Preconcentration of Trace Elements in Sea Water with 8-Hydroxyquinoline Immobilized Polyacrylonitrile Hollow Fiber Membrane for Determination by Inductively Coupled Plasma-Mass Spectrometry

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PLEASE SCROLL DOWN FOR ARTICLE

PRECONCENTRATION OF TRACE ELEMENTS IN SEA WATER WITH 8-HYDROXYQUINOLINE IMMOBILIZED POLYACRYLONITRILE HOLLOW FIBER MEMBRANE FOR DETERMINATION BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

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8-Hydroxyquinoline immobilized on polyacrylonitrile hollow fiber membrane was synthesized and used for the preconcentration of cadmium, lead, copper, mangenese, bismuth, indium, cobalt, beryllium and silver in sea water prior to their determination by inductively coupled plasma-mass spectrometry. The optimum experimental conditions such as pH, sample flow rate and volume of eluents were investigated. The concentration factor of at least 300 for analytes of interest in sea water and separation of matrix components can be achieved. The recommended method has been applied for the determination of trace elements in coastal sea water. The results indicated that the recovery ranged from 91% to 107%, and the relative standard deviations were found to be less than 5% for trace elements at ng/L level.

INTRODUCTION

Because of its excellent sensitivity, precision and accuracy, inductively coupled plasma-mass spectrometry (ICP-MS) has occupied an invaluable position in the modern analytical laboratory. It is especially suitable for trace muti-element determination and applicable to a wide range of samples. Unfortunately, its application to the analysis of sea water remains quite limited mainly due to the

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high salinity of the matrix which prevents its direct analysis by ICP-MS owing to the obvious problems of salt deposition on the torch, sampling interface, or ion lenses. Another restriction comes from the extremely low levels of some elements, which are below the detection limits of the instrument. Therefore, the development of a preconcentration technique is an important consideration in the sea water analysis.

The requirement for a preconcentration technique in ICP-MS is far more critical than for a single element determination technique. As ICP-MS is a muti-element determination technique, the preconcentration method should concentrate trace elements as many as possible. A lot of preconcentration techniques have been proposed for the determination of metals in various environmental samples. Compared with the more traditional liquid-liquid extraction methods, solid phase techniques have become increasingly popular. It is recognised that 8-hydroxyquinoline is a well-characterized chelation organic ligand which can form covalent compounds with over 60 metal ions under controlled pH conditions, and its preference for transition- and heavy − metal cations to alkali and alkaline-earth cations is well known.[1] Many research works have been done recently to find the most efficient way to immobilize 8-hydroxyquinoline on a number of different substrates, including glass beads,[2, 3] silica[4, 5] and vinyl polymers.[6] Trace elements determination methods have also involved precomplexation of analytes with ligands and then concentration on Amberlite[7].

Among these supports silica gel is the most often used material.[8, 9] It offers good mechanical strength, resistance to swelling and rapid overall exchange kinetics in column applications.[10] However, silica gel is unstable at high pH, leading to cleavage of the immobilized 8-hydroxyquinoline and potential trace metal contamination from the newly exposed silica surface.[11, 12]

The preparation and properties of condensation resins of the resorcinol-formaldehyde-8-hydroxyquinoline type have also been investigated.[13, 14] Although these resins offer higher exchange capacities, low stability in acid solution and slower overall kinetic exchange rates are their obvious drawbacks.

The immobilization of 8-hydroxyquinoline onto polystyrene-divinylbenzene resins are apparently quite stable with respect to extremes of pH and can be produced with high total exchange capacity. But their overall kinetic exchange rate is also reported to be slow.[13, 14]

In our previous work, 8-hydroxyquinoline immobilized on polyacrylonitrile (PAN) hollow fiber membrane was synthesized and applied to preconcentration of rare earth elements (REEs) from sea water sucessfully [15]. The exchange capacity for each REEs and chemical stability of the modified PAN hollow fiber membrane were also assessed. The aim of the present study is to evaluate the exchange capacity and kinetic exchange rate of this 8-hydroxyquinoline immobi-

lized on polyacrylonitril (PAN) hollow fiber membrane for preconcentration and determination of trace elements in sea water by inductively coupled plasma-mass spectrometry.

EXPERIMENTAL

Instrument

A Plasma-Quad 3 (VG Elemental, Winsford, UK) inductively coupled plasma mass spectrometer was used for the determination of analytes. The optimum instrumental parameters are given in Table I. Calcium, magnesium, sodium, potassium were determined by ICP-AES (Jarrel-Ash, Model 1155 AtomComp, USA). The operating conditions for the determinations were optimized. The corrections for background shift and spectral interferences were performed. The pH values of the solutions were measured with a Model pHS-3 C pH-meter (Shanghai Instrument Company).

TABLE I ICP-MS operating conditions

ICP system	
Forward Power	1350 W
Reflected Power	<5 W
Coolant argon flow rate	14 L/min
Auxiliary argon flow rate	0.9 L/min
Nebulizer argon 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
3rd stage pressure	1.7×10^{-1} mPa
Data acquisition	Range-scanning mode
Mass range	M/z 9–210
Total acquisition time	60 s

Reagents

Stock solutions of each element, 1000 µg/mL, were prepared by dissolving appropriate amount of metal oxide (specpure, Johnson Matthey Chemicals Limited) in 5 mL of nitric acid (67%). If complete dissolution was not achieved, 1 mL HCl (37%) was added and moderate heating was applied. Single- and multi-elements standard solutions with concentrations 10, 50 and 100 ng/mL were prepared from the concentrated stock solution before use by dilution with dilute HNO_3. The final acid concentration of all standard solutions was fixed at 0.1 mol/L HNO_3. Rhodium was added to monitor matrix effects and instrumental drift.

All other reagents were of analytical grade or better. High purity water (18M $\Omega \cdot$ 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, China).

Polyacrylonitrile hollow fiber membrane was obtained from Zhong Ke Membrane Research & Development Center of Beijing, China, and rinsed with nitric acid (1+1), hydrochloric acid (1+1) and double distilled deionized water sequentially before use.

Certified sea water reference materials, 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, tap water, then soaked in nitric acid (1+1) for 48 hours and cleaned with double deionized distilled water before use.

Immobilization procedure

The details of the immobilization procedure have been described elsewhere [15].

Fiber capacity

The chelating capacity of this 8-hydroxyquinoline immobilized PAN hollow fiber membrane was determined for each metal ion by batch technique. Membrane (~100 mg) was equilibrated with each metal ion by shaking for 24 h at pH 5 in an excess of metal ion solution (10 mL, 50 µg/mL). The membrane was then

separated from the solution by filtration and the concentration of the metal ion remaining in the solution determined by ICP-MS.

Kinetic experiments

A batch-type reactor and sequential sampling procedures were used to conduct the kinetics experiments. Kinetics runs were performed using a 400 mL, 3-neck glass flask in a circulating water bath at 25±0.01°C for the specified time period. The metal solutions (containing 100 mL, 10 μg/mL of one metal ion species) were adjusted to pH 5 by addition of dilute NaOH and HNO_3. Subsequently, the metal solutions were mixed with the membrane (~100 mg) and the mixture was stirred immediately. Sampling times varied from 0 to 1440 min. At selected time periods, a 0.5 mL of sample was taken from the reactor and immediately filtered through 0.45 μm membrane filter. The metal concentration in the filtrate was analyzed by ICP-MS.

Sampling of sea water

The polyethylene bottles (10 L) used for sampling sea water were precleaned with detergent, doubly deionized distilled water, dilute HNO_3 and doubly deionized distilled water successively, and 10 mL of high-purity HNO_3 (67%) was added to keep the final acidity of sea water at about pH 2 after sampling. Sea water samples were taken at depth of 1 m of 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 pore size of 0.45 μm and stored at temperature of 4°C

Package of 8-hydroxyquinoline immobilized PAN hollow fiber membrane column

Eight matches of 8-hydroxyquline modified PAN hollow fiber membrane (length 60 mm, i.d. 0.5 mm, weight about 0.3g) were inserted into a "T" glass column (length 60mm, i.d. 6mm). The column was drained and rinsed several times with HNO_3 (1+1) and double deionized distilled water sequentially prior to use. At each end of the glass column, 8-hydroxyquinoline immobilized PAN hollow fiber membrane was fixed with epoxy resin. One end of the glass column was sealed with Teflon stopcock. The column assembly was previously described [15].

Prior to use, the entire assembly was carefully rinsed first with sufficient distilled water, then with 100 mL 1 mol/L HCl – 0.1 mol/L HNO_3, finally with double deionized distilled water again until the pH of the eluate was neutral.

Preconcentration of trace metal ions from sea water

A 1500 mL seawater sample was adjusted to the desired pH 5 using high purity ammonium hydroxide and nitric acid, then introduced into the immobilized PAN hollow fiber membrane using a peristaltic pump at the flow rate of 10 mL/min. After washing with 50 mL doubly deionized destilled water, the trace element retained in the column was eluted with 5 mL of 1 mol/L HCl – 0.1 mol/L HNO_3 at a flow rate of 1 mL/min.

RESULTS AND DISCUSSION

Characterization and properities of 8-hydroxyquilline modified PAN hollow fiber membrane

The capacity of modified PAN hollow fiber membrane

The binding capacity is an important factor to determine how much fiber is required to quantitatively concentrate the analytes of interest from sea water. Following the procedure described in the experimental section the capacity of Be, Co, Mn, Cu, Ag, Cd, In, Pb and Bi were found to be 99.8, 28.95, 76.07, 71.55, 15.31, 50.56, 36.35, 52.5 and 16.99 μmol/g, respectively, under the optimum pH 5, which will be discussed later. Compared with the chelating capacity reported for silica-immobilized 8-hydroxyquinoline, this value is lower than Marshall's yield [16] of 185 μ mol/g Cu(II), but it is equivalent to Sturgeon's yield[17] of 61 μ mol/g Cu(II) and greater than Daihi's products[4] of 10.4 μ mol/g Cu(II). In light of the extremely minute amount of trace elements in sea water, the exchange capacity of the modified PAN hollow fiber membrane is sufficient for the preconcentration of trace elements from sea water.

Kinetics of metal uptake

The kinetics of the ion extraction of the modified PAN hollow fiber membrane are remarkably important for an assessment of the suitability of this material to serve as a packed bed ion exchanger. In this test a batch technique was used. All ions were extracted at the maximum adsorbed amounts of the modified PNA hollow fiber membrane within 60 min (Figure 1). The times for half the maximal

absorption ($t_{1/2}$) of all metal ions was less than 10 min. This indicated a fast exchange reaction for the metal extraction process.
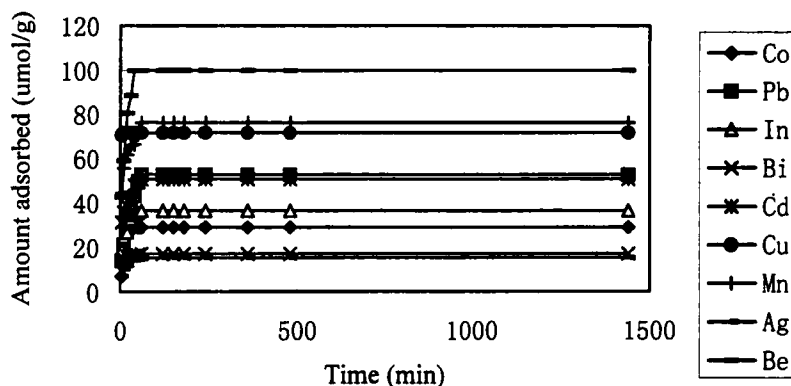
FIGURE 1 Single ion sorption kinetics for each metal reacted with modified PAN hollow fiber membrane

Optimum conditions for the preconcentration of trace elements in sea water

To obtain quantitative recoveries of metal ions on the 8-hydroxyquinoline immobilized PAN hollow fiber membrane, the experimental parameters were optimized including pH, sample volume, flow rate and matrix effect. The concentration of each metal in the model solution for this purpose was ranged from 5 to 10 µg/L.

Effect of pH on the preconcentration efficiency

The effect of pH on the preconcentration efficiency was studied from 2 to 9. The results are shown in Figure 2. Quantitative recoveries (>95%) were found for the trace metals at pH 4–9 except Ag (I). However, at the pH 3–6, Ag (I) was also quantitatively concentrated. Hence, pH 5 was chosen as the optimum acidity conditions for simultaneous multielement preconcentration.

Effect of eluent volume

An eluent of 1 mol/L HCl – 0.1 mol/L HNO$_3$ was used by many researchers to elute analytes chelated with 8-hydroxyquinoline immobilized silica gel.[4, 16] In this study, various volumes of 1 mol/L HCl – 0.1 mol/L HNO$_3$were used to elute the adsorbed metal ions after the analytes were concentrated from 1500 mL of sample solution at the level of of 5 µ g/L (Figure 3). As can be seen, when the volume of eluent is less than 4 mL, no quantitative recoveries (>95%) could be
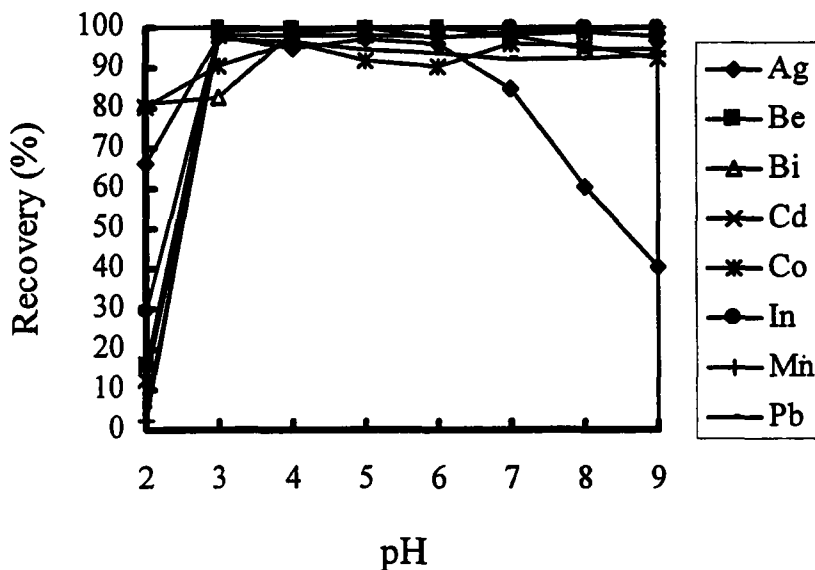
FIGURE 2 Effect of sample pH on concentration efficiency of trace metal ions (sample volume: 100 mL, each trace metal concentration: 10 μg/L, eluent volume: 5 mL)

obtained. However, quantitative recoveries were achieved over the eluent volume from 5 to 10 mL. In order to achieve a higher concentration factor, 5 mL of eluent was used in the remainder of the study.

Effect of flow rate and volume of sample

Due to the large volume of sample needed, it was desirable to pump it at maximum flow rate without sacrificing the recoveries. The effect of different flow rates of sample solution through the 8-hydroxyquinoline immobilized PAN hollow fiber membrane on the concentration efficiency was tested at the flow rate from 1 to 10 mL/min at the pH 5 (Figure 4). It can be seen that the recoveries of all elements of interest were quantitative at the flow rate from 1 to 10 mL/min and the flow rate of 10 mL/min was used in the following study.

In order to explore the possibility of enriching low concentration of analytes with a high preconcentration factor, the effect of sample volume on the concentration efficiency was also studied and the results are given in Figure 5. Quantitative recoveries (>95%) were obtained when the sample volume was less than 1500 mL. When this volume was exceeded the recoveries for all analytes decreased. The same phenomena were also found in the literature [18, 19]. The
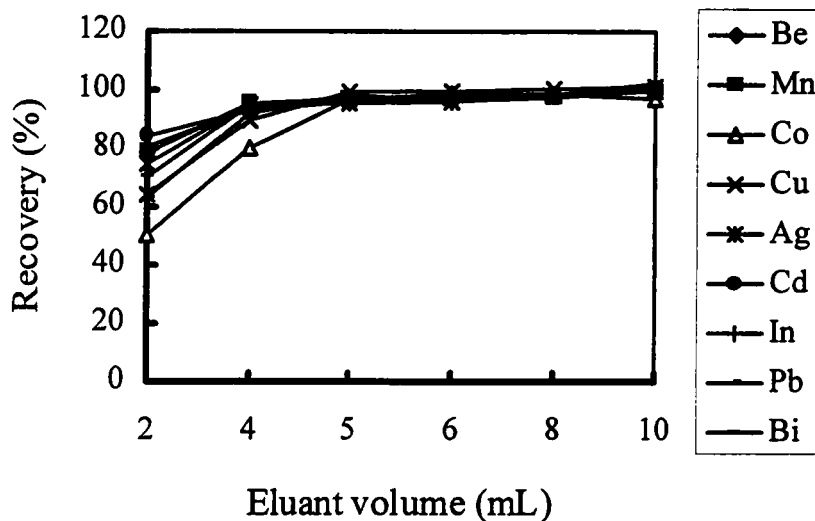
FIGURE 3 Elution efficiency of trace metal ions as a function of the eluent volumes (sample volume: 1.5 L, each trace metal concentration: 5 µg/L, eluent: 1 mol/L HCl – 0.1 mol/L HNO$_3$)
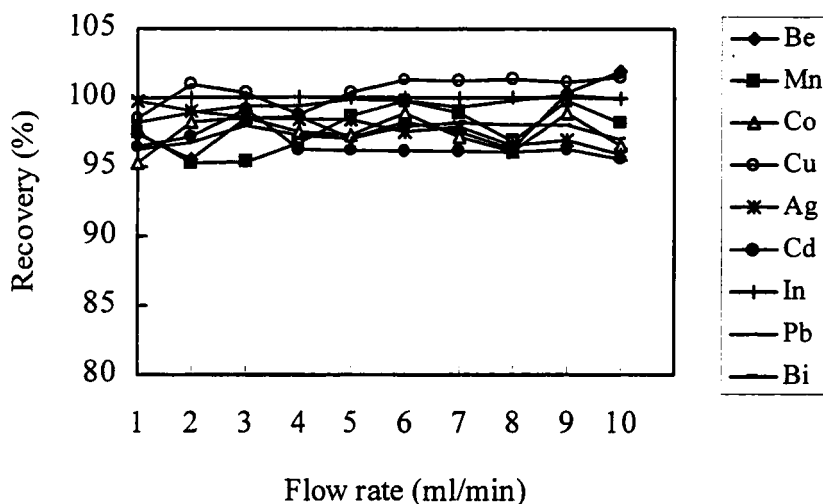

FIGURE 4 Effect of the sample flow rate on the concentration efficiency of trace metal ions (sample volume: 1500 mL, concentration of each trace metal: 10 µg/L, eluent volume: 5 mL, n = 5)

reason why the recoveries decreased with increasing sample volume may be that some ions present in the sample can act as eluents if their affinity for the fiber is sufficiently large. Therefore, when the sample volume increases, early break-through is possible [20]. In this experiment, 1.5 L of sample solution was adopted for the preconcentration of analytes in sea water, and the adsorbed analytes can be eluted with 5 mL of 1mol/L HCl – 0.1mol/L HNO$_3$, so the preconcentration factor was found to be 300.
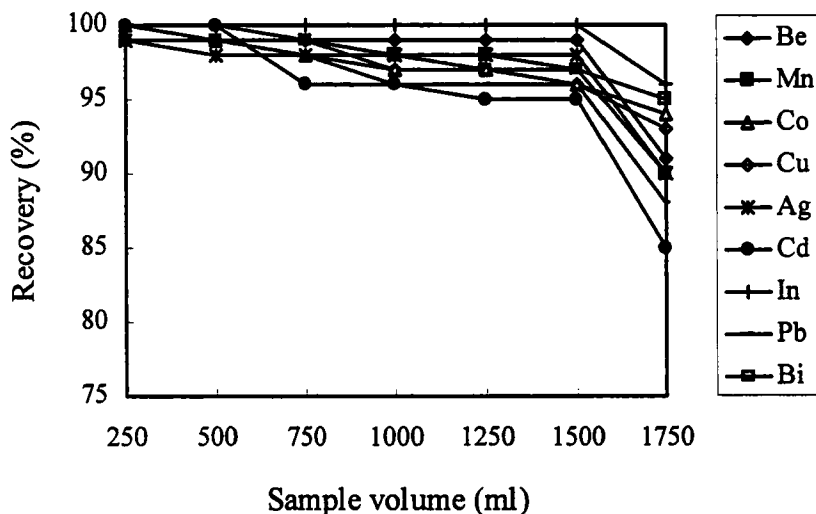
FIGURE 5 Effect of the sample volume on the concentration efficiency of trace metal ions (concentration of each trace metal: 5 μg/L, eluent volume: 5 mL, n = 5)

Effect of matrix ions

The influence of major matrix ions in sea water such as sodium, potassium, calcium and magnesium, were investigated in order to elucidate the possibilities of determination of analytes in sea water following the proposed preconcentration procedure. Fang and his co-workers [21] detailed the different types of resins in the preconcentration of trace elements in sea water prior to the determination by flow injection atomic absorption spectrometry (FIAAS), and pointed out that owing to smaller exchange capacity of 8-hydroxyquinoline immobilized silica gel and the comparatively high stability of the magnesium complexes, the recoveries of most of the heavy metals from sea water were not acceptable with 8-hydroxyquinoline immobilized silica gel. Nevertheless, Malamas and co-workers [22] successfully used 8-hydroxyquinoline immobilized silica gel for

on-line preconcentration in FIAAS. Because the high salt content of sea water prevents the direct determination of trace elements by ICP-MS, effective separation of matrix components is another requisite in addition to the preconcentration of analytes of interest. Therefore, an experimental work was conducted to verify if the 8-hydroxyquinoline immobilized PAN hollow fiber membrane could separate the matrix components of sea water without sacrifice of concentration efficiency of trace elements.

Synthetic solutions (1500 mL) in which the concentration of each analyte was fixed at 5 µg/L and the matrix concentration for Na, K, Mg and Ca chlorides was set at 20000, 500, 2500 and 500 mg/L, respectively, were passed through the column. The analytes retained on the column were eluted with 1 mol/L HCl – 0.1 mol/L HNO_3. The concentration of the analytes and matrix components in the eluent were determined. The results are shown in Table II. It is verified that the salt contents in the eluents are significantly lower and suitable for ICP-MS determination, and the recoveries of analytes are satisfactory. Therefore, no more separation procedure is needed. This indicates that the 8-hydroxyquinoline immobilized PAN hollow fiber membrane can be used to concentrate ultratrace metals from high saline sea water for the determination by ICP-MS.

TABLE II Influence of matrix ions on the concentration efficiency of trace metal ions (Sample volume: 1500 mL, each trace metal concentration: 5 µg/L, eluent volume: 5 mL, n = 3)

		Na^+	K^+	Mg^{2+}	Ca^{2+}
	Matrix ion added as	*NaCl*	*KCl*	*MgCl$_2$*	*CaCl$_2$*
	Concentration of matrix ions in the sample (mg/L))	20000	500	2500	500
	Concentration of matrix ions in the eluent (mg/L)	2.6	0.85	4.86	2.8
	Be	99.4	100	100	98.3
	Mn	100	102	98.8	99.6
	Co	99.8	99.6	98.6	96.4
	Ag	100	100	99.8	97.1
Recovery%	Cd	100.8	98.8	98.6	100.2
	In	100.5	99.5	98.8	99.4
	Pb	97.8	99.6	100.2	99.6
	Bi	97.7	96.4	99.5	99.3
	Cu	96.4	97.7	96.8	97.3

Blank and detection limits

The detection limits and the blank values are shown in Table III. The blank values were obtained by performing the preconcentration procedure using 1500 mL of doubly deionized distilled water as a sample and 5 mL 1 mol/L HCl – 0.1 mol/L HNO_3 as an eluent. The detection limits of the method were calculated based on three times the standard deviation of 11 runs of the blank solution. In the real sample analysis the reagent blanks come only from small amounts of ultrapure HNO_3 and 5mL of 1 mol/L HCl – 0.1 mol/L HNO_3. Because, HCl and HNO_3 were of ultrapure grade and the blank level of impurity was very low, quite satisfactory detection limits were obtained. Compared with the concentration of analytes present in sea water samples (Tables IV and V), the concentrations of all analytes in the eluent are much greater after preconcentration than the detection limits.

TABLE III Blanks and detection limits

Element	Blank (ng/ L)	Detection limit (ng/L)
Be	18.2	50.2
Mn	23.8	120.0
Co	3.4	0.4
Cu	5.6	7.8
Ag	9.2	5.6
Cd	4.0	6.1
In	9.2	2.6
Pb	45	11.6
Bi	17.8	31.0

TABLE IV Determination of Trace Metals in Certified Sea Water GBW(E) 080040, N=6

Elements	determined value (ng/mL)	certified value (ng/mL)
Pb	9.7 ± 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	0.0022 ± 0.0005	
Mn	0.035 ± 0.003	
Co	0.16 ± 0.01	
Ag	0.023 ± 0.002	
In	0.0025 ± 0.0004	
Bi	0.0037 ± 0.0005	

TABLE V Determination of trace elements in seawater (ng/L) sample and spiked recovery (%) (sample volume: 1.5 L, eluent volume: 5 mL).*

Elements	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	Found	Added	Total found	Recovery
Be	1.58	1.60	3.10	95	3.44	3.40	6.75	94	3.02	3.00	5.84	94	3.65	3.60	7.01	93
Mn	7.60	7.50	15.0	100	15.1	15.0	29.6	97	47.6	45.0	96	108	68.3	70.0	138.6	100
Co	27.0	27.0	56.0	107	79.7	80.0	164.3	106	80.0	80.0	157	96	53.2	53.0	1083	104
Cu	2760	2760	5430	97	1150	1150	2310	101	276	275	550	100	124	125	257	106
Ag	32.8	32.0	63.8	99	18.9	19.0	39.5	108	58.3	60.0	115	94	19.3	20.0	38.8	98
Cd	129.5	129.0	250.8	94	45.2	45.0	87.4	94	33.5	34.0	68.4	103	70.0	70.0	145	107
In	1.09	1.10	2.09	91	1.01	1.00	2.02	108	1.25	1.20	2.40	96	0.99	1.00	1.89	90
Pb	58.5	60.0	116	96	54.5	55.0	110.9	103	807	800	1600	99	76.5	76.0	153	101
Bi	8.85	8.80	17.8	102	7.88	8.00	15.3	93	3.01	3.00	5.89	96	11.9	12.0	22.8	91

* Seven measurements for each sample, the RSD % less than 5%

Determination of trace metals in sea water

To assess the accuracy of the method for the determination of trace metals in sea water, a certified sea water sample GBW(E) 080040 was used. The results are shown in Table IV. The data indicated that a good agreement was achieved between the results obtained by the method and the certified values.

Because no certified and/or reference values are available for all the 9 elements in sea water GBW(E) 080040, trace metal ions equal to the same level of the elements present in sea water were spiked into the sea water before matrix separation and preconcentration. The recoveries of spikes are given in Table V, showing sufficiently high recoveries (>90%), high reliability and validity of the method. A comparison was also made (Table VI) between the data obtained by this method and those by another method [23], and a reasonable good agreement was also achieved.

TABLE VI Comparison of trace element concentration in seawater obtained by the present method with the reported values

Element	Trace elements in sea water (ng/L)								
	Present method				Other method				
	Tianjin	Dalian	Qingdao	Qinghuan-gdao	Tianjin	Dalian	Qingdao	Qinghuan-gdao	Ref.
Be	1.58	3.44	3.02	3.65	1.60	3.44	3.12	3.65	23
Mn	7.60	15.1	47.6	68.3	7.63	14.3	49.6	69.3	23
Co	27.0	79.7	80.0	53.2	27.1	77.7	81.0	52.2	23
Cu	2760	1150	276	124	2758	1152	276	132	23
Ag	32.8	18.9	58.3	19.3	32.4	18.9	54.3	20.3	23
Cd	129.5	45.2	33.5	70.0	127.5	47.2	34.5	70.0	23
In	1.09	1.01	1.25	0.990	1.04	1.11	1.15	0.971	23
Pb	58.5	54.5	807	76.5	59.2	56.5	811	77.3	23
Bi	8.85	7.88	3.01	11.9	8.70	8.10	3.09	11.4	23

CONCLUSION

In this study, a new successful technique was developed based on the 8-hydroxy-quinoline immobilized PAN hollow fiber membrane for preconcentration of trace elements in sea water prior to the determination by ICP-MS. All analytes can be

easily concentrated 300 times with almost all matrix elements separated. This method has the following advantages over the previously reported ones: (1) Compared with the preparation time reported in the literature for 8-hydroxy-quinoline immobilized on other substrates, the present one is relatively short; (2) Only a single-stage process is required for preconcentration of trace elements and separation of matrix components from sea water. As the salinity in the eluent is considerably reduced, the final eluent can be directly run by ICP-MS; (3) All elements can be preconcentrated at the wide pH-range, therefore no buffer is required for controlling the pH, which minimizes the contamination. In this paper, only 9 trace elements were preconcentrated. However, in our previous work, the modified PAN hollow fiber membrane was used to preconcentrate REEs in sea water successfully. We expect that even more trace elements can be preconcentrated. This is particularly valuable for simultaneous multielement determination in the environmental research.

Acknowledgements

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