Separation and preconcentration of cadmium ions using octadecyl silica membrane disks modified by methyltrioctylammonium chloride

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ABSTRACT

A simple and selective method for the determination of cadmium in water samples by FAAS after solid phase extraction has been developed. The method is based on the sorption of cadmium as CdI_4^{2-} on octadecyl silica membrane disks modified by cationic surfactant of methyltrioctylammonium chloride in the pH range of 1–8. The sorbed cadmium is then eluted with 10 ml of 1 mol l^{-1} nitric acid in ethanol and is measured by flame atomic absorption spectrometry. The influence of flow rates of eluent and sample solution, iodide concentration and amount of surfactant in retention and elution of cadmium from disks was also investigated. A preconcentration factor of 100 was achieved by passing 1000 ml of sample through the membrane disk. The limit of detection (LOD) of cadmium was found to be 0.014 ng ml^{-1}. Precision at 2.5 μg l^{-1} was 1.2% ($n = 8$). The method was successfully applied to the determination of cadmium in some natural water samples. The accuracy was assessed through recovery experiment, independent analysis by graphite furnace atomic absorption spectrometry, and analysis of certified reference waters.

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1. Introduction

The contamination by heavy metals from various environmental sources including natural waters is a great concern nowadays. Water pollution by heavy metals is causing serious ecological problems in many parts of the world. Cadmium is known to be extremely toxic and accumulates in human body mainly in the kidneys and liver [1]. Prolonged intake of cadmium leads to severe dysfunction of the kidneys. It can also inhibit the action of the zinc enzymes by displacing the zinc. Moreover, cadmium has been designated as a human carcinogen [2,3]. This element occurs naturally in rocks and soils, generally associated with zinc and its compounds. Anthropogenic sources include; emissions from industrial plants, such as zinc smelters, steel works, incinerators and power stations. These practices resulted in accumulation of cadmium in soils, allowing it to enter the food chain with the potential to cause health problems [4]. Therefore, the determination of cadmium in the environmental samples is mandatory today, and requires analytical techniques exhibiting low detection limits for this toxic element.

A variety of sensitive and selective analytical techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [5], inductively coupled plasma mass spectrometry (ICP-MS) [6], hydride generation atomic fluorescence spectrometry [7], graphite furnace atomic absorption spectrometry (GFAAS) [8], spectrophotometry [9], potentiometric stripping analysis [10], and flame atomic absorption spectrometry (FAAS) [11] has been used for the determination of trace Cd in different samples. Among these methods, FAAS is still the most convenient one because of its specificity, simplicity, availability and low cost. However, due to the low concentration of cadmium in environmental samples, a separation/preconcentration step is usually necessary.

Several procedures such as coprecipitation [12], liquid–liquid [13], cloud-point [14], solid-phase extraction (SPE) [15], and dispersive liquid–liquid microextraction [16] have been developed for the separation and preconcentration of cadmium from different matrices. Liquid–liquid extractions are generally time consuming, labor-intensive, and require strict control of extraction conditions. SPE as an alternative to separation/preconcentration procedures overcomes many drawbacks of liquid–liquid extraction. Some advantages of SPE are simplicity, rapidity, ease of recovery of the solid phase, and ability to attain a high concentration factor.

Octadecyl-bonded silica membrane disks have been used extensively for the extraction of several organic environmental pollutants [17,18]. These disks also have been modified by suitable reagents for selective separation and preconcentration of metal ions [19,20]. The major advantages of SPE disks as has been claimed are: (a) shorter

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sample processing time; this is due to the large cross-sectional area of the disk and decrease in pressure drop, which allows sample processing at higher flow rates, (b) lower chance of plugging by particles due to large cross-sectional area of the disk and (c) reduced channeling; because of the use of smaller diameter sorbent and greater mechanical stability of the sorbent bed [21].

In the present work a method for the determination of cadmium after its preconcentration using octadecyl silica membrane disk modified with methyltrioctylammonium chloride is described. Cadmium as CdI_4^{2-} is preconcentrated on modified disk, eluted by ethanolic solution of nitric acid and determined by FAAS.

2. Experimental

2.1. Reagents

All the chemicals were of analytical reagent grade and obtained from Merck (Darmstadt, Germany). Doubly distilled deionized water was used throughout.

The stock standard cadmium solution ($1000\,\mu g\,ml^{-1}$) was prepared from pure cadmium nitrate in $0.5\,mol\,l^{-1}$ nitric acid. Working standard solutions were prepared by appropriate dilution of the stock standard solution.

2.2. Apparatus

A Buck Scientific flame atomic absorption spectrometer 210 VGP (East Norwalk, CT, USA) furnished with a cadmium hollow cathode lamp and air–acetylene flame, was used for the analysis. The absorbance wavelength was set at 228.8 nm and the spectral band width at 0.7 nm. A Metrohm 691 digital pH meter (Herisau, Switzerland) equipped with a combined glass electrode was used for the pH measurements.

Solid phase extractions were performed with $47\,mm \times 0.5\,mm$ (diameter $\times$ thickness) Empore membrane disks containing octadecyl (C_{18}) silica ($8\,\mu m$ particle, $60\,Å$ pore size) from 3 M (Oakdale, MN, USA). The disk was used in conjunction with the standard Millipore 47 mm filtration apparatus.

2.3. Preparation of modified extraction disks

After placing the membrane disk in filtration apparatus, it was washed with 10 ml methanol and 10 ml of acetonitrile by applying a slight vacuum. After all of the solvent had passed through the disk, it was dried by passing air through it for several minutes. Then, a solution containing 15 mg of methyltrioctylammonium chloride in 2 ml dioxan was introduced onto the disk so that the solution was sorbed on the whole disk surface. The solution was allowed to penetrate inside the membrane completely without applying any vacuum. Finally, the filtration funnel containing the modified disk was transferred into an oven and the solvent was evaporated at $50\,°C$ for about 5 min. The membrane disk modified by methyltrioctylammonium chloride was then ready for sample extraction.

2.4. General procedure

The general procedure for the extraction of Cd^{2+} ions as CdI_4^{2-} on the modified membrane disk was as follows. The modified disk was washed with 20 ml of water. This step prewets the surface of the disk prior to the extraction of Cd^{2+} ions. Then, the sample (up to 1000 ml) containing trace amounts of cadmium and $0.01\,mol\,l^{-1}$ potassium iodide was passed through the modified membrane disk at a flow rate of $50\,ml\,min^{-1}$ with the aid of a suction pump. The analyte was then eluted from the membrane disk using two 5 ml portions of $1\,mol\,l^{-1}$ nitric acid solution in ethanol at a flow rate of
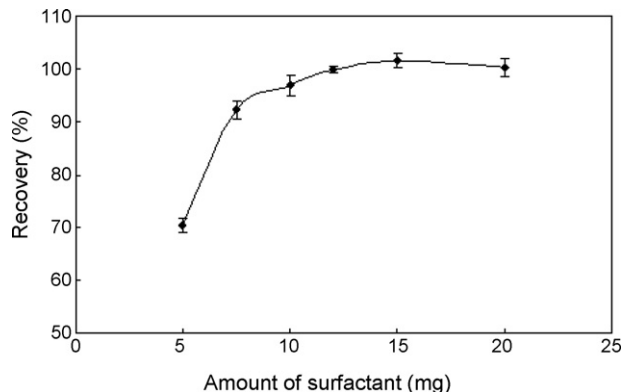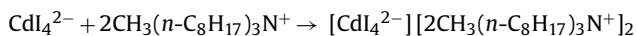

Fig. 1. Effect of the amount of methyltrioctylammonium chloride on the recovery of cadmium from the membrane disk. *Conditions*: cadmium, 10 to 20 μg; sample volume 100 ml; sample pH 5; iodide concentration, $2 \times 10^{-2}\,mol\,l^{-1}$; eluent, 10 ml of $1\,mol\,l^{-1}$ nitric acid in ethanol; sample flow rate $20\,ml\,min^{-1}$, and eluent flow rate, $2\,ml\,min^{-1}$.

$3\,ml\,min^{-1}$. The cadmium content of the eluent was then analyzed by flame atomic absorption spectrometer using standard solutions of cadmium in similar matrix.

3. Results and discussion

Because of the high molecular weight of methyltrioctylammonium chloride, it strongly adsorbs onto hydrophobic substrates, such as C_{18} sorbent and polyurethane foam [22,23]. This surfactant is quaternary ammonium salt which is used as a counter ion in solvent extraction of anionic metal complexes. Cadmium(II) easily forms anionic complex with iodide (CdI_4^{2-}, $\log \beta_4 = 5.35$) which is extractable into the organic solvent in the form of a lipophilic ion-pair with a suitable cation [24]. The preliminary experiments showed that CdI_4^{2+} can be retained on octadecyl silica membrane disk modified with methyltrioctylammonium chloride due to the formation of ion pair.

$$CdI_4^{2-} + 2CH_3(n\text{-}C_8H_{17})_3N^+ \rightarrow [CdI_4^{2-}][2CH_3(n\text{-}C_8H_{17})_3N^+]_2$$

Therefore, octadecyl silica membrane disks modified with methyltrioctylammonium chloride was chosen as a sorbent for solid phase extraction of cadmium.

The optimal amount of methyltrioctylammonium chloride which must be adsorbed on the octadecyl silica membrane disks for quantitative recovery of 20 μg of Cd^{2+} from 100 ml of aqueous sample was investigated by varying the amount of surfactant from 5 to 20 mg (Fig. 1). As can be seen, the extraction of cadmium is quan-
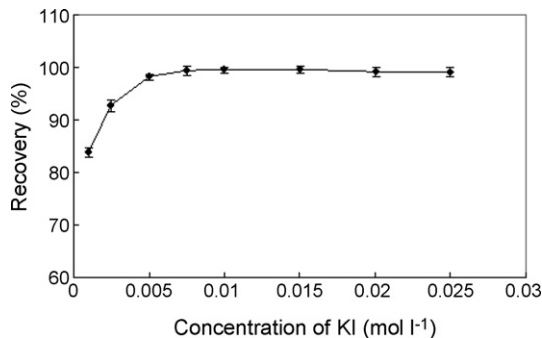
Fig. 2. Effect of the potassium iodide concentration on the recovery of cadmium from the membrane disk. *Conditions*: cadmium, 10 μg; sample volume 100 ml; sample pH 5; eluent, 10 ml of $1\,mol\,l^{-1}$ nitric acid in ethanol; sample flow rate $20\,ml\,min^{-1}$, and eluent flow rate, $2\,ml\,min^{-1}$.

Table 1
Percent recovery of cadmium from modified disk using different stripping solutions as a function of stripping solutions and volume of eluent

| Stripping solution	Volume (ml)		
	5	10	15
HCl (1 mol l^{-1})	19.8 ± 0.1	36.5 ± 0.1	52.5 ± 0.7
CH$_3$COOH (1 mol l^{-1})	35.6 ± 0.8	61.9 ± 0.6	65.1 ± 0.9
HNO$_3$ (1 mol l^{-1})	28.1 ± 0.7	49.8 ± 0.4	60.5 ± 0.5
HNO$_3$ (2 mol l^{-1})	72.3 ± 0.6	85.5 ± 1.2	90.4 ± 1.0
HNO$_3$ (1 mol l^{-1}) in EtOH	84.3 ± 0.9	100.1 ± 0.9	–

titative above 12 mg of the surfactant. Therefore, for subsequent extractions, the disk was modified with 15 mg of the surfactant.

Potassium iodide was added to the solution containing Cd^{2+} to form CdI_4^{2-}. The effect of its concentration in the range of 1×10^{-3} to 2.5×10^{-2} mol l^{-1} on the retention of 10 µg cadmium from 100 ml of aqueous sample by the modified disk was studied. The results showed that cadmium recovery increased with sodium iodide concentration up to 7.5×10^{-3} mol l^{-1} and level off at higher concentration (Fig. 2). Hence, 1×10^{-2} mol l^{-1} was selected as optimum concentration for further studies.

In order to choose the most effective eluent for quantitative stripping of the cadmium retained by the disk, various eluents such as nitric acid, hydrochloric acid, acetic acid, and acidified ethanol were tested. After the extraction of 10 µg of cadmium in 100 ml of solutions by the modified disk, the cadmium was stripped with varying volumes of different concentrations of eluents. From the data given in Table 1, it is obvious that 10 ml of 1 mol l^{-1} nitric acid in ethanol can strip the retained cadmium ions quantitatively.

The influence of pH of aqueous samples on the recovery of 10 µg of Cd^{2+} from 100 ml solutions was studied in the pH range of 1.0–8.0. The pH was adjusted by either diluted nitric acid or sodium hydroxide solution. The sample was passed through the modified membrane disk and the deposited cadmium was eluted with 10 ml of 1 mol l^{-1} nitric acid in ethanol. It was found that the retention of cadmium is quantitative in the pH range of 1.0–8.0. The pH values (>8.0) were not tested because of the possibility of hydrolysis of the octadecyl silica in the disks.

The influence of sample flow rate on the retention of cadmium ion was investigated by processing 100 ml of the solution containing 10 µg of Cd through the modified membrane disk at different flow rate (Fig. 3). It was found that, in the range of 10–60 ml min^{-1}, the retention of cadmium by the membrane disk was not considerably affected by the sample solution flow rate. The effect of the eluent flow rate on the recovery of cadmium was also studied.
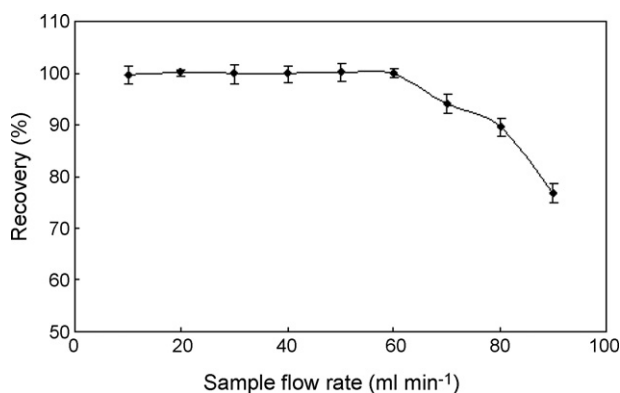
Table 2
Effect of foreign ions in binary mixtures on percent recovery of 2.5 µg cadmium from 100 ml of sample[a]

Foreign metal ion	Amount taken (M^{n+}/Cd^{2+})	Recovery (%)
Na$^+$	5000	99.3 ± 1.1
K$^+$	5000	99.2 ± 0.8
Mg^{2+}	5000	100.1 ± 1.6
Ca^{2+}	3000	98.4 ± 1.5
Co^{2+}	900	99.5 ± 1.0
Zn^{2+}	500	97.2 ± 1.6
Fe^{3+}	1000[a]	99.6 ± 0.6
Bi^{3+}	100	98.9 ± 1.2
Hg^{2+}	100	99.4 ± 1.4
Cu^{2+}	400	98.6 ± 1.3
Pb^{2+}	500	97.8 ± 1.1
Ni^{2+}	2000	99.2 ± 0.9
Mn^{2+}	2000	99.6 ± 1.2
Cl$^-$	3000	99.2 ± 0.9
PO$_4^{3-}$	1000	99.6 ± 1.2
SCN$^-$	2000	98.7 ± 2.1
SO$_4^{2-}$	1000	99.1 ± 1.0

[a] Masked with F$^-$ (3 ml 5% NaF).

The maximum recovery was achieved at flow rates between 1 and 4 ml min^{-1}, with 10 ml of eluent. At higher flow rates, quantitative stripping of cadmium needed larger volumes of eluent.

3.1. Analytical performance

The breakthrough volume of the sample solution was tested by processing 10 µg of cadmium in different volumes of water (200–1300 ml) according to recommended procedure under optimum conditions. The results showed that up to 1000 ml, the extraction by the modified membrane disk was quantitative. Thus the breakthrough volume of the method is 1000 ml. Consequently, by considering the final elution volume of 10 ml and the breakthrough volume of 1000 ml, a concentration factor of 100 was calculated.

The limit of detection (LOD) of the proposed method for the determination of cadmium was studied under the optimal experimental conditions. The LOD was calculated as LOD $= kS_b/m$, where k is equal to 3 according to the desired confidence level (95%), S_b is the standard deviation of the blank signal and m is the slope of the analytical curve. The LOD was found to be 0.014 ng ml^{-1}.

The reproducibility of the proposed method for the extraction and determination of 2.5 µg cadmium from 1000 ml water was investigated and for 8 replicate measurements a R.S.D. of 1.2% was obtained.

The maximum capacity of the membrane disk modified with 15 mg of surfactant was determined by processing 100 ml of an aqueous solution containing 2000 µg of cadmium, followed by the

Fig. 3. The effect of sample flow rate on the recovery of cadmium from 100 ml of water by modified membrane disk. *Conditions*: cadmium, 10 µg; sample volume 100 ml; sample pH 5; iodide concentration, 1×10^{-2} mol l^{-1}; eluent, 10 ml of 1 mol l^{-1} nitric acid in ethanol and eluent flow rate, 2 ml min^{-1}.

Table 3
Determination of cadmium in water samples (sample volume, 1000 ml)

Sample	FAAS		GF-AAS	
	Added (µg l^{-1})	Found[a] (µg l^{-1})	Recovery (%)	(µg l^{-1})[a]
Tap water	0	0.74 ± 0.01	–	0.75 ± 0.02
	5	5.71 ± 0.15	99.4	–
Sea water	0	3.92 ± 0.08	–	3.94 ± 0.12
	5	8.86 ± 0.18	98.8	–
Well water	0	2.55 ± 0.05	–	2.54 ± 0.11
	5	7.51 ± 0.23	99.2	–
River water	0	0.66 ± 0.03	–	0.67 ± 0.04
	5	5.67 ± 0.15	100.2	

[a] Mean and standard deviation of three determinations.

Table 4
Comparative data from some reported SPE methods for FAAS determination of cadmium

Sorbent	Reagent	pH	PF	DL ($\mu g\,l^{-1}$)	Reference
Silica gel	DHAQ	6.0–8.0	200	0.62	[25]
Amberlite XAD-4	ABA	4.0–6.0	400	–	[26]
Chromosorb-106	PAN	8.0–9.0	250	0.19	[27]
Silica gel	Cupferron	4.0–6.0	30	0.5	[28]
Naphthalene	1-BPzDC	4.0–6.0	500	34	[29]
Dowex Optipore V-493	DBDTC	1.0–6.0	50	0.43	[30]
Alumina	PAN	9.5–10.5	100	0.024	[31]
Activated carbon	KPPzDC	5.0–9.0	400	11	[32]
Activated carbon	MTB	9	1000	1	[15]
Chelex-100	Chelex-100	7	50	0.017	[33]
Naphthalene	Iodide	1.2–10	40	0.6	[34]
Benzophenone	DBQ	6–8	400	0.1	[12]
Poly-Cd-DAAB-VP	DAAB	6–8	200	0.093	[35]
Chromosorb-108	BCDSA	8–9.5	80	0.24	[36]
C_{18} membrane disk	MTOAC	1.0–8.0	100	0.014	Present work

PF: preconcentration factor; DL: detection limit; DHAQ: 1,8-dihydroxyanthraquinone; ABA: *o*-aminobenzoic acid; PAN: 1-(2-pyridylazo)2-naphthol; 1-BPzDC: 1-benzylpiperazinedithiocarbamate; DAAB: diazoaminobenzene; BCDSA: bathocuproinedisulfonic acid; DBQ: 5,7-dibromoquinolne-8-ol; DBDTC: dibenzyldithiocarbamate; KPPzDC: potassium phenylpiperazine dithiocarbamate; MTB: methyl thymol blue; MTOAC: methyltrioctylammonium chloride.

determination of the retained cadmium on the disk using FAAS. The maximum capacity of the disk was found to be $626 \pm 7\,\mu g$ of Cd^{2+}.

3.2. Effect of foreign ions

The effects of various foreign ions on the determination of $2.5\,\mu g$ cadmium from 100 ml of solution were investigated under the optimum conditions. Table 2 shows the tolerance limits with a relative error of less than 5%. As can be seen the effect of various ions are negligible and cadmium can be determined quantitatively in real samples without interference from the matrix ions of the sample.

3.3. Application

The proposed method was applied to the determination of cadmium in tap water, sea water, well water and river water. The samples were first filtered through a Millipore $0.45\,\mu m$ pore-size membrane into cleaned polyethylene bottles and were treated according to the given procedure. Reliability of the method was checked by spiking experiment and comparing the results with data obtained by graphite furnace atomic absorption spectrometry. The results are given in Table 3. It can be seen that the method gives good recoveries of added cadmium ions, and at 95% confidence level there is good agreement between the results and data obtained by GFAAS.

Furthermore, the procedure was applied to the determination of cadmium in two different certified reference waters, TM-15 and TM-DWS.2 (Measurement Standard Laboratories, Lower Hutt, New Zealand) with cadmium concentration of 13.20 and $4.20\,\mu g\,l^{-1}$, respectively. The amount of cadmium in TM-15 and TM-DWS.2 was found to be 13.35 ± 0.23 and $4.20 \pm 0.12\,\mu g\,l^{-1}$, respectively. Results were in agreement with the certified values, indicating the suitability of the method for water samples.

4. Conclusions

A simple, sensitive and selective method was developed for the preconcentration of cadmium in water samples. Cadmium as CdI_4^{2-} can be adsorbed on the octadecyl silica membrane disk modified with methyltrioctylammonium chloride even in the presence of high concentration of foreign ions. Moreover, the procedure can be performed over a wide range of pH (1–8) and no buffer is required; which minimizes the possibility of contamination. Comparative data from some recent reported SPE methods for FAAS

determination of cadmium are given in Table 4 [25–36]. As it can be seen, the present method has several advantages such as wider pH range and lower detection limit. Furthermore, the preparation of the modified disk is very simple and the reagents used in this work are environmentally safe and less expensive. Although no improvement in the preconcentration factor is observed, but in term of selectivity and the speed of analysis, the proposed method is superior to the reported methods.

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