0.14	95	1.23 ± 0.04	2	3.15 ± 0.03	93