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Solid-phase extraction and determination of ultra trace amounts of lead, mercury and cadmium in water samples using octadecyl silica membrane disks modified with 5,5'-dithiobis(2-nitrobenzoic acid) and atomic absorption spectrometry

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Solid-phase extraction and determination of ultra trace amounts of lead, mercury and cadmium in water samples using octadecyl silica membrane disks modified with 5,5'-dithiobis(2-nitrobenzoic acid) and atomic absorption spectrometry

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A simple and fast method for preconcentration and determination of ultra trace amounts of lead(II), mercury(II) and cadmium(II) in water samples is presented. Lead, mercury and cadmium adsorbed quantitatively during passage of water samples (pH = 7, flow rate = 20 mL min⁻¹) through octadecyl silica membrane disks modified with 5,5'-dithiobis(2-nitrobenzoic acid). The retained lead, mercury and cadmium are then stripped from the disk with a minimal amount of 1 M hydrochloric acid solution as eluent, and determined by atomic absorption spectrometry. The influence of flow rates of the eluent and sample solution, the amount of ligand, type and least amount of eluent, pH of sample, effect of other ions and breakthrough volume are determined. The breakthrough volume of the method is greater than 2000 mL for lead and greater than 1500 mL for mercury and cadmium, which results in an enrichment factor of 200 for lead and an enrichment factor of 150 for both mercury and cadmium. The limit of detection of the proposed method is 177, 2 and 13 ng l⁻¹ for lead, mercury and cadmium, respectively.

Keywords: lead; mercury; cadmium; preconcentration; octadecyl silica membrane disks; atomic absorption spectrometry

1. Introduction

Environmental pollution monitoring requires determination of toxic heavy elements in trace and ultra trace levels. Among the toxic heavy metals lead, mercury and cadmium are of major interest in environmental protection due to their cumulative toxicity and well-known health risk to animals and humans [1,2]. The atomic absorption spectrometry (AAS) technique [3,4], which is one of the most common methods employed for the determination of metals in solutions, suffers from poor sensitivity in the determination of heavy elements in environmental samples like natural water and other real samples. This drawback can be overcome by a combination of a suitable preconcentration technique

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with subsequent AAS determination. The most common preconcentration methods that can be used for water samples are solvent extraction [5,6], coprecipitation [7,8], ion exchange and chelating resin [9,10] and cloud point extraction [11,12].

These preconcentration methods provide low detection limits and also help to avoid matrix interferences in the analysis of real samples. Solid-phase extraction (SPE) for the analysis of trace concentrations of heavy metals in water samples has received much attention in recent years. This technique reduces solvent usage and exposure, disposal costs, and extraction time [11,12].

Various adsorbents, such as octadecyl functional groups bonded on silica gel, C18 [13–15], glycerol-silica gel [16], chelating adsorbents [17–19], Amberlite XAD resins [20,21], Chromosorb resins [22–24] and other sorbents [25,26] have been used for adsorption of metal chelates in the preconcentration and separation of heavy metal ions.

Octadecyl-bonded silica (ODBS) membrane disks have been utilized for the extraction and analysis of many different organic and environmental matrices [27,28]. Moreover, these membrane disks modified by suitable ligands can be successfully used for the separation and sensitive determination of metal ions [29–32].

In this study, we used 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB) as a suitable modifier for octadecyl silica membrane disks, which exhibits significantly high selectivity to lead, mercury and cadmium ions over alkali, alkaline earth and several transition metal ions. The aim of this work was to develop a rapid and efficient method for the selective extraction, preconcentration and determination of lead, mercury and cadmium ions in water samples using octadecyl silica membrane disks modified with 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB), and atomic absorption spectrometry. Different experimental conditions, e.g. the type and volume of eluting solvent, the effect of pH, the effect of sample and eluent flow rates and the amount of DTNB, on the extraction efficiency and breakthrough volume, limit of detection and maximum capacity of the disks for lead, mercury and cadmium ions recovery have been studied.

2. Method

2.1 Reagents

Extra pure methanol, dimethylsulfoxide, nitric acid, hydrochloric acid, acetic acid (all from Merck, Germany) were used as received. The nitrate or chloride salts of the cations used (all from Merck, Germany) were of the highest purity available and used without any further purification, except for vacuum drying over P_2O_5 .

Reagent grade 5,5'-dithiobis(2-nitrobenzoic acid) (Aldrich, USA) was used as received. Doubly distilled deionized water was used throughout. The standard stock solution of lead(II) ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving 1.598 g of lead nitrate, $\text{Pb}(\text{NO}_3)_2$, in 10 mL of 5 M HNO_3 and dilution to 1000 mL with water. The standard stock solution of mercury(II) ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving 1.3535 g of HgCl_2 in 5 mL concentrate HNO_3 , and dilution to 1000 mL with water. The standard stock solution of cadmium(II) ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving 1.0000 g of cadmium metal (analytical reagent grade) in 20 mL of 5 M HCl and dilution to 1000 mL with water. Working solutions were prepared by appropriate dilution of the stock solution with water.

Table 1. Parameters for AAS determination of lead, mercury and cadmium.

	Pb	Hg	Cd
Wavelength (nm)	217.0	253.7	228.8
Slit width (nm)	1.0	0.5	0.5
Lamp current (mA)	5.0	3.0	3.0

2.2 Apparatus

The determination of all cations was performed on a GBC 932 Plus atomic absorption spectrometer (Australia). The determination of lead and cadmium was carried out using an adjusted air-acetylene flame. Mercury determination was done by cold vapor atomic absorption spectrometry (CVAAS). The analytical parameters for the AAS determinations of lead, mercury and cadmium are presented in Table 1. The AAS determination of all other cations was performed under the recommended conditions for each metal. A Metrohm model 744 digital pH meter equipped with a combined glass-calomel electrode (Netherlands) was used for the pH adjustments.

Extractions were performed with 47 mm diameter \times 0.5 mm thickness Empore membrane disks containing octadecyl-bonded silica (8 μ m particles, 6 nm pore size) distributed by VWR Scientific. The typical composition of the disks was 90% w/w octadecyl-bonded silica and 10% w/w PTFE fibers. The disks were used in conjunction with a standard Sartorius 47 mm filtration apparatus (Germany).

2.3 Sample extraction

In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, disk cleaning and conditioning were done prior to use. Thus, after placing the membrane disk in the filtration apparatus, 10 mL methanol was poured onto the disk and immediately drawn through it by applying a slight vacuum. After all of the solvent passed through the disk, the disk was dried by passing air through it for a few minutes. Disk conditioning was then begun by pouring 10 mL methanol onto the 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. Note that the disk should not be allowed to soak without vacuum, and no air should be allowed to contact the surface of the disk. Immediately 20 mL water was introduced onto the disk and drawn through it. The disk was then dried under vacuum for 5 min (or longer, if necessary). Then a solution of 5 mg DTNB dissolved in 2 mL DMSO was introduced into the reservoir of the apparatus and drawn slowly through the disk by applying a slight vacuum, until the ligand penetrated the membrane completely. Finally, the disk was washed with 25 mL water and dried by passing air through it. The membrane disk modified by DTNB was now ready for sample extraction.

The general procedure for the extraction of Pb^{2+} , Hg^{2+} and Cd^{2+} ions on the modified membrane disk was as follows. The disk was first washed with 25 mL water. This step pre-wets the surface of the modified disk prior to ion extraction. Then 50 mL of the sample solution containing 10 μ g Pb^{2+} , 5 μ g Cd^{2+} and 1 μ g Hg^{2+} (pH = 7), was passed

Table 2. Percent recovery of lead, mercury and cadmium from the modified membrane disk using different stripping acid solutions^a.

% Recovery												
20 mL			15 mL			10 mL			5 mL			Stripping acid solution
Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	
100	96	100	100	92	94	100	86	85	78	74	77	HCl (0.1 M)
100	100	100	100	100	100	100	100	100	83	80	84	HCl (1 M)
95	93	97	89	89	91	77	84	83	68	69	76	HNO ₃ (0.1 M)
100	100	100	100	100	100	92	90	100	78	77	81	HNO ₃ (1 M)
77	84	66	76	79	64	75	73	60	63	60	49	CH ₃ COOH (0.1 M)
80	90	86	79	86	85	77	80	82	66	67	67	CH ₃ COOH (1 M)

Notes: Conditions: sample volume, 50 mL; pH, 7; amounts of DTNB, 5 mg; flow rate, 20 mL min⁻¹.
^aInitials samples contained 10 µg Pb²⁺, 5 µg Cd²⁺ and 1 µg Hg²⁺ in 50 mL water.

through the membrane (flow rate = 20 mL min⁻¹). After extraction, the disk was dried completely by passing air through it for a few minutes. The extracted lead, mercury and cadmium were then stripped from the membrane disk using 10 mL of a 1 M solution of hydrochloric acid (flow rate = 5 mL min⁻¹) into a 10.0 mL volumetric flask. The lead and cadmium concentrations were determined by flame atomic absorption spectrometry, and the mercury concentration was determined by cold vapor atomic absorption spectrometry. It is interesting to note that the reagent DTNB is quite stable in acidic solutions; it was sparingly washed out from the surface of the disks with the eluent. Thus, each modified disk could be used at least 10 times.

3. Results and discussion

The sulphur donor atoms are well known to coordinate strongly with heavy metal ions [33,34]. Due to its negligible solubility in water and the existence of two donating sulphur atoms in its structure, DTNB seemed to be a suitable reagent for solid phase extraction and preconcentration of heavy metal ions using octadecyl silica membrane disks.

Some preliminary experiments were carried out in order to investigate the quantitative retention of lead, mercury and cadmium ions by the membrane disks in the absence and presence of DTNB. It was found that the disks modified with 5 mg of the ligand are capable of quantitatively retaining Pb²⁺, Hg²⁺ and Cd²⁺ ions from solutions, while the bare membrane disk can not retain cations.

3.1 Choice of eluent

In order to choose a proper eluent for the retained Pb²⁺, Hg²⁺ and Cd²⁺ ions, after extraction by the modified disks, the ions were stripped with different volumes of varying concentrations of different acids (Table 2). From the data provided in Table 2, it is clear that among the three different acid solutions used, 10 mL of 1 M hydrochloric acid can accomplish the quantitative elution of lead, mercury and cadmium from the membrane disk, while 10 mL of each of the other acids used are ineffective for the complete simultaneous elution of lead, mercury and cadmium.

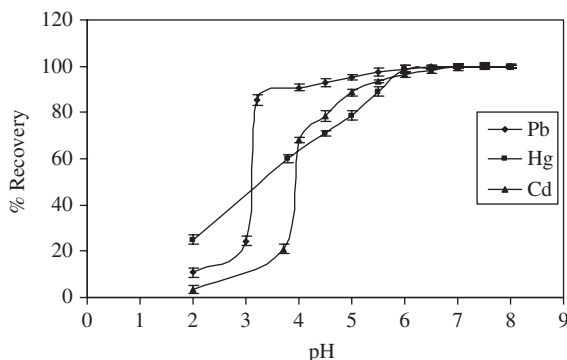


Figure 1. Effect of pH of sample solutions on extraction efficiency of Pb^{2+} , Hg^{2+} and Cd^{2+} ions ($n=3$). Conditions: sample volume, 50 mL; amounts of DTNB, 5 mg; eluent, 10 mL of 1.0 M HCl; flow rate, 20 mL min^{-1} .

3.2 Effect of flow rate

The effect of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of lead, mercury and cadmium was investigated. It was found that, in the range of $5\text{--}20 \text{ mL min}^{-1}$, the retention of lead, mercury and cadmium by the membrane disk is not affected by the sample solution flow rate. On the other hand, quantitative stripping of Pb^{2+} , Hg^{2+} and Cd^{2+} ions from the disk was achieved in a flow rate range of $0.5\text{--}5 \text{ mL min}^{-1}$, using 10 mL of 1 M hydrochloric acid. At higher flow rates, quantitative stripping of lead, mercury and cadmium required larger volumes of 1 M HCl.

3.3 Effect of pH

Most chelating ligands are conjugate bases of weak acid groups and, accordingly, have a very strong affinity for hydrogen ions. The pH of the sample solution is a very important factor in the separation of metal ions by chelation, and determines the values of the conditional stability constants of the metal complexes on the surface of the sorbent. Due to the presence of two carboxylic acid groups on the DTNB structure, it was expected that the extent of its complexation is sensitive to pH. Thus, the effect of pH on the extraction of lead, mercury and cadmium ions was studied.

To do this, the pH of aqueous samples containing $10 \mu\text{g Pb}^{2+}$, $5 \mu\text{g Cd}^{2+}$, and $1 \mu\text{g Hg}^{2+}$ was varied from 2.0 to 8.0. The pH was adjusted by using 0.1 M of nitric acid and potassium hydroxide solutions. The resulting percent recovery versus pH plot is shown in Figure 1, and indicates that the Pb^{2+} , Hg^{2+} and Cd^{2+} ions can be retained quantitatively by the membrane disk in the pH range 7.0–8.0. Higher pH values (>8) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.

3.4 Effect of amount of ligand

In order to investigate the optimum amount of DTNB for the quantitative extraction of lead, mercury and cadmium by the membrane disk, extraction of $10 \mu\text{g Pb}^{2+}$, $5 \mu\text{g Cd}^{2+}$ and $1 \mu\text{g Hg}^{2+}$ from 50 mL sample solutions under the optimal experimental conditions was conducted by varying the amount of ligand from 0 to 8 mg (Figure 2). As seen, the

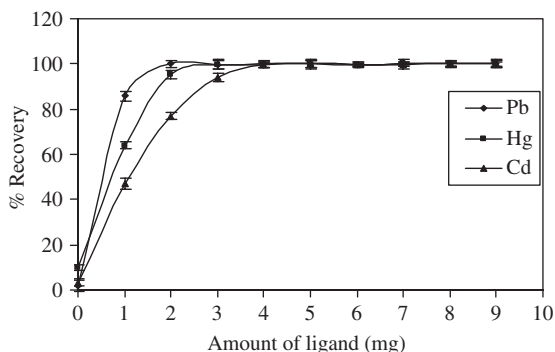


Figure 2. Effect of amounts of DTNB on extraction efficiency of Pb^{2+} , Hg^{2+} and Cd^{2+} ions ($n=3$). Conditions: sample volume, 50 mL; pH, 7; eluent, 10 mL of 1.0 M HCl; flow rate, 20 mL min^{-1} .

extraction of lead, mercury and cadmium is quantitative above 4 mg of the DTNB ligand. Hence, subsequent SPE experiments were carried out with 5 mg of the ligand.

3.5 Analytical performance

The measurement of breakthrough volume is important in solid-phase extraction because it represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample.

The breakthrough volume of the sample solution was examined by passing 50, 100, 250, 500, 750, 1000, 1500, 2000 and 2500 mL water containing 10 μg Pb^{2+} , 5 μg Cd^{2+} and 1 μg Hg^{2+} ions through the modified membrane, and the recommended procedure under optimal conditions was followed. The results showed that, in the case of lead up to 2000 mL, and in the cases of mercury and cadmium up to 1500 mL, extraction by membrane was quantitative. Thus, the breakthrough volume of the proposed method for lead should be greater than 2000 mL, and for mercury and cadmium should be greater than 1500 mL. Consequently, by considering the final elution of 10 mL and the sample solution volume, an enrichment factor of 200 was achievable for lead and the enrichment factor of 150 was achievable for mercury and cadmium.

The maximum capacity of the membrane disk modified by 5 mg of DTNB for each cation was determined by passing 50 mL portions of an aqueous solution containing 2000 mg cation through the disk, followed by determination of the retained metal ions using AAS. The maximum capacity of the membrane disk for lead, mercury and cadmium was found to be 480, 435 and 357 μg , respectively.

The limit of detection (LOD) of the proposed method for the determination of lead, mercury and cadmium was studied under the optimal experimental conditions. The LOD based on 3σ of the blank [35] is 0.177, 0.002 and 0.013 $\mu\text{g L}^{-1}$ for lead, cadmium and mercury, respectively.

The reproducibility of the proposed method for the extraction and determination of 10 μg lead, 5 μg cadmium and 1 μg mercury from 50 mL water was also studied. The results obtained on 10 replicate measurements revealed an RSD of 2%.

The effect of other cations on the determination of lead, mercury and cadmium was studied by adding a known quantity of the desired ion to a 50 mL aliquot of aqueous solution containing 10 μg lead, 5 μg cadmium and 1 μg mercury, and the recommended

Table 3. Separation of lead, mercury and cadmium from binary mixtures in the presence of different diverse ions^a.

% Recovery of Cd ²⁺	% Recovery of Hg ²⁺	Recovery of Pb ²⁺	Amount taken (mg)	Diverse ion
99.3 (0.9)	99.7 (0.6)	99.4 (0.6) ^b	20.0	Na ⁺
99.5 (1.5)	99.5 (1.2)	99.1 (0.8)	20.0	K ⁺
98.9 (1.0)	98.8 (1.5)	98.9 (1.1)	10.0	Ca ²⁺
99.0 (1.2)	99.3 (1.3)	99.5 (1.0)	10.0	Mg ²⁺
97.7 (1.8)	99.6 (0.7)	99.8 (1.6)	5.0	Fe ³⁺
98.3 (1.2)	98.3 (1.4)	98.6 (1.4)	5.0	Mn ²⁺
97.3 (1.9)	98.6 (1.3)	98.7 (1.6)	2.0	Ni ²⁺
96.7 (1.8)	99.2 (1.0)	97.3 (2.1)	2.0	Co ²⁺
98.5 (1.6)	99.1 (0.8)	98.4 (2.5)	1.0	Cu ²⁺
95.3 (2.2)	98.5 (1.3)	99.1 (1.5)	1.0	Zn ²⁺

Notes: Conditions: sample volume, 50 mL; pH, 7; amounts of DTNB, 5 mg; eluent, 10 mL of 1.0 M HCl; flow rate, 20 mL min⁻¹.

^aInitials samples contained 10 µg Pb²⁺, 5 µg Cd²⁺ and 1 µg Hg²⁺ and different amounts of diverse ions in 50 mL water.

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

Table 4. Recovery of 10 µg Pb²⁺, 5 µg Cd²⁺ and 1 µg Hg²⁺ added to 500 mL solution of the synthetic and water samples.

% Recovery of Cd ²⁺	% Recovery of Hg ²⁺	% Recovery of Pb ²⁺	Sample
98.3 (0.8)	99.3 (1.7)	100.1 (1.5) ^a	Synthetic sample 1 (Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , 5 mg of each cation)
95.8 (2.1)	98.4 (0.9)	98.7 (1.4)	Synthetic sample 2 (Ni ²⁺ , Co ²⁺ , Cu ²⁺ , Zn ²⁺ , 0.5 mg of each cation)
98.5 (1.7)	99.7 (1.2)	101.3 (2.5)	Tap water
97.8 (0.9)	100.0 (1.3)	99.9 (1.6)	Well water
98.9 (1.9)	99.3 (1.1)	99.6 (2.3)	Spring water

Notes: Conditions: sample volume, 500 mL; pH, 7; amounts of DTNB, 5 mg; eluent, 10 mL of 1.0 M HCl; flow rate, 20 mL min⁻¹.

Values in parentheses are RSDs based on three replicate analyses.

procedure was followed. The results obtained are summarized in Table 3, and show that the lead, mercury and cadmium ions are retained almost completely by the modified membrane disk. It is interesting to note that, with the exception of Cu²⁺ and Zn²⁺ ions, the retention of other cations by the modified disk is low, and they can be separated from the Pb²⁺, Hg²⁺ and Cd²⁺ ions.

The applicability of the method to real samples was examined by its use in separation and recovery of Pb²⁺, Hg²⁺ and Cd²⁺ from 500 mL of five different synthetic and water samples; the results are summarized in Table 4. As is evident, the lead, mercury and cadmium ions added can be quantitatively recovered from the synthetic and water matrices.

3.6 Comparison with other solid-phase extraction methods

The comparative data from some recent papers on solid-phase extraction of trace heavy metal ions on the various adsorbent for the figure of the merits are summarized

Table 5. Comparative data from some recent studies on solid-phase extraction of heavy metal ions.

Analytes	Complexing agent	Absorbent	Eluent	Enrichment factor	Detection limit ($\mu\text{g l}^{-1}$)	RSD (%)	Reference
Pb, Cd	Na-dibenzylthiocarbamate	Dowex Optipore V-493	1 mol L^{-1} HNO_3 in acetone	50	0.43, 0.65	<5	[36]
Pb, Cu	Diethyldithiophosphate	Polychlorotrifluoroethylene	Isobutyl methyl ketone	250	0.07, 2.0	<2.2	[37]
Pb	4-(4-methoxybenzylidene)thiophenole	Alumina-sodium dodecyl sulfate	1 mol L^{-1} HNO_3 in acetone	200	1.6	<0.9	[38]
Cr, Pb	Ammonium pyrrolidine dithiocarbamate	Poly-chlorotrifluoroethylene	Isobutyl methyl ketone	94, 220	0.4, 1.2	<2.1	[39]
Pb, Ni	EDTA	Ambersorb-572	1 mol L^{-1} HNO_3	50, 75	1.42, 3.65	<2	[40]
Cu, Cd, Pb, Bathocuproinedisulfonic acid		Chromosorb 108	2 mol L^{-1} HNO_3	80	0.18, 0.24, 0.60, 0.27, 0.33, 0.20, 0.50, 0.44, 0.25	<5	[22]
Zn Mn, Fe, Cr, Ni, Co							
Cd, Cu	2-Aminothiophenol	Amberlite XAD-2	0.5 mol L^{-1} HCl	14, 28	0.14, 0.54	<5	[41]
Hg	Isopropyl 2-[(isopropoxycarbonyl)disulfanyl]ethane thioate	Octadecyl silica	0.5 mol L^{-1} HBr	150	0.005	<1	[42]
Pb, Hg, Cd	5,5'-dithiobis (2-nitrobenzoic acid)	Octadecyl silica	1 mol L^{-1} HCl	200, 150	0.177, 0.002, 0.013	<2	Present work

in Table 5. The preconcentration factors of the octadecyl silica membrane disks modified with 5,5'-dithiobis(2-nitrobenzoic acid) for Pb^{2+} , Hg^{2+} and Cd^{2+} ions is better than many of the methods given in Table 5. Only for Pb, adsorption as diethyldithiophosphate and ammonium pyrrolidine dithiocarbamate complexes on polychlorotrifluoroethylene shows better preconcentration factor values than the present study. Similarly, the detection limits of proposed method are the highest compared with various solid phase extraction procedures excepting diethyldithiophosphate-polychlorotrifluoroethylene. The elution was easily performed with 10 ml of 1 M HCl and there is no need to use any organic solvent for desorption of metal ions (as is needed in some cases). The lower acid concentration required for desorption of metal ions avoids the requirement of further dilution for AAS measurement and is among the advantages of the present adsorbent, which also does not suffer from leaching problems. The low matrix effects, as evident from the tap and well water sample analyses, good tolerance towards many foreign ions and low values of relative standard deviations are additional advantages of the present adsorbent. To summarize: the octadecyl silica membrane disks modified with 5,5'-dithiobis(2-nitrobenzoic acid) appears to be a promising metal ion collector for lead, mercury and cadmium ions.

4. Conclusions

The proposed SPE method based on octadecyl silica membrane disks modified with DTNB is a simple, rapid, selective and reproducible method for the separation, preconcentration and determination of lead, mercury and cadmium ions. The RSD of the method is about 2%, and the time taken for the separation and analysis of lead, mercury and cadmium from a 500 mL sample is at most 40 min. The method can be successfully applied to the separation and determination of lead, mercury and cadmium in real samples.

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