

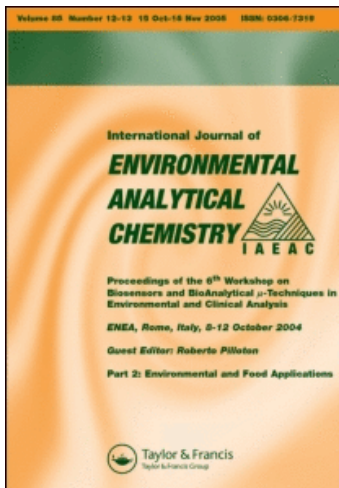
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Preconcentration of Ultra Trace Hg(Ii) in Aqueous Samples on Octadecyl Silica Membrane Disks Modified by Dibenzodiazathia-18-Crown-6-Dione and Its Determination by Cold Vapor Atomic Absorption Spectrometry

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PRECONCENTRATION OF ULTRA TRACE Hg(II) IN AQUEOUS SAMPLES ON OCTADECYL SILICA MEMBRANE DISKS MODIFIED BY DIBENZODIAZATHIA-18-CROWN-6-DIONE AND ITS DETERMINATION BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

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A simple and reliable method has been developed to selectively separate and concentrate ultra trace amounts of mercury ion from aqueous samples for the subsequent measurement by cold vapor atomic absorption spectrometry (CVAAS). The Hg²⁺ ions are adsorbed selectively and quantitatively during passage of aqueous samples through octadecyl-bonded silica membrane disks modified by dibenzodiazathia-18-crown-6-dione. The retained mercury ions are then stripped from the disk with a minimal amount of 0.5M hydrobromic acid solution as eluent, and determined by CVAAS. The proposed method permitted large enrichment factors of about 300 or higher. The limit of detection of the proposed method is 3 ng Hg²⁺ per 1000 ml. The method was applied to the recovery determination in four water samples.

Keywords: Hg(II); SPE; Octadecyl silica disks; Dibenzodiazathia-18-crown-6-dione; CVAAS

INTRODUCTION

During the past decades, concentration of mercury in air, soil, and water have been increasing because of greater utilization of fossil fuels and for the expanded use in industry and agriculture. Accurate and sensitive determination of mercury is now a challenging problem, because it is a hazardous contaminant of environment and is toxic at low levels to the biota^[1,2]. In natural waters, it is converted by bacteria to organic mercury species that are well known to bioaccumulate in fish tissue. The permissible criterion of mercury in drinking water is 1 µg l⁻¹^[3]. Thus, there is a growing interest by biologists and environmentalists to establish sources of mercury

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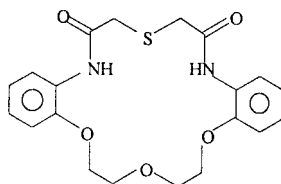
contamination and to evaluate levels of pollution, and this necessitates the development of new methods for selective separation, preconcentration and determination of mercury in sub-micro levels at different matrices.

The determination of mercury is carried out by several analytical methods described in the literature. These methods are based upon a wide range of analytical techniques such as spectrophotometry^[4–6] neutron activation analysis^[7–9], inductively coupled plasma mass spectrometry^[10], electrothermal atomic absorption spectrometry^[11], atomic fluorescence spectrometry^[12,13] and cold vapor atomic absorption spectrometry (CVAAS)^[14–20]. The CVAAS is the most widely used method for this purpose because of its simplicity, high sensitivity, relative freedom from interferences and relatively low operation costs.

Among different separation methods of mercury, liquid–liquid extraction in the presence of co-extract and ligands such as thiocyanate, acetylacetone, 8-hydroxyquinoline, tri-*n*-butylphosphate, tri-*n*-octylphosphine oxide, tenoyltrifluoroacetone, *bis*(2-ethylenyl) phosphoric acid, dithizone, diethyldithiocarbamate, pyrodinedithiocarbamate and crown ethers has attracted considerable attention^[5, 7, 9, 11, 17, 20, 21–23]. However, the use of classical extraction methods for this purpose is usually time-consuming, labor-intensive and requires large amounts of high purity solvents for extraction. Nevertheless, several other techniques for the preconcentration of mercury have been proposed including preconcentration by cryogenic trapping^[24, 25], amalgam preconcentration into a gold wire absorber^[3], concentration in a palladium-coated graphite tube^[26] and solid phase extraction^[12, 27–29].

Solid phase extraction (SPE) is a popular and growing techniques that is used to prepare samples for analysis, and sometimes referred to as liquid–solid extraction^[30]. It is an attractive alternative for classical liquid–liquid extraction that reduces solvent usage and exposure, disposal cost, and extraction time for sample separation and concentration purposes^[30–32]. In recent years, the SPE disks have been successfully utilized for the extraction and separation of many different organic compounds from environmental matrices^[33–35]. Moreover, the SPE cartridges and disks modified by suitable ligands have been successfully used for the selective separation and sensitive determination of metal ions^[32–39].

The aim of this work was the development of a rapid and efficient method for the selective extraction, concentration, and determination of $\mu\text{g l}^{-1}$ levels of Hg^{2+} ion in aqueous media using octadecyl silica membrane disks modified by dibenzodiazathia-18-crown-6-dione (DBDAT18C6DO) and CVAAS. It should be noted that we have recently reported the successful use of DBDAT18C6DO as a suitable ionophore for the construction of a PVC-based Hg^{2+} ion-selective electrode^[40].



DBDAT18C6DO

EXPERIMENTAL

Reagents

All acids were of the highest purity available from Merck and were used as received. All organic solvents were of HPLC grade from Aldrich. Analytical grade sodium tetrahydroborate, sodium hydroxide, and EDTA (disodium salt, trihydrate) were purchased from Merck and used as received. Reagent grade mercuric chloride and the nitrate or chloride salts of other cations used (from Merck or Fluka) were of the highest purity available and used without any further purification except for vacuum drying over P₂O₅. Dibenzodiazathia-18-crown-6-dione was synthesized and purified as described elsewhere^[41]. Doubly distilled deionized water was used throughout. The standard stock solution of mercury(II) was prepared by dissolving an appropriate amount of mercuric chloride in 1% (v/v) nitric acid solution. Working solutions were prepared by appropriate dilution of the stock solution with water.

Apparatus

The Hg determinations were performed on a Philips Pye Unicam 9100X atomic absorption spectrometer mounting a Hg electrodeless discharge lamp (EDL) and equipped with a deuterium background corrector. The absorbance wavelength was set at 253.7 nm (resonance line) and the spectral bandwidth at 0.5 nm. The experimental set-up was completed with a PU9360X continuous flow system for the re-circulation of Hg vapors. The determination of all other cations were carried out with a Philips Pye Unicam 9100X atomic absorption spectrometer under the recommended conditions for each metal ion. A model 691 Metrohm pH equipped with a combined glass-calomel electrode was used for the pH adjustments. Extractions were performed with 47 mm diameter × 0.5 mm thickness Empore membrane disks containing octadecyl-bonded silica (8-μm particle, 60-pore size, 3M Co., St. Paul, MN) with a standard Millipore 47-mm filtration apparatus.

Preparation of the SPE membrane disks

To remove potential interferences and to ensure optimal extraction of the analyte of interest, the disk cleaning and conditioning should be done before its use. Thus, after placing the membrane disk in the filtration apparatus, 10 ml of methanol was poured onto the disk and immediately drawn through the disk by applying a slight vacuum. The disk conditioning was then began by pouring 5 ml of dimethylsulfoxide onto disk. Immediately, a low vacuum was applied and the solvent was drawn through the disk until the solvent surface almost reached the surface of the disk. The disk should not be allowed to soak without vacuum, and air should not be allowed to make contact with the surface of the disk. It is preferable to leave extra solvent above the disk rather than to allow any air to make contact with the surface of the disk. Immediately, 10 ml of water was introduced onto the disk and was drawn through the disk. The disk was then dried under vacuum for 5 min or longer if necessary. This is especially important for the disks that are used for the first time. Then, a solution of 10 mg of DBDAT18C6DO dissolved in 2 ml of dimethylsulfoxide (a pale yellow solution) was introduced onto the disk so that the solution was spread on the whole disk surface,

and was drawn slowly through the disk by applying a slight vacuum. The passed solution was collected in a test tube. Then a few drops of water added to the test tube (until just before appearance of a colloidal suspension) and the resulting mixture was again introduced to the reservoir and passed through the disk slowly. The filtration step was repeated (if necessary) until the passed solution was completely clear and colorless. Finally, the disk was washed with 10 ml of water and dried by passing air through it. The membrane disk modified by the crown ether derivative is now ready for sample extraction. It should be noted that the modified disk thus prepared can be kept at room temperature for over a week, before its use for the extraction of Hg^{2+} ions.

Solid-phase extraction and quantification of Hg^{2+}

After drying, the modified disk was washed with 10 ml of water. This step presets the surface of the disk prior to the extraction of Hg^{2+} ions from water. Then 500 ml of the sample solution containing $1\ \mu\text{g}$ of Hg^{2+} was passed through the disk at a flow rate of $50\ \text{ml}\ \text{min}^{-1}$. The disk was dried completely by passing air through it. A proper test tube was then placed under the extraction funnel. The extracted mercury was stripped from the membrane disk using a 10 ml portion of 0.5 M hydrobromic acid at a flow rate of $10\ \text{ml}\ \text{min}^{-1}$. Then the extract was evaporated slowly to dryness. The remaining material was dissolved in a *ca.* 5 ml of 5%(v/v) nitric acid, transferred into a 10-ml volumetric flask, and diluted to the mark with 5%(v/v) nitric acid and the mercury concentration was determined by CVAAS.

General procedure for determination of Hg(II) in sea water samples

The general procedure for the determination of mercury in the sea water samples was as follows: After sampling, the samples were acidified and stored in refrigerator using PVC containers to the time when the determination possibility was brought about. Then the samples were passed through bare membrane disks to remove all particulates and organics that usually exist in such natural waters. Then, the samples were passed through a modified membrane disk and the recommended procedure for mercury determination was carried out.

RESULTS AND DISCUSSION

The Hg^{2+} ion as a soft acid possesses a coordination number of 4 and exhibits a high tendency to form complexes with ligands containing S or N donor atoms with soft and intermediate base properties respectively^[42]. Thus, the existence of a donating sulfur atom as well as two-NH-groups in DBDAT18C6DO was expected to increase both the stability and selectivity of its mercury(II) complex over other metal ions, especially alkali and alkaline earth cations^[40,43,44]. The presence of two benzo rings and two carbonyl groups on the 18-crown's cavity may also contribute to the cation selectivity by providing a rigid cavity with suitable size for the Hg^{2+} ion^[45]. Thus, we have recently used DBDAT18C6DO as an excellent neutral ion carrier for the construction of mercury(II)-PVC membrane electrode^[40].

TABLE I Percent recovery of mercury from the modified membrane disk using different eluents^a

Stripping acid solution	Volume (ml)	Recovery (%)					
		5	10	20	30	40	50
HNO ₃ (1 M)	–	0.0	0.0	0.0	0.0	0.0	0.0
HCl (1 M)	–	56.8	89.0	98.1	102.8	100.2	100.2
HCl (2 M)	–	71.5	99.3	–	–	–	–
H ₂ SO ₄ (1 M)	–	7.7	14.2	19.3	23.4	27.2	27.2
CH ₃ COOH (1 M)	–	0.0	0.0	0.0	0.0	0.0	0.0
HBr (0.5 M)	–	11.0	19.8	38.8	53.5	63.5	63.5
HBr (0.5 M)	99.2	101.3	–	–	–	–	–
HBr (1 M)	100.4	–	–	–	–	–	–

^a Initial samples contained 1 µg Hg²⁺ in 500 ml water.

Some preliminary experiments were carried out in order to investigate the quantitative retention of Hg²⁺ ions by the octadecyl silica membrane disks in the absence and presence of DBDAT18C6DO. It was found that, while the membrane disk itself shows a very low tendency for the extraction of mercury ions^[46], the disks modified by DBDAT18C6DO are capable of retaining Hg²⁺ ions in the sample solution quantitatively (the test solutions contained 1 µg Hg²⁺ in 50 ml solution).

In order to choose a proper eluent for the retained Hg²⁺ ions, after the extraction of 1 µg mercury from 500 ml sample solution, the Hg²⁺ ions were stripped using different volumes of various acids (Table I). The data given in Table I show that, among different stripping acid solutions used, 5 ml of hydrobromic acid at a concentration ≥ 0.5 M can accomplish the quantitative elution of mercury from the membrane disk. It is interesting to note that, even utilizing 50 ml of 1 M nitric acid has no effect on retained Hg²⁺ ions on the modified membrane disks; thus, this solution can be used for the elution of some interfering ions which may be co-extracted with Hg²⁺ ions by the membrane disk.

Effects of pH, amount of ligand and flow rates

The optional amount of DBDAT18C6DO for the proper modification of the membrane disks was investigated. The results showed that the membrane disks modified with 5–20 mg of the ligand are capable of retaining 1 µg of Hg²⁺ ions quantitatively. Thus, 10 mg of DBDAT18C6DO was used for further studies.

In order to investigate the effect of pH on the extraction of Hg²⁺ ions by the modified membrane disks, the pH of aqueous samples was varied in the range of 1–8, by using 1 M solutions of either HNO₃ or NaOH, and the recommended procedure was followed. It was found that percent extraction of mercury is independent of pH at the range studied. It is interesting to note that similar pH effects have been reported for the extraction and separation of different metal ions with crown ethers^[20]. However, higher pH values (> 8) were not tested because of the possibility of the hydrolysis of octadecyl silica in the membrane disks, resulting in the decreased useful life time of the disks^[20].

The influence of the flow rates of the sample and stripping solutions through the modified membrane disks on the retention and recovery of Hg²⁺ ion was investigated. It was found that, in the range of 10–70 ml min⁻¹, the retention of mercury by the modified membrane disk is not affected by the sample flow rate significantly. On the other hand, quantitative stripping of Hg²⁺ from the disk was achieved in a flow rate

range of 1–20 ml min⁻¹, using 10 ml of 0.5 M HBr. At higher flow rates, quantitative stripping of mercury needed larger volumes of 0.5 M HBr.

Analytical performance

When solutions of 1 µg of mercury in 50, 100, 200, 500, 1000, 2000 and 3000 ml sample solutions were passed through the modified disks, the Hg²⁺ was retained quantitatively. Thus, the break-through volume for the method should be greater than 3000 ml, resulting in a concentration factor greater than 300. This property of the proposed method together with the special characteristics of octadecyl silica membrane disks for the preconcentration and preservation of analytes^[30] make it suitable for easy field preconcentration and sample preparation.

The minimal capacity of the membrane disks modified by 10 mg of the DBDAT18C6DO was determined by passing 500 ml portions of an aqueous solution containing 5000 µg mercury, followed by the CVAAS determination of the retained metal ions. The maximal capacity of the disk was found to be 342 ± 35 µg of Hg²⁺ ion on the disk. The stability and re-use of a modified disk was tested for its ability to perform the SPE of more than one sample. It was found that the use of the same disk modified with 10 mg DBDAT18C6DO for at least five times resulted in no change on the recovery of Hg²⁺ ion.

The limit of detection (LOD) of the proposed method for the determination of mercury was studied under the optimal experimental conditions. The LOD obtained from 3σ of blank is 3 ng/1000 ml.

In order to investigate the selective separation and determination of mercury from its binary mixtures with different metal ions, an aliquot of aqueous solutions (500 ml) containing 1 µg Hg²⁺ and mg amounts of different foreign cations was taken and the recommended procedure was followed. The results are summarized in Table II.

TABLE II Separation of mercury from binary mixtures^a

Diverse cation	Amount taken (mg)	% Found ^b	Recovery of Hg ²⁺ ion (%)
Na ⁺	51.4	1.30 (1.7) ^c	99.0 (1.7)
K ⁺	52.4	1.24 (0.4)	100.3 (0.9)
Ca ²⁺	26.4	1.61 (1.6)	98.7 (3.7)
Mg ²⁺	25.3	0.48 (1.2)	103.5 (4.2)
Fe ³⁺	2.8	1.85 (1.4)	99.8 (1.8)
Zn ²⁺	2.8	8.83 (0.4)	103.1 (2.9)
Mn ²⁺	4.4	3.30 (1.3)	99.1 (1.3)
Co ²⁺	2.9	8.95 (0.7)	100.7 (3.9)
Ni ²⁺	2.8	6.47 (1.3)	101.9 (3.8)
Cu ²⁺	3.6	3.80 (1.6)	97.9 (3.3)
Cr ³⁺	2.8	1.32 (1.1)	102.1 (2.7)
Al ³⁺	2.5	3.42 (0.5)	102.8 (4.3)
Cd ²⁺	3.8	6.25 (0.9)	99.4 (2.1)
Pb ²⁺	3.4	8.72 (0.4)	97.8 (1.8)
UO ₂ ²⁺	2.7	–	103.1 (0.5)

^a Initial samples contained 1 µg Hg²⁺ and different amounts of diverse cations in 500 ml water.

^b Percentage of the retained diverse cations reduced to zero by washing the disks with 20 ml of 1 M HNO₃, prior to elution of the retained Hg²⁺ ions by 10 ml of 0.5 M HBr.

^c Values in parentheses are % RSDs of three replicate analyses.

TABLE III Recovery of 1 µg Hg²⁺ from 1000 ml solution of the synthetic and water samples

<i>Sample</i>	<i>Recovery of Hg²⁺ ion (%)</i>
Synthetic sample 1 (Na ⁺ , K ⁺ , Ca ⁺ and Mg ²⁺ , 25 mg of each cation)	99.7 (1.0) ^a
Synthetic sample 2 (Na ⁺ , K ⁺ , Ca ²⁺ and Mg ²⁺ , 25 mg) of each cation and Zn ²⁺ , Mn ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Pb ²⁺ , Cd ²⁺ , 2 mg of each cation)	96.9 (0.7)
Synthetic sample 3 (composition of sample 2 in addition to 0.01 M EDTA)	98.1 (2.2)
Tap water (Tehran, July 29, 1999) ^b	99.6 (2.5)
Spring water (Manjil, May 15, 1999) ^b	98.5 (1.1)
River water (Manjil, May 17, 1999) ^b	97.7 (1.2)

^aValues in parentheses are %RSDs based on three replicate analyses.

^bDirect CVAAS experiment did not show any mercury in initial samples.

TABLE IV Determination of mercury(II) in five water samples from different civic-coastal sites in Bandar-Anzaly^a

<i>Sample site</i>	<i>Mercury concentration (ng ml⁻¹)</i>
Gol-Laleh	1.6 (0.2) ^b
Shanbeh-Bazar	1.8 (0.2)
Rasteh-Khaleh	2.1 (0.3)
Soosar-Rooga	1.2 (0.1)
Hendoo-Khaleh	1.7 (0.3)

^a250 ml of each sample was taken.

^bValues in parentheses are %RSDs based on three replicate analyses

The data given in Table II show that the Hg²⁺ ions in the binary mixtures are retained completely by the modified membrane disks even in the presence of up to 50 mg of the other cations studied. It should be noted that the retention of foreign cations by the disk is at the most 9% of the amounts taken. However, quantitative separation of foreign cations for the Hg²⁺ ion can achieve by washing the disks with 20 ml of 1 M HNO₃ solution prior to elution of the retained Hg²⁺ ions by the hydrobromic acid solution.

To evaluate the applicability of the proposed method to samples with different matrices containing varying amounts of a variety of diverse ions, it was applied to the separation and recovery of Hg²⁺ ions from two different synthetic samples as well as three different natural water samples (Table III). The results show that, in all samples, the mercury recovery is almost quantitative.

The proposed method was also applied to determination of Hg²⁺ ions in the five sea waters, taken from different civic-coastal sites in Bandar-Anzaly, Caspian Sea, and the results are given in Table IV. It is noteworthy that the direct CVAAS analysis did not show any mercury in these samples, However, by using the mercury content of different samples it was found to be from 1.2 to 2.1 ng ml⁻¹.

CONCLUSIONS

The proposed SPE procedure based on octadecyl silica membrane disks modified with a novel crown ether derivative (DBDAT18C6DO) is simple, highly sensitive, selective, reproducible and rapid, when compared with most of the previously reported

methods^[7–9, 14–20, 28, 47]. The time taken for separation, concentration, and analysis of mercury in a 1000 ml sample is at the most 20 min. The method can be successfully applied to the separation and determination of mercury in a variety of real samples.

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