

Preconcentration of Rare Earth Elements in Seawater with Poly(acrylamino-phosphonic dithiocarbamate) Chelating Fiber Prior to Determination by Inductively Coupled Plasma Mass Spectrometry

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A new ion-exchange chelating fiber with aminophosphonic and dithiocarbamate groups based on polyacrylonitrile was developed for the preconcentration of rare earth elements (REEs) in seawater prior to their determination by inductively coupled plasma mass spectrometry. REEs can be easily separated from the high-saline matrix using the fiber. The optimum experimental parameters such as pH, flow rate, sample volume, and effect of matrix ions for preconcentration of REEs were investigated. All REEs in water can be quantitatively retained in the acidity range of pH 3–6 by the fiber and then eluted quantitatively with 0.01 mol L⁻¹ ammonium citrate. The fiber has been applied to the concentration of REEs in seawater. The relative standard deviations for the determination of REEs in seawater at nanogram per liter levels were found to be less than 5%. A reasonably good agreement is obtained with the data reported in the literature.

The chemistry of rare earth elements (REEs) makes them particularly useful in studies of marine geochemistry.¹ But the determination of REEs in seawater at ultratrace levels has always been a difficult task. Of the various methods applied, instrumental neutron activation analysis (INAA) and isotope dilution mass spectrometry (IDMS) were the main techniques used for the determination of REEs in seawater. However, sample preparation is tedious and large amounts of water are required in INAA. In addition, the method can only offer relatively low sample throughputs and some of REEs cannot be determined. The main drawbacks of IDMS are that it is time-consuming and expensive and monoisotopic elements cannot be determined as well.

At present, inductively coupled plasma mass spectrometry (ICPMS) provides a unique, powerful, alternative for the determination of REEs in natural samples.^{2,3} Nevertheless, its application to the determination of REEs at ultratrace concentration level in seawater is limited because highly saline samples can cause both spectral interferences and matrix effects.⁴ Therefore, a

separation of the matrix components and preconcentration of the analytes are prerequisites. To achieve this goal, many preconcentration techniques have been used including coprecipitation with iron hydroxide,^{5–7} ion exchange with Chelex 100,^{8–11} treatment with silica-immobilized 8-hydroxyquinoline,^{12,13} solvent extraction with bis(2-ethylhexyl)hydrogen phosphate/2-ethylhexyl dihydrogen phosphate (HDEHP/H₂MEHP),^{14,15} and sorption on activated carbon.¹⁶ It should be pointed out that coprecipitation with iron hydroxide requires an additional separation step, usually cation-exchange chromatography, to remove magnesium, calcium, and iron before determination. Chelation with Chelex 100 requires removal of calcium and magnesium by careful washing with ammonium acetate or by cation- and anion-exchange chromatography prior to elution of REEs. The solvent extraction technique reported by Shabani et al.^{14,15} involves many manipulations such as scrubbing, stripping from the organic phase, washing the aqueous solution, and evaporating the final solution. The concentration technique reported by Esser et al.¹² and Halicz et al.¹³ can only concentrate REEs at pH 8–9, and sorption on activated carbon¹⁶ is time consuming.

The aim of the present study is to report the application of a new ion-exchange chelating fiber with aminophosphonic and

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Table 1. ICPMS Operating Conditions

ICP System	
forward power	1350 W
reflected power	<5 W
coolant argon flow rate	14 L/min
auxiliary gas flow rate	0.9 L/min
nebulizer gas flow rate	0.8 L/min
sample uptake rate	1.0 mL/min
sampling depth	15 mm
Mass Spectrometer	
sampler (nickle) orifice	1.0 mm
skimmer (nickle) orifice	0.7 mm
first-stage pressure	1.6 mbar
second-stage pressure	1.0×10^{-4} mbar
third-stage pressure	1.7×10^{-6} mbar
data aquisition	range-scanning mode
mass range	85–175 μ
total acquisition time	60 s

dithiocarbamate groups synthesized on polyacrylonitrile fiber for the preconcentration of REEs in seawater prior to the determination by ICPMS.

EXPERIMENTAL SECTION

Instrument. A Plasma-Quad 3 (VG Elemental, Winsford, U.K.) inductively coupled plasma mass spectrometer was used for the determination of REEs. The optimum instrumental parameters are given in Table 1. A Hitachi model 180-80 Zeeman atomic absorption spectrometer was used for the determination of calcium and magnesium. A Perkin-Elmer model 2280 atomic absorption spectrometer (in emission mode) was used to determine sodium and potassium.

Reagents and Solutions. The polyacrylonitrile fiber (a common commercial product, diameter <10 μm) was purchased from a Chinese chemical factory.

The stock solutions of each REE (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of their high-purity oxides (Specpure, Johnson Matthey Chemicals Limited) in 5 mL of HNO_3 (67%) with moderate heating. If the metal oxide did not completely dissolve, 1 mL of HCl (37%) was also added. Standard solutions of 10, 50, and 100 $\mu\text{g L}^{-1}$ were prepared for single REEs and multi-REEs before use by diluting the stock solutions in two steps with diluted HNO_3 . The final acid concentration was fixed at 0.1 mol L^{-1} HNO_3 . Indium was added as an internal standard to monitor matrix effects and instrumental drift.

All other chemicals were of analytical grade or better (Beijing Chemicals), and doubly deionized distilled water was used throughout.

The pH of solutions in the experiments was adjusted by addition of high-purity ammonium hydroxide and nitric acid.

Prior to any sampling and sorption work, all beakers, funnels, and calibrated flasks, together with other glassware used for experiments were soaked with 1 + 1 nitric acid and cleaned sequentially with tap water, neutral detergent, tap water, and doubly deionized distilled water before use.

Synthesis of the Fiber. The poly(acrylamino-phosphonic dithiocarbamate) was synthesized according to the following four stages:

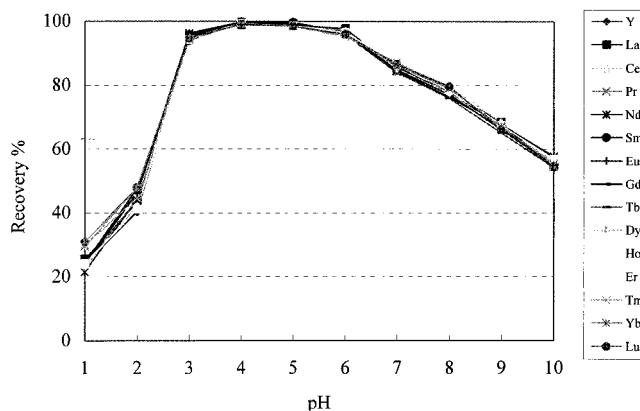


Figure 1. Effect of pH on recovery of REEs (sample volume, 100 mL; containing REEs 2 $\mu\text{g L}^{-1}$).

Step 1. The hydrazine-modified polyacrylonitrile fiber was synthesized following the method of Zhang et al.¹⁷ Twenty grams of polyacrylonitrile fiber and 800 mL of hydrazine hydrate were reacted in a 1-L flat-flange reaction vessel for 2.5 h at 90–94 $^{\circ}\text{C}$, then suction-filtered, washed with ethanol, and dried at 55–60 $^{\circ}\text{C}$ overnight.

Step 2. A mixture of 10 g of dry hydrazine-modified polyacrylonitrile fiber and 400 mL of diethylenetriamine was heated for 5–10 h at 95 ± 1 $^{\circ}\text{C}$. Afterward the mixture was cooled, suction-filtered, successively washed with alcohol and distilled water until neutral, and then dried at 60–65 $^{\circ}\text{C}$ overnight.¹⁸

Step 3. The poly(acrylamino-phosphonic carboxylhydrazide) fiber was prepared by the reaction of 10 g of the above fiber aminated with 400 mL of phosphorous acid for 6 h at 85–90 $^{\circ}\text{C}$, then suction-filtered, washed with distilled water, and dried at 60–65 $^{\circ}\text{C}$ overnight.¹⁹

Step 4. The poly(acrylamino-phosphonic dithiocarbamate) chelating fiber was synthesized by reacting 10 g of poly(acrylamino-phosphonic carboxylhydrazide) fiber with 200 mL of sodium hydroxide and 200 mL of carbon disulfide at 60–65 $^{\circ}\text{C}$ for 2 h. The fiber was washed with alcohol and distilled water and dried at 40–50 $^{\circ}\text{C}$ overnight.²⁰

Fiber Capacity. The binding capacity of the fiber was determined for each REE by the batch technique. Fiber (100 mg each) was equilibrated by shaking for 24 h in the excess REE solution (50 mL, 10 mg L^{-1}) at optimum adsorption pH 5. Then, fiber was filtered off and the concentration of the remaining REEs in the solution was determined by ICPMS.

Column Package. A small plug of glass wool was placed at the bottom of the column (i.d. 0.4 cm, height 5 cm), and the empty column and glass wool plug were soaked in concentrated nitric acid for 24 h before use. The column was drained and rinsed several times with deionized water prior to filling with fiber. To increase the adsorption surface area of the fiber, the fiber was sheared by stainless steel scissors and passed a 0.25-mm nylon sieve before packing. Then, 100 mg of the fiber suspended in water was slurry-packed in the column and rinsed first with sufficient

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Table 2. Influence of Matrix Ions on the Concentration Efficiency of REEs^a

matrix ions	concn (mg L ⁻¹)	added as	matrix ion concn in eluent (mg L ⁻¹)	recovery (%)															
				Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Na ⁺	20000	NaCl	3.10 ± 0.2	99.2	98.8	100	99.1	98.4	97.5	98.0	99.6	98.1	99.8	98.8	97.3	97.8	100	99.0	
K ⁺	500	KCl	0.90 ± 0.05	99.9	102	101	99.6	98.7	98.6	99.4	97.7	99.1	100	96.9	101	99.5	98.6	97.2	
Mg ²⁺	2500	MgCl ₂	1.50 ± 0.1	98.6	99.3	99.1	98.0	100	97.7	97.0	97.6	99.4	98.3	97.9	99.5	100	98.2	98.9	
Ca ²⁺	500	CaCl ₂	0.50 ± 0.02	99.7	102	101	98.5	99.5	98.4	98.1	100	97.1	98.8	99.6	99.7	97.1	99.0	98.0	

^a Sample volume, 1000 mL; concentration of each REE, 2 μg L⁻¹, *n* = 3.

Table 3. Instrument Absolute Blanks and Detection Limits of REEs

element	blank (ng L ⁻¹)	detectn limit (ng L ⁻¹)	element	blank (ng L ⁻¹)	detectn limit (ng L ⁻¹)
Y	4	2	Tb	0.9	0.5
La	4	2	Dy	0.9	0.7
Ce	2	1	Ho	0.8	0.7
Pr	2	0.9	Er	0.3	0.2
Nd	2	1	Tm	0.8	0.6
Sm	3	1	Yb	0.7	0.5
Eu	2	0.7	Lu	0.6	0.3
Gd	2	1			

distilled water, then with 5 mL 0.01 mol L⁻¹ ammonium citrate, and finally with deionized water again before use.

Sampling of Seawater. The polyethylene bottles used for sampling seawater were precleaned with detergent, doubly deionized distilled water, dilute HNO₃, and doubly deionized distilled water, respectively, and then high-purity HNO₃ was added to keep the final acidity of seawater at about pH 2 after sampling. Seawater samples were taken at a depth of 1 m beneath the surface from four locations 10 miles from Tianjin, Qinghuangdao, Dalian, and Qingdao along the eastern and northern coasts of China in October 1997. The samples were filtered through a Millipore cellulose membrane of pore size 0.45 μm and stored at temperature of about 4 °C.

Preconcentration of REEs in Seawater. A 1000-mL seawater sample was adjust to the desired pH 5 and passed through the column using a peristaltic pump at a flow rate of 7 mL min⁻¹. After washing with 25 mL of deionized water, the REEs retained in column was eluted with 5 mL of 0.01 mol L⁻¹ ammonium citrate at a flow rate of 1 mL min⁻¹. The eluted REEs were determined by ICPMS. The used fiber was washed with deionized water until neutral prior to next use.

RESULTS AND DISCUSSION

Effect of pH on Recovery of REEs from Water Samples.

The effect of various pHs of the water sample solution on the recovery of REEs was studied, and the results are shown in Figure 1. As can be seen, when the pH values of the water samples were lower than 3, all the REEs were recovered poorly. However, a quantitative sorption of REEs (>95%) on the fiber occurs in the acidity range of pH 3–6. When the pH value was higher than 6, the recovery for all the REEs decreased again. Hence, pH 5 was fixed as the optimum for the quantitative preconcentration.

Fiber Capacity. The binding capacity of the fiber is an important factor to determine how much fiber is required to quantitatively concentrate REEs from water samples. The capacity

for Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were 0.705, 0.206, 0.216, 0.219, 0.220, 0.217, 0.215, 0.202, 0.202, 0.194, 0.190, 0.181, 0.183, 0.183, and 0.178 mmol g⁻¹, respectively, under the optimum pH 5. It was concluded that the column capacity did not vary much for the different elements except Y. As can be seen, the capacity of the fiber is high enough for use in the simultaneous concentration and determination of REEs in seawater.

Selection of Eluent and Its Volume. In general, mineral acids such as hydrochloric acid, nitric acid, and sulfuric acid were used as the eluents of REEs,^{12,15,16} but the concentrations of these acids used for elution are too high for ICPMS determination. Ammonium citrate and ethylenediaminetetraacetic acid (EDTA) are also good eluents for REEs²¹ because they can form stable chelates with REEs. It was also found that 0.01 mol L⁻¹ ammonium citrate eluted REEs quantitatively.²² To achieve quantitative elution of REEs from the fiber, different concentrations of various eluents such as nitric acid, EDTA, and ammonium citrate were tried. A detailed comparison of elution performance of HNO₃, EDTA, and ammonium citrate demonstrated that no quantitative elution was obtained when HNO₃ and EDTA were used. However, it should be stressed that 97–100% of REEs retained on the fiber was eluted if 0.01 mol L⁻¹ ammonium citrate was used. Therefore, 0.01 mol L⁻¹ ammonium citrate is recommended for the remainder of the study. To study the effect of eluent volume on the elution efficiency, different volumes of 0.01 mol L⁻¹ ammonium citrate was used to elute REEs after REEs was concentrated from 1000 mL of the solution to a level of 2 μg L⁻¹. The experimental results indicated that 4–10 mL of 0.01 mol L⁻¹ ammonium citrate is sufficient for the quantitative elution of all REEs. Therefore, 5 mL of 0.01 mol L⁻¹ ammonium citrate was used for the elution of REEs after preconcentration from 1 L of real seawater.

Effect of Flow Rate and Volume of the Sample on Concentration. The effect of different flow rates of the sample solution on the concentration efficiency of REEs was studied at flow rates from 1 to 10 mL min⁻¹ under the condition of optimum pH 5. The recoveries of all REEs were quantitative at a flow rate of 8 mL min⁻¹ or less.

To explore the possibility of enriching REEs from solution of low concentration equivalent to REEs concentration in seawater with a high preconcentration factor, the effect of sample volumes from 100 to 2000 mL was studied using the column described in the Experimental Section with a flow rate of 7 mL min⁻¹ and pH

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Table 4. Determination of REEs in Seawater (ng L⁻¹) and Recovery (%) of Spiked REEs^a

element	Tianjin seawater				Dalian seawater				Qingdao seawater				Qinghuangdao seawater			
	found	added	total found	rec	found	added	total found	rec	found	added	total found	rec	found	added	total found	rec
Y	13.8	13.5	27.1	98	13.6	13.5	26.7	97	12.9	13.0	25.8	99	11.8	12.0	23.5	98
La	3.74	3.70	7.36	98	3.34	3.30	6.57	98	3.57	3.50	6.93	96	3.50	3.50	6.86	96
Ce	7.16	7.10	14.0	96	6.82	6.80	13.3	95	6.32	6.30	12.5	98	7.30	7.30	14.3	96
Pr	1.12	1.10	2.18	96	1.86	1.80	3.60	97	1.06	1.00	2.03	97	1.71	1.70	3.39	99
Nd	2.82	2.80	5.48	95	3.17	3.10	6.15	96	3.66	3.60	7.08	95	3.01	3.00	5.92	97
Sm	1.05	1.00	2.02	97	1.23	1.20	2.38	96	1.36	1.30	2.64	98	1.29	1.30	2.52	96
Eu	0.411	0.41	0.808	97	0.448	0.44	0.879	98	0.352	0.35	0.688	96	0.423	0.42	0.830	97
Gd	1.19	1.10	2.28	99	1.45	1.40	2.79	96	1.26	1.20	2.40	95	1.32	1.30	2.58	97
Tb	0.332	0.33	0.649	96	0.286	0.28	0.563	99	0.248	0.25	0.493	98	0.387	0.38	0.759	98
Dy	0.851	0.85	1.67	96	1.06	1.00	2.03	97	0.954	1.00	1.95	100	1.09	1.00	2.05	96
Ho	0.354	0.35	0.697	98	0.250	0.25	0.500	100	0.230	0.23	0.453	97	0.305	0.30	0.602	99
Er	1.06	1.00	2.03	97	1.04	1.00	2.00	96	0.955	1.00	1.92	96	1.07	1.00	2.04	97
Tm	0.207	0.20	0.401	97	0.240	0.24	0.473	97	0.237	0.23	0.462	98	0.208	0.20	0.402	97
Yb	1.13	1.10	2.20	97	0.925	0.90	1.79	96	0.938	0.94	1.84	95	0.994	1.00	1.97	98
Lu	0.198	0.20	0.392	98	0.151	0.15	0.296	97	0.194	0.20	0.392	99	0.209	0.20	0.400	96

^a Sample volume, 1 L; eluent volume, 5 mL. Three measurements for each sample, RSD less than 5%.

Table 5. Comparison of REEs Concentration in Seawater Obtained by the Present Method with That Reported in the Literature

element	REEs in seawater (ng L ⁻¹)						
	present method				lit. report		
	Tianjin	Dalian	Qingdao	Qinghuangdao	ref 15	ref 16	ref 13
Y	13.8	13.6	12.9	11.8			
La	3.74	3.34	3.57	3.50	3.49		3.8
Ce	7.16	6.82	6.32	7.30	5.03	6.53	6.1
Pr	1.12	1.86	1.06	1.71	0.731	2.61	0.7
Nd	2.82	3.17	3.66	3.01	3.26	6.05	2.7
Sm	1.05	1.23	1.36	1.29	0.607	2.62	0.5
Eu	0.411	0.448	0.352	0.423	0.180	2.09	0.2
Gd	1.19	1.45	1.26	1.32	0.985	1.28	0.7
Tb	0.332	0.286	0.248	0.387	0.17	0.31	0.2
Dy	0.851	1.06	0.954	1.09	0.976	1.67	0.9
Ho	0.354	0.250	0.230	0.305	0.25	0.31	0.3
Er	1.06	1.04	0.955	1.07	0.730	1.02	0.7
Tm	0.207	0.240	0.237	0.208	0.105	1.35	0.2
Yb	1.13	0.925	0.938	0.994	0.634	0.31	0.8
Lu	0.198	0.151	0.194	0.209	0.102		0.2

5. All REEs were quantitatively recovered (95–100%) when the sample volume was less than 1250 mL. When the sample volume exceeded 1250 mL, the recovery was decreased gradually for all REEs, the larger the sample volume, the lower the recovery of REEs. The same phenomena were reported previously.^{15,23} The reason for this may be that there are many ions present in the sample solution; some ions may act as eluents if their affinity for the ion-exchange fiber is greater than the affinity of the REE ions associated with the fiber. So when the sample volume increases, early breakthrough is possible.²⁴ Therefore, the sample volume of 1 L was adopted for the preconcentration of REEs in seawater. As mentioned above, 5 mL of eluent is sufficient; thus, an enrichment factor of 200 is achievable.

Effect of Matrix Ions. To evaluate the feasibility of the method for the determination of REEs in seawater, the effects of the major matrix ions such as sodium, potassium, calcium, and magnesium in seawater were studied (Table 2). Table 2 shows that the presence of a manifold amount of alkali and alkaline earth

metals in the water have no significant influence on the recoveries of REEs from the water sample, and the salt content in the eluent is very low and suitable for ICPMS determination. Therefore, no additional separation procedure is needed. This indicates that the fiber can be successfully used to concentrate ultratrace REEs from high-saline seawater before the determination by ICPMS.

Blanks and Detection Limits. The blanks for individual REE are derived from repeated measurements of signals obtained from running 0.1 mol L⁻¹ nitric acid as sample. The detection limit is defined as 3 times the standard deviation of 10 runs of the blank solution. The results are presented in Table 3. The content of REEs in seawater ranges between 0.1 and 10 ng L⁻¹; therefore, the concentrations of all REEs after the 200-fold preconcentration are high enough to allow precise and accurate determination with ICPMS.

Determination of REEs in Seawater. Since no certified seawater is available for REEs, trace REEs were spiked into the seawater before matrix separation and REE preconcentration. The recoveries of spikes are shown in Table 4. The experimental results demonstrated that the recoveries of all added REEs were greater than 95%. This indicates the high reliability and validity of the technique developed here.

Based on the above study, the developed method has been applied for the determination of REEs in seawater. The results of four seawater samples are given in Table 5. A comparison was also made between the data obtained by this method and those reported in the literature,^{13,15,16} and a reasonably good agreement was achieved.

CONCLUSION

In this study, a new successful technique was developed based on the preconcentration of REEs in seawater with poly(acrylamino-phosphonic dithiocarbamate) chelating fiber prior to the determination by ICPMS. In this method, all REEs can be concentrated 200 times in a short time with almost all matrix elements separated. The recommended method has advantages over the previously reported methods: (1) Only a single-stage process is required for preconcentration and separation of REEs from seawater; the salinity in the eluted REEs fraction is considerably

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reduced, so that the final solutions can be run by ICPMS. (2) The preconcentration is performed in acidic solutions; therefore, no buffer is required for controlling the pH, thus minimizing the contamination of blanks. (3) Generally, fibrous ion exchangers have some features associated with their structure. The synthesized fiber has several functional groups with different exchange characteristics, so that it has high metal binding capacities. (4) The kinetics of the fiber has verified that the extraction reaction is sufficiently fast in most cases not only for rare earth elements but also for other heavy metals, which will be published in a separate paper. And nearly the same extraction behavior is observed for many elements; therefore, a simultaneous multielement separation and preconcentration is feasible. This is particu-

larly important in environmental research for simultaneous multielement determination techniques such as ICP-AES and ICPMS.

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