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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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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 HNO_3 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.

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 C_{18} 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-µL aliquot of sample was manually injected into the furnace, and absorbance signals in the form of peak height were measured.

Table 1
Instrumental operating conditions (GFAAS)

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

Temperature program

Stage	Temperature (°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

2.2. Reagents and materials

The stock standard solution of Cd (II) (1000 µg 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 A 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 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 (K_2SO_4) 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 µm i.d., 200 µm wall thickness, 0.2 µm pore size) was purchased from Membrana, Wuppertal, Germany. A 25-µL 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 °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 µL 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