ORIGINAL PAPER

Bei Wen · Xiao-Quan Shan · Rui-Xia Liu
Hong-Xiao Tang

Preconcentration of trace elements in sea water with poly(acrylamino-phosphonic – dithiocarbamate) chelating fiber for their determination by inductively coupled plasma mass spectrometry

Received: 1 May 1998 / Revised: 30 July 1998 / Accepted: 8 August 1998

Abstract A new ion exchange chelating fiber with aminophosphonic and dithiocarbamate groups based on polyacrylonitrile was used for the simultaneous preconcentration of beryllium, bismuth, cobalt, gallium, silver, lead, cadmium, copper, manganese and indium in sea water. The optimum experimental parameters, such as fiber capacity, pH, sample flow rate and volume, eluant and effect of matrix ions on the preconcentration were investigated. The separation of analytes can be achieved from sea water with a concentration factor of at least 200 times. The method has been applied for the determination of trace elements in coastal sea water. The data obtained by this method agreed well with certified values.

Introduction

Since its introduction more than one decade ago, inductively coupled plasma mass spectrometry (ICP-MS) has been found widespread application in spectrochemical analysis because of the many advantages of this technique. Unfortunately, its application to the analysis of saline waters remains quite limited due to the low tolerance of the instrument to dissolved solids, the highest recommended level being approximately 0.2% [1]. Therefore, the development of preconcentration techniques to separate analytes from the sample matrix is an important prerequisite for environmental analysis.

Many preconcentration techniques have been proposed for the determination of metals in various environmental samples, including solvent extraction [2, 3], ion exchange [4, 5], coprecipitation [6, 7] and sorption [8, 9]. Recently, solid phase techniques have become increasingly popular in comparison with the more traditional liquid-liquid extraction methods [10].

To meet the growing demands of ecological and environmental research, new chelating resins are continuously being developed. Among these, iminodiacetate based [11–13] and quinoline-8-ol based [14–16] exchangers are showing promising qualities for the separation and concentration of trace metals. However, ion exchange with Chelex 100 requires the removal of calcium and magnesium by careful washing with ammonium acetate or by cation- and anion-exchange chromatography, resulting in time-consuming, sample manipulation and possible contamination [17]. The use of quinoline-8-ol based resins is limited to stability of the resins at high pH. Cleavage of the immobilized 8-hydroxyquinoline decreased the capacity of the resin obviously. Recently, many efforts have been made to synthesize dithiocarbamates onto suitable substrates, for example, bound silica [18, 19], C₁₈ [20, 21] or Amberlite XAD-2 [22]. The most commonly used dithiocarbamate ligand is diethylammonium, but bis(carboxymethyl) [23] and ammonium tetramethylene [21] dithiocarbamates have also been reported. Generally, all dithiocarbamates form strong complexes with many metal ions [24] and have been employed for the effective concentration of trace elements.

In this study we developed a new ion exchange chelating fiber with aminophosphonic and dithiocarbamate groups bound to a polyacrylonitrile fiber for the separation of beryllium, bismuth, cobalt, gallium, silver, lead, cadmium, copper, manganese and indium from sea water. The experimental conditions for the separation process were studied in detail. The recommended technique was applied to the determination of trace elements in coastal sea water by ICP-MS.

Experimental

Instruments

A Plasma-Quad 3 (VG Elemental, Winsford, UK) ICP-MS was used for the determination of trace elements. General instrumental operating conditions are given in Table 1. A Hitachi model 180-80 Zeeman atomic absorption spectrometer (AAS) was used for the

B. Wen · X.-Q. Shan (✉) · R.-X. Liu · H.-X. Tang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences,
P.O.Box 2871, Beijing 100085, China
e-mail: Xiaoquan@mail.rcees.ac.cn

Table 1 ICP-MS 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 (nickel) orifice	1.0 mm
Skimmer (nickel) orifice	0.7 mm
1st stage pressure	1.6×10^5 mPa
2nd stage pressure	1.0×10 mPa
3rd stage pressure	1.7×10^{-1} mPa
Data acquisition	Range-scanning mode
Mass range	m/z 9–210
Total acquisition time	60 s

determination of calcium and magnesium. A Perkin-Elmer model 2280 AAS (in emission mode) was used to determine sodium and potassium concentrations.

Reagents and solutions

Stock solutions of each element, $1000 \mu\text{g} \cdot \text{mL}^{-1}$, were prepared by dissolving appropriate amounts of metal oxide (specpure, Johnson Matthey Chemicals Limited) in 5 mL of nitric acid (67%). For complete dissolution 1 mL HCl (37%) was added and moderate heating was applied. Single- and multielement standard solutions with concentrations of 10, 50 and 100 ng mL^{-1} were prepared from the stock solution by dilution with HNO_3 up to a final acid concentration of $0.1 \text{ mol L}^{-1} \text{ HNO}_3$.

All other reagents were of analytical grade or better. High purity water ($18 \text{ M}\Omega \times \text{cm}$) was prepared by double distillation of deionized water in a fused quartz still (Westdeutsche Quarzschmelze, Geesthacht, Germany). Nitric acid was purified by sub-boiling distillation in a quartz still using ultrapure grade HNO_3 as feed. All other acids used were of ultrapure grade (Beijing Chemicals, P.R. China).

Certified sea water reference material, GBW(E) 080040, was purchased from the Second Research Institute of National Oceanography Agency, Hangzhou, China.

Prior to use, all beakers, funnels, calibrated flasks and other glassware were cleaned sequentially with tap water, neutral detergent, doubly deionized distilled water; this was followed by soaking in nitric acid (1+1) and a rinse with doubly deionized distilled water.

Synthesis of the fibers

The poly(acrylamino-phosphonic-dithiocarbamate) fiber was prepared in a four steps procedure:

Step 1: The hydrazine-modified polyacrylonitrile fiber was prepared following the method of Zhang et al. [25] using polyacrylonitrile and hydrazine hydrate. Step 2: This fiber was modified with diethylenetriamine according to Egawa [26]. Step 3: The reaction product was phosphorylated according to [27]. Step 4: Finally, the poly (acrylamino-phosphonic-carboxyl-hydranide) fiber was reacted with carbon disulfide in NaOH according to [28] resulting in the poly(acrylamino-phosphonic-dithiocarbamate) fiber.

Fiber capacity

The exchange capacity of the fiber was determined for each metal ion by a batch technique. 100 mg fiber was equilibrated with each metal ion for 24 h at pH 6 with an excess of metal ion solution (30 mL , $10 \mu\text{g} \cdot \text{mL}^{-1}$). After filtration the concentration of the metal ion in the solution was determined by ICP-MS.

Packing of columns

Glass columns (i.d. 4 mm, 50 mm high) were packed with a small glass wool plug treated with 1% HNO_3 at the end. After thorough draining and rinsing with doubly deionized distilled water, 100 mg of fiber, suspended in water, was slurry-packed and another small glass wool plug was inserted on the top of the fiber bed. The column was rinsed first with 100 mL distilled water, then with 20 mL $2 \text{ mol L}^{-1} \text{ HCl}$, and finally with doubly deionized distilled water until the pH of the eluant was neutral.

Sampling of sea water.

The polyethylene bottles (10 L) used for the collection of sea water were successively precleaned with detergent, doubly deionized distilled water, dilute HNO_3 and doubly deionized distilled water. 10 mL of high-purity HNO_3 were added to keep the final acidity of sea water at about pH 2 after sampling. Sea water samples were taken in a depth of 1 m at four locations in October 1997. The sample localities are situated at a distance of approximately 10 miles from the cities of Tianjin, Qinghuangdao, Dalian and Qingdao along the eastern and northern coasts of China. The samples were filtered through a Millipore cellulose membrane with a pore size of $0.45 \mu\text{m}$ and stored at 4°C .

Preconcentration of trace metal ions from sea water

A 1000 mL sea water sample was adjusted to pH 6 and then passed through the fiber column using a peristaltic pump at a flow rate of 5 mL min^{-1} . After washing with 25 mL doubly deionized distilled water, the trace metal ions retained on the column were eluted with 5 mL of $2 \text{ mol L}^{-1} \text{ HCl}$ at a flow rate of 1 mL min^{-1} . The eluants were collected in Teflon beakers and 0.5 mL of concentrated HNO_3 was added. The solution was then evaporated on a hot plate to near dryness. Care should be taken to avoid baking of the residue. Another 0.5 mL of concentrated HNO_3 were then added to the beaker and the procedure was repeated in order to ensure complete removal of HCl, which could disturb the ICP-MS determination. Finally, several portions of dilute HNO_3 were added. Following moderate heating on a hot plate, the solution was transferred to a 5 mL volumetric flask and diluted to the mark with dilute HNO_3 . Prior to reuse, the used fiber was cleaned with doubly deionized distilled water until the eluate was neutral.

Results and discussion

The experimental parameters, such as pH, fiber capacity, sample volume and flow rate, matrix effect, and eluants were carefully optimized with metal samples of 5 to $10 \mu\text{g L}^{-1}$.

Effect of pH on the preconcentration efficiency

The effect of sample pH, which was adjusted by the addition of high purity ammonium hydroxide and nitric acid, on the preconcentration efficiency of trace metal ions was studied (Fig. 1) It is obvious that all the metals were ab-

sorbed poorly at $\text{pH} < 4$. However, a quantitative recovery ($> 95\%$) was found for Cd(II) , Ga(III) , Pb(II) , In(III) and Ag(I) at the pH range of 4–8. The optimum acidity conditions for the preconcentration of Be(II) , Bi(II) and Cu(II) were in the pH range 5–8. For Mn(II) and Co(II) , the

highest recovery was obtained in the pH range of 5–7. In order to preconcentrate all considered elements simultaneously a pH of 6 was selected.

Fiber capacity

The binding capacity is an important factor, because it determines how much fiber is required to quantitatively concentrate the analytes from a given solution. Following the procedure described in the experimental section, the capacity of the fiber for Be , Mn , Co , Cu , Ga , Ag , Cd , In , Pb and Bi was found to be 74.1, 59.2, 69.2, 31.9, 4.05, 9.57, 0.834, 3.06, 27.6 and $3.06 \mu\text{mol g}^{-1}$, respectively, at pH 6. As can be seen the capacity of the fiber is high enough for the concentration of analytes from sea water.

Effect of eluant type, concentration and volume

The elution efficiencies of hydrochloric acid and nitric acid were compared at different concentrations (Table 2). The data show that neither 2 mol L^{-1} nor $3 \text{ mol L}^{-1} \text{ HNO}_3$ can elute any of the metal ions quantitatively. However, higher recoveries for all metal ions were achieved with $2 \text{ mol L}^{-1} \text{ HCl}$ than with 0.5 to $1.0 \text{ mol L}^{-1} \text{ HCl}$ eluant. In addition, 2, 4, 5, 6, 8 and 10 mL of $2 \text{ mol L}^{-1} \text{ HCl}$ were used to elute the adsorbed metal ions following the adsorption of the metal ions from 1000 mL of solution with a concentration of $5 \mu\text{g L}^{-1}$. With eluant volumes of less than 4 mL , quantitative recoveries ($> 95\%$) could not be obtained. Therefore, 5 mL of eluant were used in the following experiments.

Effect of flow rate and sample volume

The effect of different flow rates for sample solutions on the concentration efficiency was tested at flow rates from

Fig. 1a, b Effect of pH on the concentration efficiency of trace metal ions (sample volume: 100 mL , trace metal ion concentration: $10 \mu\text{g L}^{-1}$, eluant volume: 5 mL)

Table 2 Trace metal ion recovery (in %) as a function of eluant (sample volume: 1000 mL , trace metal ion conc. $5 \mu\text{g L}^{-1}$, eluant volume: 5 mL)

Eluant	Be	Mn	Co	Cu	Ga	Ag	Cd	In	Pb	Bi
$2 \text{ mol L}^{-1} \text{ HNO}_3$	21	47	40	5.7	31	1.2	40	1.1	4.2	1.2
$3 \text{ mol L}^{-1} \text{ HNO}_3$	41	72	68	10	49	5.6	50	3.6	8.2	3.3
$0.5 \text{ mol L}^{-1} \text{ HCl}$	80	61	57	58	72	55	86	55	84	80
$1 \text{ mol L}^{-1} \text{ HCl}$	90	83	79	76	89	76	95	71	90	91
$2 \text{ mol L}^{-1} \text{ HCl}$	99	99	99	98	99	96	100	95	99	100

Table 3 Influence of matrix ions on the concentration efficiency of trace metal ions (Sample volume: 1000 mL , trace metal ion concentration: $5 \mu\text{g L}^{-1}$, eluant volume: 5 mL)^a

Matrix ions	added as	Concentration of matrix ions in the sample (mg L^{-1})	Concentration of matrix ions in the eluant (mg L^{-1})	Recovery %									
				Be	Mn	Co	Cu	Ga	Ag	Cd	In	Pb	Bi
Na^+	NaCl	20000	3.00	100	99.2	99.8	98.4	99.4	100	97.4	99.5	97.8	99.4
K^+	KCl	500	0.96	100	99.6	99.4	98.6	97.8	100	98.4	99.8	98.2	98.7
Mg^{2+}	MgCl_2	2500	1.50	100	98.8	97.6	97.8	98.9	99.8	99.6	96.5	97.6	99.5
Ca^{2+}	CaCl_2	500	0.50	99.6	98.4	98.8	98.5	99.5	97.1	99.6	98.4	98.6	96.3

^aThree measurements for each sample, the RSD was less than 5%

Table 4 Blanks and detection limits

Element	Blank/ng L ⁻¹	Detection limit/ng L ⁻¹
Be	17.2	0.301
Mn	22.8	0.605
Co	2.9	0.002
Cu	4.2	0.040
Ga	8.3	0.024
Ag	9.2	0.028
Cd	4.0	0.033
In	9.2	0.013
Pb	41	0.058
Bi	17	0.155

Table 5 Determination of trace metals in certified sea water GBW(E) 080040^a

	Determined value, ng mL ⁻¹		Reference value, ng mL ⁻¹
Pb	9.5	± 0.6	10.0 ± 0.6
Cu	4.8	± 0.4	5.0 ± 0.4
Cd	0.94	± 0.09	1.0 ± 0.06
Be	0.0021	± 0.0005	
Mn	0.035	± 0.003	
Co	0.15	± 0.01	
Ga	0.083	± 0.01	
Ag	0.025	± 0.002	
In	0.0026	± 0.0004	
Bi	0.0036	± 0.0005	

^aSix measurements for each sample

1 to 10 mL min⁻¹ and pH 6. Quantitative recoveries of all studied metal ions were obtained at flow rates less than 6 mL min⁻¹.

In order to explore the possibility of enriching low concentrations of analytes from large sample volumes, the effect of sample volume on the concentration efficiency was also studied. Quantitative recoveries (> 95%) were obtained for sample volumes of less than 1200 mL. This phenomenon was also found by other authors [29, 30]. The reason why the recoveries decreased with increasing sample volume may be that some ions present in the sample can act as eluants, if their affinity for the fiber is sufficiently large. Therefore, when the sample volume increases, an early breakthrough is possible [31]. In this experiment, 1 L of sample solution was adopted for the pre-concentration of analytes from sea water, the adsorbed analytes can be eluted with 5 mL of 2 mol L⁻¹ HCl, and a pre-concentration factor of 200 is achieved by the concentration technique.

Effect of matrix ions

It is well recognized that high concentrations of Na, K, Ca and Mg in sea water cause serious salt deposition on the torch, sampling interface or ion lenses and prohibit the direct determination of trace elements in sea water by ICP-MS. Therefore, pre-separation of the major matrix of sea water

Table 6 Analytical data (ng L⁻¹) and recovery (%) of trace metal ions added to sea water samples (sample volume: 1000 mL, eluant volume: 5 mL)^a

Element	Tianjin sea water			Dalian sea water			Qingdao sea water			Qinghuangdao sea water		
	Found	Added	Total found	Recovery	Found	Added	Total found	Recovery	Found	Added	Total found	Recovery
Be	1.60	1.50	3.2	107	3.44	3.50	6.75	94	3.65	3.60	7.00	93
Mn	7.63	7.50	15.0	98	14.3	14.5	28.6	97	69.3	70.0	138.6	99
Co	27.1	27.0	55.0	103	77.7	77.0	154.3	99	52.2	52.0	103	98
Cu	2758	2760	5520	100	1152	1150	2305	100	132	132	262	98
Ga	4.05	4.00	8.00	99	16.8	16.0	32.0	95	103	103	262	98
Ag	32.4	32.0	64.0	99	18.9	19.0	38.5	103	20.3	20.0	39.8	97
Cd	127.5	127.0	253.8	99	47.2	47.0	93.4	98	70.0	70.0	142	103
In	1.04	1.00	1.98	94	1.11	1.10	2.20	99	0.971	1.00	2.01	104
Pb	59.2	60.0	118	98	56.5	56.0	110.9	97	77.3	78.0	156	101
Bi	8.70	8.70	16.8	93	8.10	8.00	16.3	102	11.4	11.4	22.4	96

^aThree measurements for each sample, the RSD was less than 10%

is required. The potential of the separation of high salt contents from sea water by the fiber was examined. Synthetic solutions of 1000 mL containing 500–20 000 mg L⁻¹ Ca, Mg, Na, K as their chlorides were used as samples. The results obtained in these experiments (Table 3) demonstrate that the presence of large amounts of alkali and alkaline earth metals in the sample have no significant effect on the recoveries of the studied metal ions. Furthermore, the salt content of the eluant is sufficiently low for direct ICP-MS analysis. Therefore, no additional separation procedure is required. This indicates that the newly developed fiber can be used for the concentration of ultra-traces of metal ions from high saline sea water prior to the analytical determination by ICP-MS.

Blank and detection limits

The detection limits and the blank values are shown in Table 4. The blank value was obtained by performing the preconcentration procedure using 1000 mL of doubly deionized distilled water as sample. The detection limits of the method were calculated based on three times the standard deviation of 11 runs of the blank solution and a concentration factor of 200. Compared to the concentration of the analytes in sea water samples (Tables 5 and 6), all metal concentrations in the real samples are higher than the detection limits after preconcentration.

Determination of trace metals in sea water

The accuracy of the method for the determination of trace metals in sea water was assessed by analyzing a certified sea water sample GBW(E) 080040. The results are shown in Table 5. The data indicated excellent agreement between the results obtained by our new method and the certified values.

Because the certified sea water sample did not provide reference values for the 10 analytes, trace metal ions in similar concentrations to the elements of interest present in sea water were added to the sea water before matrix separation and preconcentration. The recoveries of all analytes added are given in Table 6, showing sufficiently high recoveries (> 90%), high reliability and validity of this method.

Conclusion

Solid-phase extraction using a poly(acrylamino-phosphonic dithiocarbamate) chelating fiber sorbent column provides an effective preconcentration procedure for the determination of trace levels of Be, Cu, Co, Cd, In, Pb, Ga, Mn, Bi and Ag in sea water. The analytes of interest can be concentrated 200 times in a short time. Furthermore,

the salinity of the eluted metal fractions are considerably reduced. Because the procedure is a one stage process and no buffer is required, sample contamination is minimized. The combination of this preconcentration technique with sample analysis by ICP-MS provides a promising method for the determination of trace elements in sea water.

Acknowledgements The study was supported by the National Natural Science Foundation of China

References

- Houk RS (1986) *Anal Chem* 58 (1):97A–105A
- Malvankar PL, Shinde VM (1991) *Analyst* 116:1081–1084
- Namboothiri KK, Balasubramanian N, Ramakrishna TV (1991) *Talanta* 8:945–949
- Kiriyama T, Kuroda R (1988) *Fresenius Z Anal Chem* 332:338–340
- Kubova J, Nevoral V, Stresko V (1994) *J Anal At Spectrom* 9:241–243
- Lan CR, Tseng CL, Yang MH, Alfassi ZB (1991) *Analyst* 116:35–38
- Frigge C, Jackwerth E (1991) *Anal Chim Acta* 242:99–105
- Soylak M, Elci L, Dogan M (1995) *Fresenius J Anal Chem* 351:308–310
- Lee ML, Tölg G, Beinrohr E, Tschöpel P (1993) *Anal Chim Acta* 272:193–203
- Nickson RA, Hill SJ, Worsfold PJ (1995) *Anal Proc Sep* 32:387–395
- Miyazaki A, Reimer RA (1993) *J Anal At Spectrom* 8:449–452
- Haraldsson C, Lyven B, Pollak M, Skoog A (1993) *Anal Chim Acta* 284:327–335
- Bloxham MJ, Hill SJ, Worsfold PJ (1994) *J Anal At Spectrom* 9:935–938
- Beauchemin D, Berman SS (1989) *Anal Chem* 61:1857–1862
- Orians KJ, Boyle EA (1993) *Anal Chim Acta* 282:63–74
- Watanabe H, Goto K, Taguchi S, McLaren JW, Berman SS, Russell DS (1981) *Anal Chem* 53:738–739
- Shabani MB, Akagi T, Masuda A (1992) *Anal Chem* 64:737–743
- Sperling M, Yin X, Welz B (1991) *J Anal At Spectrom* 6:615–625
- Sperling M, Yin X, Welz B (1991) *J Anal At Spectrom* 6:295–300
- Liu ZS, Huang SD (1992) *Anal Chim Acta* 267:31–37
- Sperling M, Yin X, Welz B (1992) *Analyst* 117:629–635
- Elci L, Soyak M, Dogan M (1992) *Fresenius J Anal Chem* 342:175–178
- Plantz MR, Fritz JS, Smith FG, Houk RS (1989) *Anal Chem* 61:149–153
- Starry J (1964) *Solvent Extraction of Metal Chelates*, Pergamon Oxford
- Zhang BW, Fischer K, Bieniek D, Kettrup A (1994) *React Polym* 24:49–58
- Egawa H, Takahara M (1973) *Nippon Kagaku Kaishi* 9:1786–1791
- Fields EK (1952) *J Amer Chem Soc* 74:1528–1531
- Saehusa T, Kobayashi S, Hayashi K, Yamada A (1978) *Polymer J* 10:403–407
- Soylak M, Elci L (1997) *Intern J Environ Anal Chem* 66:51–59
- Shabani MB, Akagi T, Shimizu H, Masuda A (1992) *Anal Chem* 64:737–743
- Technical Note 8 (1994) Dionex Corporation, Sunnyvale, CA