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Preconcentration and Determination of Cd(II) Using Octadecyl Silica Membrane Disks modified Cyanex 272 and Flame Atomic Absorption Spectrometry

Ali Moghimi

Department of Chemistry, Varamin Campus, Islamic Azad University, Varamin, (IRAN)

E-mail: Kamran9537@yahoo.com

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ABSTRACT

A novel and selective method for the fast determination of trace amounts of Cd(II) in water samples has been developed. The procedure is based on the selective formation of Cd(II) bis(2,4,4-trimethylpentyl)phosphinic complexes at different pH in the presence of acetate as an enhancement agent of Cd(II) signals followed by elution with organic eluents and determination by atomic absorption spectrometry. The maximum capacity of the employed disks was found to be $471 \pm 3 \mu\text{g}$ for Cd(II). The detection limit of the proposed method is $105 \text{ ng} \cdot \text{L}^{-1}$ for Cd(II). The effect of potential interfering ions, ligand amount, stripping solvent, and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to be about 1000 mL providing a preconcentration factor of 500. The proposed method was successfully applied for determination of Cd(II) in different water samples.

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KEYWORDS

Solid phase extraction;
Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272);
Flame atomic absorption spectrometry;
Octadecyl silica membrane disk.

INTRODUCTION

Cd(II) is an essential micronutrient for life. Determination of low levels of Cd(II) by flame atomic absorption spectrometry (FAAS) often demands separation and preconcentration steps because of insufficient sensitivity or matrix interference. Several procedures of enrichment have been developed for Cd(II) determination involving different analyti-

cal techniques, such as coprecipitation^[1], or liquid-liquid^[2], cloud point^[3] or solid-phase^[4] extraction. Processes involving solid-phase extraction^[5] show several advantages, like availability and easy recovery of sorbent, attainability of high preconcentration factors, and facility of handling. Therefore, these procedures avoid or minimize the use of organic solvents that are generally toxic.

Online preconcentration systems using solid-

phase extraction are opportune for metal determination, due to their flexibility, simplicity, high sample throughput and versatility. These characteristics permit the use of online systems coupled with different detectors. Many online procedures using solid-phase extraction can be found in the literature. The materials generally used are ion-exchangers^[6,7], silica^[8,9], activated alumina^[10,11], carbon^[12], fullerene^[13], polyurethane foam^[14,15] and chelating resins^[16].

There is continued interest in development of chelating sorbents for use in metal preconcentration systems. To produce these matrices, chelating ligands can be loaded on solid supports^[17-20], or can be covalently bonded to a polymeric matrix through an azo^[21,22] or methylene group^[23]. Coupling by covalent bond reduces problems of leaching of the ligand from the column.

When multielemental determinations are required, such as systems that use flame atomic absorption spectrometry (FAAS) as the detection technique, the use of unselective ligands is convenient. However, in some determinations in which the goal is reduction of interference problems, the use of selective reagents is more suitable.

Cd(II) is known to be essential at trace levels to man, animals and plants for metabolic processes^[27]. It is clear that the determination of the trace amounts of Cd(II) in biological and environmental samples is important in the fields of environmental analysis, process control and medicine. The determination of trace amounts of Cd(II) in natural waters is of great interest because Cd(II) is important for living species as complexed Vitamin B₁₂. The deficiency of Cd(II) in ruminants usually results in different types of anemia. Toxicological effects of large amounts of Cd(II) include vasodilation, flushing and cardiomyopathy in humans and animals. Investigations have been extended to the biochemistry of Cd(II) in animals, microorganisms and enzymes^[28]. The maximum recommended concentration of toxic ions such as nickel and Cd(II) in drinking water for livestock is: Cd-1.0mg l⁻¹^[29]. For drinking water for human consumption the upper limits are even less. It is therefore clear that a reliable analytical method must be established to test waters and soils on a regular basis. Previously, trace elements in natural waters were

typically analyzed using flame atomic absorption techniques, which although almost interference free, were labor intensive owing to their one element at a time analytical mode. At the present time, even the furnace atomic absorption technique, for years the standard bearer of low-level trace metal analysis is giving way to FAAS techniques.

The ability of the FAAS system to perform multi-element trace metal analysis of environmental samples provided commercial laboratories with the needed incentive to enter into the business of trace metal analysis. Despite the selectivity and sensitivity provided by this technique, there is a crucial need for the preconcentration of ultra trace elements before their analysis due to their frequent low concentrations in numerous samples. Additionally, since FAAS emission is normally subjected to high levels of interferences that usually accompany analytes; a cleanup step is often required. Many methods have been developed for the preconcentration of trace heavy metals from various samples. These include coprecipitation, electrodeposition, liquid-liquid extraction and solid phase extraction. Solid phase extraction (SPE) has received much attention in recent years for the analysis of trace concentrations in samples. This technique reduces the use of solvents, which reduces disposal costs and extraction times^[30,31]. Many solid phases, such as activated carbon, polymeric fibers, Amberlite XAD, silica gel and modified alkyl-bonded silica gel have been used to preconcentrate trace metal ions from various media. Silica with chemically bounded alkyl chains modified by the use of suitable ligands has been an excellent and widely used extractor of metal ions^[32-36]. Some works dealing with the adsorption of trace metal chelates on C₁₈-silica adsorbent materials packed into columns or cartridges and their determination by FAAS can be found in literature^[37,38]. The use of extraction disks with a high cross-sectional area may largely prevent all the problems encountered with columns, cartridges and tubes and usually offer higher breakthrough volumes^[39].

8-aminoquinoline derivatives are known as chromogenic reagents for spectrophotometric determination of micro-amounts of gold^[40] and palladium^[41], and for the fluorimetric determination of iron^[42] and

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gold^[43]. Cyanex272, has been used as a selective chelating agent for the simultaneous spectrophotometric determination of Cd(II) ions^[44,47-49]. In this work, Cyanex272 is synthesized and used to modify the C₁₈-silica extraction disks. Using these disks, a highly efficient and simple method for the preconcentration of ultra trace amounts of Cd(II) in natural water samples is developed and the simultaneous determination of these elements is achieved using FAAS.

EXPERIMENTAL

1. Apparatus

An inductively coupled plasma-optical emission spectrometer (FAAS, Varian Vista-Pro, Australia) coupled to a V-groove nebulizer and equipped with a charge-coupled device (CCD) detector was used. The operating parameters are listed in TABLE 1. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (30µm particles, 70Å pore size) obtained from Supelco in conjunction with a standard Millipore 47mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

2. Reagents

All metal salts, acids and solvents and Cyanex272 used were purchased from Merck (Darmstadt, Germany) and were of analytical reagent grade. Deionized double distilled water was used throughout. Multi-elemental standard solution containing Cd at 100µg ml⁻¹ was prepared by dissolving Cd in appropriate amounts of nitrate salts. Single standard solutions of Cd at 1000µg ml⁻¹ were also used (Merck). Phosphate buffer was prepared by dissolving 1.179g of potassium dihydrogen phosphate and 4.30g of disodium hydrogen phosphate in deionized double distilled water to give 1000 ml of solution.

3. Preparation of modified extraction disks

Extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47mm diameter × 0.6 mm

thickness containing octadecyl silica bonded phase (30µm particles, 70Å pore size) obtained from Supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. In order to remove potential interferences and to ensure optimal extraction of the analytes, disk cleaning and conditioning should be performed before use. Thus, after placing the disk in the filtration apparatus, 10 ml methanol was poured onto the disk and immediately drawn through it by applying a slight vacuum to remove all contaminants arising from the manufacturing process and the environment. This procedure is especially important for the disks, which are used for the first time. After all of the solvent passed through the disk, air was drawn through it for 5min to dry it. After drying the disk, a 5ml solution of chloroform containing 6mg of Cyanex272 was introduced onto the disk and allowed to penetrate inside the disk completely. Then, the solvent was evaporated at 60°C and the modified disk was washed and preconditioned by passing a 20 ml portion of the buffer solution to pre-wet the surface of the disk prior to the extraction of ions from aqueous samples. In order to ensure complete wetting of the disk with the buffer solution it is preferable to leave extra buffer above the disk rather than to allow any air to come in contact with the surface of the disk.

4. Procedure of extraction, elution and determination

The general procedure for the extraction and determination of Cd(II) ions was as follows: A 250.0ml volume of solution containing 0.5µg of each metal was adjusted to the pH=6.0 by the addition of 5ml phosphate buffer and then passed through the modified disk at 20ml min⁻¹ flow rate. The disk was dried completely by passing air through it for 5min. After the extraction, a 25×200 mm test tube was then placed under the extraction funnel. The extracted ions were stripped from the modified disk using 10ml solution of 0.01M of nitric acid at 7ml min⁻¹ flow rate. The analyte ion concentrations were then determined at recommended conditions FAAS.

5. Analytical procedure for Cd(II) in water samples

Water samples were acidified with HNO_3 to 0.5% v/v prior to storage in order to avoid metal adsorption onto the inner bottles walls. 1000ml aliquot of water samples was first passed through 2.5 μm pore size filter paper(Whatman) to remove suspended particulate matter and was stored at 6°C in the dark. Then complete the determination as discussed in Section 2.4.

RESULTS AND DISCUSSION

1. Effect of pH on the adsorption of metal ions

The pH of the sample solution is one of the influencing factors in solid phase extraction process. The analyte solutions were adjusted by the addition of appropriate amounts of 0.1 M either nitric acid or ammonia solutions to a fixed pH and passed through modified octadecyl silica disks at a flow rate of 20ml min^{-1} . The pH range studied was between 2.0 and 8.0. Higher pH values(>8) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks. Then the metal ions were eluted from the disks and their determination by FAAS gave the percentage recoveries of the eluted metal ions at various pHs. Figure 1 shows the effect of pH on the retention of metal ions on the modified octadecyl silica extraction disks. Both Cd(II) ions have been quantitatively retained in the pH>6.0. Thus for subsequent experiments, pH=6.0 was chosen as working pH. Addition of 5.0 ml phosphate buffer was sufficient for achieving this pH.

2. Choice of eluent

In order to choose a proper eluent for the retained ions after their extraction, the analyte ions were stripped with varying amounts of 0.01M concentrations of different acids and the results are summarized in TABLE 2. It is seen that their elution from the modified membrane disk was quantitative with 10.0ml of 0.01M nitric acid, while this could not be done even if greater than 10.0ml volumes of the other acids tested. In other experiments it was found that the lower the concentration of nitric acid, the larger the volume of the acid solution needed for the quantitative stripping of the cations. Thus, 10 ml portions of 0.01M nitric acid were used for

TABLE 2 : Percent recovery of Cd(II) from modified octadecyl silica extraction disks using varying amounts of different 0.01M of acid solutions^a

Hydrobromic acid	Recovery (%)			Volume (ml)
	Nitric acid	Hydrochloric acid	Acetic acid	
43.5	85.8	60.5	35.6	6.0
61.5	93.4	81.5	52.3	10.0
80.0	98.7	95.4	70.6	15.0

^aSample solution: 250ml of multi-elemental solution containing 0.5 μg of Cd(II) ions (pH=6.0)at 25ml min^{-1} flow rate, Eluent flow rate: 7ml min^{-1} , Amount of ligand: 10mg.

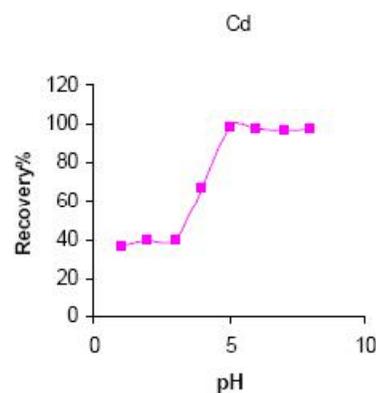


Figure 1: Effect of pH on the recovery of Cd(II). (Sample solution: 250 ml of solution containing 0.5 μg of each metal at 25ml min^{-1} flow rate. Eluent: 10ml of 0.01M of nitric acid solution at 7ml min^{-1} flow rate. Amount of ligand: 10mg)

further studies. It is noteworthy that when nitric acid of concentrations higher than 0.01M was used, there was some leaching of Cyanex272 from the disk.

3. Effect of the amount of ligand

In order to investigate the optimum amount of Cyanex272on the quantitative extraction of metal ions by the modified extraction disks, extraction from 250ml solutions containing 0.5 μg of Cd(II) ions under the optimal conditions was conducted by varying the amounts of ligand from 5 to 20mg. In all cases, the extraction of metal ions found to be quantitative. Hence, subsequent experiments were carried out with 10mg of the ligand.

4. Effect of flow rates

The dependency of uptake of the metal ions on the flow rate was studied. The flow rate of the solution through the modified disk was being varied from 10 to 30ml min^{-1} . Adsorption of cations was quanti-

Full Paper

tative and reproducible in this range and not considerably affected by the sample solution flow rate. Similar results for the extraction of organic^[45] and inorganic^[32-36] materials by octadecyl silica extraction disks have been reported in the literature. Thus, the flow rate of the sample solution was maintained at 20ml min⁻¹ throughout the experiment. Quantitative stripping of metal ions from the modified disk was achieved in a flow rate range of 2-10ml min⁻¹, using 10ml of 0.01 M HNO₃ as a stripping solution. At higher flow rates, a large volume of eluent was necessary for the quantitative stripping of ions. Hence, subsequent experiments were carried out with a flow rate of 7ml min⁻¹.

5. Disk efficiency

Undoubtedly, one of the major parameters affecting in the SPE determinations is the efficiency of the used membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimum experimental conditions, it was found out that each ENV-18 DISKTM disk could perform at least 15 replicate analyses if organic eluting solvents are used. On the other hand, acidic, eluents practically decrease the number of time a disk could be used to 10 replicates. These observations are represented in figure 2.

6. Analytical figures of merit

The measurement of breakthrough volume is important in solid phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without the loss of analyte during elution of the sample. The breakthrough volume of the sample solution was tested by dissolving 0.5µg of Cd(II) ions in 500, 750 and 1000 ml of buffered solution and the recommended procedure was followed. In all cases, the extraction by modified disk was found to be quantitative. Thus the breakthrough volume for the method should be around 1000 ml. Consequently, by considering the final elution volume of 10 ml and the sample solution volume of 1000 ml, an enrichment factor of 500 was easily available. The maximum capacity of the modified disk for each ion was determined by passing 250 ml portions of buffered aqueous solu-

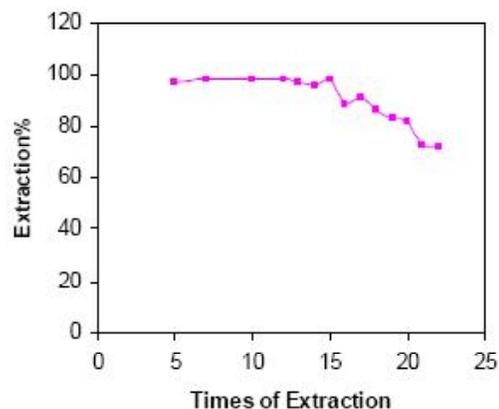


Figure 2 : Influence of eluent type on disk efficiency

TABLE 3 : Effect of foreign ions on the recovery of Cd(II) ions^a

Cd	Concentration (ppm)	Ions
98.9	0.7	Zn ⁺²
97.7	0.09	Cu ⁺²
-	0.5	Co ⁺²
97.0	0.5	Ni ⁺²
97.8	0.7	Fe ⁺³
98.8	0.5	Al ⁺³
95.8	0.4	Mn ⁺²
97.6	300	Mg ⁺²
96.4	1200	Na ⁺
98.4	1200	K ⁺
98.7	450	Ca ⁺²
98.4	0.7	Hg ⁺²
96.8	0.8	Cd ⁺²
97.3	0.6	Cr ⁺³
98.4	8	Ag ⁺
97.6	0.6	Pb ⁺²
97.8	49	Ba ⁺²
97.8	48	As ⁺³

^aSample solution: 250ml of multi-elemental solution containing 0.5µg of Cd(II), nickel(pH=6.0) at 25ml min⁻¹ flow rate, Eluent: 10ml of 0.01M of nitric acid solutions at 7ml min⁻¹ flow rate, Amount of ligand: 10 mg.

^aConcentration values are confidence intervals based on three replicate analyses at 95%; n.d.: not determined.

tions through the disk in which each of the solutions contains 500µg of one of the ions. The conditions were as recommended procedure. The maximum capacities of the disks obtained from three replicate measurements were 471±3µg of loaded ligand for Cd(II). The limits of detection(LOD) of the proposed method were studied under the optimal experimental conditions.

This parameter was calculated by $LOD = k_s/m$, where k is equal to 3 according to the desired confi-

TABLE 4 : Determination of Cd(II) ions in 1000 ml of different water samples and recovery test ^a

Recovery (%)	Concentration ($\mu\text{g l}^{-1}$), $\bar{X} \pm s_b \sqrt{n}$		Added (μg)	Element	Sample
	Proposed method	Reference method			
-	12.26 \pm 0.35	12.32 \pm 0.67	-	Cd	Sea water
87.8	-	16.64 \pm 0.54	5		
94.9	-	21.75 \pm 0.67	10		
-	1.30 \pm 0.37	1.23 \pm 0.58	-	Cd	Tap water
109.3	-	6.73 \pm 0.48	5		
102.5	-	11.55 \pm 0.55	10		
-	n.d.	n.d.	-	Cd	Synthetic water
95.5	-	4.50 \pm 0.77	5		(K ⁺ , Na ⁺ , Li ⁺ , Mg ²⁺ , Ba ²⁺ , Na ⁺ , Ag ⁺ , Ca ²⁺ , Fe ³⁺ , Mn ²⁺ , 0.01 mg of each cation)
97.6	-	9.64 \pm 0.68	10		

dence level(95%), s_b is the standard deviation of the blank signal and m is the slope of the analytical curve. The LODs were 105ng l⁻¹ for Cd(II). The reproducibility of the proposed method for the extraction and determination of 0.5 μg of analyte ions from 250ml buffered solution at pH=6.0 was also studied. The results obtained on 10 successive extractions and elution cycles revealed relative standard deviations of 1.8 for Cd(II).

7. Effect of foreign ions

The effect of other cations on the determination of analyte ions was studied. Known quantities of the foreign ions were added to 250ml aliquot of aqueous solution(pH=6.0) containing 0.5 μg of Cd(II) ions, and the recommended procedure was followed. As shown in TABLE 3, most of the cations examined did not interfere considerably with the extraction of analyte ions and their recoveries were quantitative in the presence of other cations.

8. Analysis of water samples

To test the applicability of the developed procedure, it was applied to the extraction and determination of Cd(II) contents from some water samples. Tap water(Saveh, 20 February ,2007), seawater (taken from the Caspian sea, Anzali port, 11 November 2006) and a synthetic sample were analyzed. As can be seen in TABLE 4, the added analyte ions can be quantitatively recovered from the water samples by the aforementioned procedure. The accuracy of the results given in TABLE 4 was demonstrated by the use of a cloud point extraction procedure^[46]. According to the 95% confidence level, there

was no significant difference between the results obtained from the two methods.

CONCLUSION

The results presented in this work well demonstrate the tremendous possibilities offered by the solid phase extraction of ultra trace amounts of Cd(II) in water samples using C₁₈-silica extraction disks modified by Cyanex272 and its determination by FAAS. This method is a rapid, simple, precise and accurate alternative to conventional procedures for determining these ions in natural water samples. Low detection limits, up to 105ng l⁻¹ for Cd(II), and an enrichment factor of 500 are the main advantages of this analytical procedure used in environmental ultra trace analysis. In conclusion, the developed method can be applied in order to simultaneously determine ultra trace amounts of these elements in various natural water samples.

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Full Paper

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