Analytical note

Ultrasensitive determination of cadmium in seawater by hollow fiber supported liquid membrane extraction coupled with graphite furnace atomic absorption spectrometry

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Received 19 December 2006; accepted 11 April 2007

Available online 22 April 2007

Abstract

A new procedure, based on hollow fiber supported liquid membrane preconcentration coupled with graphite furnace atomic absorption spectrometry (GFAAS) detection, was developed for the determination of trace Cd in seawater samples. With 1-octanol that contained a mixture of dithizone (carrier) and oleic acid immobilized in the pores of the polypropylene hollow fiber as a liquid membrane, Cd was selectively extracted from water samples into 0.05 M HNO₃ that filled the lumen of the hollow fiber as a stripping solution. The main extraction related parameters were optimized, and the effects of salinity and some coexisting interferants were also evaluated. Under the optimum extraction conditions, an enrichment factor of 387 was obtained for a 100-mL sample solution. In combination with graphite furnace atomic absorption spectrometry, a very low detection limit (0.8 ng L⁻¹) and a relative standard deviation (2.5% at 50 ng L⁻¹ level) were achieved. Five seawater samples were analyzed by the proposed method without dilution, with detected Cd concentration in the range of 56.4–264.8 ng L⁻¹ and the relative spiked recoveries over 89%. For comparison, these samples were also analyzed by the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method after a 10-fold dilution for matrix effect elimination. Statistical analysis with a one-way ANOVA shows no significant differences (at 0.05 level) between the results obtained by the proposed and ICP-MS methods. Additionally, analysis of certified reference materials (GBW (E) 080040) shows good agreement with the certified value. These results indicate that this present method is very sensitive and reliable, and can effectively eliminate complex matrix interferences in seawater samples.

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Keywords: Cadmium; Seawater; Hollow fiber; Supported liquid membrane extraction; Graphite furnace atomic absorption spectrometry**1. Introduction**

The determination of trace or ultratrace Cd in seawater is of great interest since it is a way to assess the early impact of human activities on the marine environment [1]. High concentration of salt (approximately 3%) and very low content of cadmium in seawater are the two major problems that preclude the development of a simple approach for this determination. Nowadays, a few sensitive analytical tools such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are available for the determination of trace heavy metals. However, the very high cost of the ICP-MS instrument and its operating expenses are a

heavy burden for a common laboratory. Furthermore, it is very difficult to achieve satisfactory results for seawater analysis due to the serious interferences related to its high salinity. Because of its high sensitivity, low cost and easy operation, graphite furnace atomic absorption spectrometry (GFAAS) has been frequently used for the determination of trace Cd in seawater [1–3]. To eliminate the matrix effects, several separation and preconcentration procedures have been proposed, based on solution-phase chelation followed by adsorption onto reversed-phase C₁₈ substrates [4–6], or retention on chelating resins or activated carbon [7–9], coprecipitation [10], cloud point extraction [11,12] and flow injection on-line preconcentration techniques [13,14].

As an alternative, supported liquid membrane (SLM) extraction was successfully applied to enrich trace metals [15]. In the SLM extraction of metals, a key issue is how to select the

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appropriate solvent for extraction as well as the carrier for transporting the metal ions from the sample solution to the stripping solution. Dihexyl ether, isooctane, *n*-undecane, toluene, kerosene, and 1-octanol were used as the membrane liquid. Macrocyclic crown ethers like 1,10-didecyl-1,10-diaza-18-crown-6, organophosphorus extractants like di-2-ethylhexyl phosphoric acid (DEHPA) and tri-*n*-butyl phosphate (TBP), thiourea and dithizone were commonly used as the carrier to form complexes with the metal ions.

There are many SLM extraction devices, but the hollow fiber supported liquid membrane (HFSLM) extraction system is one of the most efficient devices that have been developed. HFSLM is usually composed of three distinct compartments: an internal stripping solution (filled in the hollow fiber lumen), a hydrophobic liquid membrane (immobilized in the hollow fiber pores), and an external sample solution (containing the analytes). HFSLM has some specific advantages: the hollow fiber itself can effectively exclude high molecular weight species and particles present in the sample solution; the extraction system can be easily set up; and the hollow fiber is disposable and therefore eliminates the carry-over between determinations.

In this study, 1-octanol that dissolved the mixture of oleic acid and dithizone was immobilized in the pores of the polypropylene hollow fiber to form a liquid membrane for the extraction of Cd. Dithizone was used as a carrier, while oleic acid was adopted to prevent the loss of the liquid membrane. This proposed HFSLM procedure can eliminate the interferences from seawater samples, as well as the complex matrix effects in graphite furnace atomic absorption spectrometry analysis.

2. Experimental

2.1. Apparatus

GFAAS measurements were carried out using a Hitachi Z-5700 graphite furnace atomic absorption spectrometer with Zeeman-effect background correction (Hitachi High-Technologies Corporation, Japan). A cadmium hollow cathode lamp (Beijing ShuGuangMing Electronic Lighting Instrument Co., Ltd., Beijing, China) was used as radiation source at 228.8 nm. The optimum operating parameters for the spectrometer are shown in Table 1. A 10- μ L aliquot of sample was manually injected into the furnace, and absorbance signals in the form of peak height were measured.

2.2. Reagents and materials

The stock standard solution of Cd (II) (1000 μ g mL⁻¹) was purchased from the National Research Center for Reference Material (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution with 2% nitric acid (v/v). Dithizone ($\geq 98\%$) and 1-octanol ($\geq 99\%$) were obtained from Alfa Johnson Matthey Company (Alfa Aesar, USA). Oleic acid ($\geq 97\%$) and 1,10-dicyclohexano-18-crown-6 ($\geq 98\%$) were purchased from Acros Organics (Acros, Belgium). The nitric acid used in the experiments (suprapure grade) was obtained from Beijing Chemicals Corporation (Beijing, China). Other standard solutions of

Table 1

Instrumental operating conditions (GFAAS)

Analyte	Wavelength (nm)	Injection mode	Sample volume (μ L)	Modifier	Spectral band width (nm)	Lamp current (mA)
Cd	228.8	Manual	10	–	0.4	5.0

Temperature program

Stage	Temperature ($^{\circ}$ C)		Time (s)	
	Start	End	Ramp	Hold
Drying	80	140	40	0
Pyrolysis	350	350	20	0
Atomization	1700	1700	0	5
Cleaning	1800	1800	0	4

metal ions like Pb (II), Mo (II), Sn (II), Ca (II), Fe (III), Mg (II), Zn (II), Ba (II) used in the interference experiments were purchased from the National Research Center for Reference Material. Sodium chloride (NaCl) (spectroscopically pure) was purchased from Beijing Chemicals Corporation. The anions (sulfate and chloride) were prepared by dissolving spectroscopically pure potassium sulfate (K₂SO₄) and potassium chloride (KCl) (Beijing Chemicals Corporation, Beijing) in ultrapure water (Easypure LF). The certified reference materials, GBW (E) 080040 (seawater), were from the Second Oceanography Institute of China (Hangzhou, China).

The pH of the sample solutions was adjusted with 0.04 mol L⁻¹ lithium hydroxide or 1% (v/v) nitric acid. A pH 211 pH meter (Hanna Instruments, Italy) was used for the pH determination. All the other chemicals were at least of analytical grade and ultrapure water produced by an Easypure LF (Barnstead International, Dubuque, IA, USA) equipment was used throughout. The vessels used for trace analysis were kept in 30% (v/v) nitric acid for at least 48 h and subsequently washed four times with ultrapure water. To avoid blank contributions from the reagents, tests by AAS were performed prior to use.

The Q 3/2 Accurel polypropylene hollow fiber membrane (600 μ m i.d., 200 μ m wall thickness, 0.2 μ m pore size) was purchased from Membrana, Wuppertal, Germany. A 25- μ L microsyringe (Agilent, USA) with a needle of 0.5-mm outer diameter was used to flush the inner wall of the hollow fiber and introduce the stripping solutions into the lumen of the hollow fiber for extraction. Seawater samples were collected from Yantai, the Bohai Sea of China. The samples were all stored at the temperature of 4 $^{\circ}$ C.

2.3. Extraction procedure

Extraction was performed as follows: the porous hollow fiber that was cut carefully into 4.5-cm length pieces was immersed in 1-octanol solution containing dithizone or mixture of dithizone and oleic acid, for a prescribed time. The hollow fiber was taken out and washed outside and inside five times with water. The needle of the microsyringe holding ~ 20 μ L of the stripping solution was connected to the fiber and the plunger of the microsyringe was depressed to flush out its content to wash and fill the lumen of the hollow fiber. Care was taken to

avoid any air bubbles. After that, the two ends of the fiber were sealed with heated tweezers. By this preparation, the obtained HFSLM device had an effective fiber length of ~ 4.0 cm with acceptor phase volume of ~ 10 μL . The extraction was carried out by placing the hollow fiber in 100 mL of aqueous solution in a 150-mL beaker. After stirring for a prescribed time, the hollow fiber was taken out from the solution and one of the sealed ends was cut to allow its connection with the microsyringe needle; the other sealed end was then cut to permit the flushing of the stripping solution to a 200- μL glass vial. This solution in the glass vial was directly injected into the AAS or after an appropriate dilution. The used fiber was discarded and a fresh one was used for the next extraction.

2.4. Enrichment factor

For investigating the relevant parameters affecting the extraction, the enrichment factor (E_e) defined as: $E_e = C_A/C_S$ was selected as response, in which C_A and C_S are the concentrations of analytes in the acceptor (stripping solution) and extracted sample solutions, respectively.

3. Results and discussion

3.1. Selection of the carrier and its concentration

Macrocyclic crown ethers have been extensively applied as chelating agent in the determination of many metallic elements in the past decades. But preliminary experiments showed that 1,10-dicyclohexano-18-crown-6 did not extract Cd^{2+} from the sample solution efficiently. Therefore, dithizone that can selectively complex many transition metal ions [16] was adopted as the carrier in the present study.

In general, the transport of metal ions through SLM is based on one of the three possible mechanisms: proton-drive, anion-drive, and metal ion counter gradient-drive [17]. According Ref. [18], the most probable transport mechanism for Cd^{2+} through HFSLM is proton-drive. In the sample/membrane interface, the proton of dithizone was exchanged by Cd^{2+} to form a Cd–dithizone complex in the liquid membrane and released H^+ into the sample, then the Cd–dithizone complex diffused to the membrane/stripping solution interface where dithizone was protonated and Cd^{2+} was released into the stripping solution.

Concerning the effect of the carrier concentration, E_e increased with the concentration of dithizone up to 0.8 mg L^{-1} , and remained constant up to 1.2 mg L^{-1} . A further increase was observed at 1.6 mg L^{-1} , followed by a decrease back to the previous value at 2.0 mg L^{-1} . Thus, 1.6 mg L^{-1} dithizone in 1-octanol was selected for the following experiments.

3.2. Optimization of extraction conditions

3.2.1. Effect of sample solution acidity

The pH influence was studied by adding 0.05 mol L^{-1} nitric acid or 0.04 mol L^{-1} lithium hydroxide into the sample solution, and maximum E_e values were observed between pH 5.2 and 6.4. When sample solution pH was 8.2, 9% of E_e decrease was

observed. With the further increase of pH, E_e decreased from 322 (pH 8.2) to 233 (pH 8.9). The possible reason is that dithizone is much more easily dissolved in basic solution [19]. Taking this into account, pH 5.2 was selected as the optimum sample solution acidity for the following investigations.

3.2.2. Effect of the stripping solution concentration

For stripping of the metal ions from supported liquid membrane phase, strong acidic solutions are used. Therefore, nitric acid solutions with concentrations ranging from 0.01 mol L^{-1} to 1.0 mol L^{-1} were investigated as stripping solution. E_e increased with HNO_3 concentration up to 0.05 mol L^{-1} and decreased with the further increase of the HNO_3 concentration. Thus, 0.05 mol L^{-1} nitric acid was used as the stripping solution. Further studies showed that E_e decreased with the addition of lithium nitrate (0.05 to 1.0 mol L^{-1}) to the stripping solution (0.05 mol L^{-1} HNO_3). This probably is due to the decreased H^+ activity and thus the proton driving force was weakened with the addition of lithium nitrate.

3.2.3. Effect of stirring rate

Usually, a higher stirring rate can accelerate the diffusion of the analytes and reduce the time necessary to reach the dynamic equilibrium in HFSLM. In this experiment, the stirring rate was divided into three different classes: low, medium and high. The results showed that the medium stirring rate was appropriate to obtain the highest extraction efficiency. A too high stirring rate caused many bubbles to attach on the surface of the hollow fiber, and impeded the transfer of the analyte. Therefore, a medium stirring rate was chosen in the following studies.

3.2.4. Effect of extraction period

Experimental results indicate that, with no oleic acid addition, E_e reached its maximum at an extraction time of 30 min and then decreased rapidly. This may be attributed to the loss of the dithizone in HFSLM when it was exposed to the aqueous solution for a long time. Based on the optimum result of Ref. [20], 2.08 g L^{-1} of oleic acid was added into the membrane phase to prevent the loss of dithizone from the membrane phase to the aqueous phase. The results demonstrate that the maximum E_e is reached with the extraction period in the range of 25–35 min. Consequently, 30 min was selected as the optimum extraction period and 2.08 g L^{-1} oleic acid was added into the membrane liquid.

3.3. Interference evaluation

When HFSLM is used for the treatment of real samples, potentially interfering ions might be present. According to the composition of common seawater [21], a series of metal ions (Table 2) (the corresponding anions are nitrate or chloride) were selected for evaluation of the robustness of the proposed method in relation to this kind of interference. Fluoride, chloride, bromide, iodide, sulfate and phosphate (the corresponding cation is potassium) were also investigated as interfering species. The ratios of interferant to analyte are at least equal to or larger than those in common seawater. The results shown

in Table 2 indicate that the recoveries are 91–108% in the presence of all studied ions.

In addition, it is well known that the high concentration of salt in seawater may seriously affect the AAS determination of Cd. Therefore, varied amounts of sodium chloride that covered the normal concentration of salt in seawater were added into the aqueous solutions to evaluate the interference of salt. When the sample solutions spiked with $0.5 \mu\text{g L}^{-1}$ Cd were added with 3% and 4% (w/v) sodium chloride, relative spiked recoveries of 91.7% and 90.4% respectively could be achieved. Therefore, the influence of salinity in seawater is not significant for the extraction.

3.4. Analytical performance and validation

Some characteristics of the proposed method such as enrichment factor, linear range, correlation coefficients, limit of detection (LOD) and repeatability were all investigated by extracting 100 mL of Cd standard solutions. The results indicated that an enrichment factor of 387 can be obtained under the optimum extraction conditions. Analytical curves performed after HFSLM preconcentration exhibited good linearity with correlation coefficient $r^2 > 0.999$, in the range of $0.01\text{--}1 \mu\text{g L}^{-1}$ Cd. The limit of detection, calculated from the standard deviation of 5 blank measurements of the whole analytical procedure, was 0.8 ng L^{-1} , which is far lower than the instrumental detection limit ($0.2 \mu\text{g L}^{-1}$) and is comparable to that obtained with ICP-MS [22]. The relative standard deviation calculated from five replicate experiments at 200 ng L^{-1} was lower than 3.0%.

For validation, five seawater samples were analyzed by both the proposed method and the ICP-MS method. Sample analysis by the proposed method was conducted without dilution, whereas the analysis by the ICP-MS method was performed after a 10-fold dilution for eliminating the matrix interferences.

Table 2
Influence of interferants on the extraction and determination of Cd ($0.5 \mu\text{g L}^{-1}$)

Interferant	Interferant to analyte ratio (w/w)	Recovery (%), mean $\pm$ S.D., $n=3$
K^+ (IA)	4×10^7	91 ± 1
Na^+ (IA)	2.7×10^8	92 ± 3
Li^+ (IA)	2000	100 ± 1
Ca^{2+} (IIA)	4×10^6	99 ± 6
Mg^{2+} (IIA)	1.2×10^7	98 ± 1
Ba^{2+} (IIA)	200	103 ± 2
Pb^{2+} (IVA)	50	94 ± 1
Sn^{2+} (IVA)	1000	100 ± 9
Cu^{2+} (IB)	10	98 ± 3
Hg^{2+} (IIB)	10	97 ± 4
Mo^{2+} (VIB)	500	104 ± 1
Mn^{2+} (VIIB)	1000	100 ± 2
Co^{2+} (VIII)	10	108 ± 3
Fe^{3+} (VIII)	30	91 ± 2
F^-	1.2×10^5	97 ± 2
Cl^-	3.8×10^7	91 ± 1
Br^-	6×10^5	94 ± 1
I^-	600	92 ± 5
SO_4^{2-}	2.4×10^7	94 ± 1
PO_4^{3-}	3×10^4	92 ± 3

Table 3
Analytical results of real samples (mean $\pm$ S.D., $n=3$)

Sample	Found in natural sample (ng L^{-1}) (HFSLM-AAS)	Spiked (ng L^{-1})	Recovery (%)	Found in natural sample (ng L^{-1}) (ICP-MS)
S1	264.8 ± 2.8	200	89.0 ± 1.0	246.0 ± 1.6
S2	56.4 ± 1.1	50	89.3 ± 2.0	54.0 ± 1.8
S3	127.3 ± 1.0	100	99.7 ± 1.0	122.0 ± 1.6
S4	104.0 ± 4.0	100	96.9 ± 1.0	116.0 ± 0.9
S5	125.6 ± 3.2	100	97.5 ± 2.0	123.0 ± 1.9

The analytical results shown in Table 3 demonstrate that the results by using the present method are consistent with those obtained by ICP-MS. Statistical analysis with a one-way ANOVA showed no significant differences (at 0.05 level) between the results obtained by these two methods. In addition, the cadmium content of certified reference materials (GBW (E) 080040 seawater) determined by the proposed method ($0.95 \pm 0.07 \mu\text{g L}^{-1}$, mean $\pm$ S.D., $n=3$) shows good agreement with the certified values ($1.00 \pm 0.06 \mu\text{g L}^{-1}$) [23].

4. Conclusion

A novel preconcentration procedure for determination of trace Cd in seawater has been developed in this study. The hollow fiber supported liquid membrane extraction device showed an interference free performance. After optimization of the extraction conditions, an enrichment factor as high as 387 could be achieved. Coupled with graphite furnace atomic absorption spectrometry, Cd concentration down to a few nanograms per liter level in seawater samples could be determined.

Acknowledgements

This work was jointly supported by the Chinese Academy of Sciences (KJCX2-SW-H06, KZCX3-SW-431) and the National Basic Research Program of China (2002CB412308).

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