



Solid phase extraction of lead and cadmium using solid sulfur as a new metal extractor prior to determination by flame atomic absorption spectrometry

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ABSTRACT

A new method using a mini-column packed with sulfur as a new solid phase extractor has been developed for simultaneous preconcentration of lead and cadmium in water samples prior to flame atomic absorption spectrometric determinations. The effects of various parameters such as pH, flow rate of sample and eluent, type and concentration of eluent, sample volume, amount of adsorbent and interfering ions have been studied. The calibration graph was linear in the range of 10–300 and 1–20 ng mL⁻¹ for lead and cadmium, respectively. The limit of detection based on three times the standard deviation of the blank ($3S_b$) was 3.2 and 0.2 ng mL⁻¹ ($n = 10$) for lead and cadmium, respectively. A preconcentration factor of 250 was achieved in this method. The proposed procedure was applied to the determination of metal ions in tap, river and wastewater samples.

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1. Introduction

Solid phase extraction (SPE) as a preconcentration-separation technique coupled with flame atomic absorption spectrometric (FAAS) has been applied for determination of trace heavy metals in water (tap, river, sea and industrial), soil, food, pharmaceutical, marine sediment and biological samples [1–7]. FAAS is one of the most popular techniques for determination of metal ions because of its high specificity and low cost. However its sensitivity is usually insufficient for determination of trace metal ions in environmental samples. In order to overcome this problem and prevent interference effects, the method usually requires an efficient preconcentration step [8,9].

Many methods, either on-line or batch systems, have been developed for the preconcentration of trace metals from various samples, including coprecipitation [10–13], liquid–liquid extraction [14–17], solid phase extraction [18–20] and cloud point extraction [21–24]. Among these techniques, SPE is one of the most important preconcentration methodologies because of its simplicity, flexibility to choose the solid phase, high preconcentration factor, low consumption of the organic solvents, low cost and extraction time for sample preparation [25–32].

Nowadays, investigation for finding new materials as solid phase extractor is an important issue to preconcentrate transition metals

at trace levels. In the present paper, a simple SPE procedure has been developed using a mini-column loaded with sulfur as a new non-toxic and low cost adsorbent for simultaneous preconcentration of Pb(II) and Cd(II). The optimum analytical conditions for quantitative recoveries of metal ions were investigated.

2. Experimental

2.1. Instrumentation

A Chemtech Analytical Instrument model CTA-3000 (Bedford, England) atomic absorption spectrometer with air–acetylene flame and lead and cadmium hollow cathode lamps were used for analysis. All instrumental settings were those recommended by the manufacturer. The selected wavelengths for the determination of lead and cadmium were 283.23 and 228.78 nm, respectively. pH adjustments were carried out by Metrohm model 632 (Herisau, Switzerland) pH-Meter. A Shimadzu (Kyoto, Japan) rotary oil vacuum pump type SA18 and a Metrohm model E649 (Switzerland) stirrer were used.

2.2. Reagents

All chemicals were analytical reagent grade and all solutions were prepared with doubly distilled water. A stock solution of 1000 µg mL⁻¹ of lead was prepared by dissolving 0.1599 g of Pb(NO₃)₂ (Merck, Darmstadt, Germany) in water and diluting to 100 mL in a volumetric flask. A stock solution of 1000 µg mL⁻¹ of

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cadmium was prepared by dissolving 0.2282 g of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (Merck) in water and diluting to 100 mL in a volumetric flask. More dilute solutions were prepared daily and standardized using EDTA titration [33]. pH adjustments were performed with $0.01\text{--}1.0\text{ mol L}^{-1}$ HCl and NaOH solutions. A phosphate buffer pH 8 was prepared by mixing appropriate volumes of 0.026 mol L^{-1} solution of NaH_2PO_4 with 0.16 mol L^{-1} solution of Na_2HPO_4 .

2.3. Column preparation

2.5 g sulfur (Merck) particle size $<40\ \mu\text{m}$ and purity $>99\%$ was slurried and conditioned in about 5 mL of methanol to wet and convert sulfur to a more colloidal form with higher surface area and then packed in a glass column (10 cm long and 0.7 cm internal diameter). A small amount of glass wool was used to prevent adsorbent leakage. The column was connected to a vacuum pump via a büchner system.

2.4. Sampling

Water samples were collected from three main sources: (1) tap water which provides drinking water for Ahvaz (in Iran), (2) Karoon river water which supplies water to Ahvaz and (3) wastewater from petrochemical industries. Water samples were acidified with 5 mL of nitric acid and stored in polyethylene bottles that were thoroughly washed with detergent, tap water and distilled water. The water samples were kept in the refrigerator and filtered prior to analytical procedure.

2.5. Preconcentration procedure

An off-line column procedure was applied for the preconcentration process. Hundred millilitres of solutions containing $10\text{--}300\text{ ng mL}^{-1}$ of lead, $1\text{--}20\text{ ng mL}^{-1}$ of cadmium and 2 mL of phosphate buffer (pH 8) was passed through the column at a flow rate of 3 mL min^{-1} using a vacuum pump via a büchner system. The retained metal ions were eluted from the column by 2 mL of 1 mol L^{-1} of HNO_3 in methanol solution and the concentrations of metal ions were determined by FAAS. A blank solution was also run under the same conditions without adding the analytes.

3. Results and discussion

Sulfur exists in different forms at room temperature. Colloidal sulfur usually contains a mixture of different chemical species. It has been shown that colloidal sulfur can contain polythionates of the formula $\text{SO}_3^- \text{--} \text{S}_x \text{--} \text{SO}_3^-$ ($X = 10\text{--}25$) and polymeric allotropes. Orthorhombic and monoclinic sulfur are the most stable forms which contain crown-shaped S_6 , S_8 and S_{12} molecules [34]. Therefore, it is suggested that the interaction between solid sulfur and M^{n+} is probably similar to host–guest interaction such as those occurring between crown ethers and metal ions.

The optimized conditions for preconcentration of the investigated analyte ions on sulfur adsorbent were established.

3.1. Effect of pH

The influence of pH on the retention of metal ions sorption was studied by applying the proposed procedure to the sample solutions. The pH of each solution was adjusted to values ranging from 2 to 10 with HNO_3 and NaOH solutions. According to the results (Fig. 1), quantitative recoveries ($>95\%$) for analytes were obtained at pH 8. Therefore, pH adjustment in each sample was carried out by adding 2 mL of phosphate buffer (pH 8). However at pH values

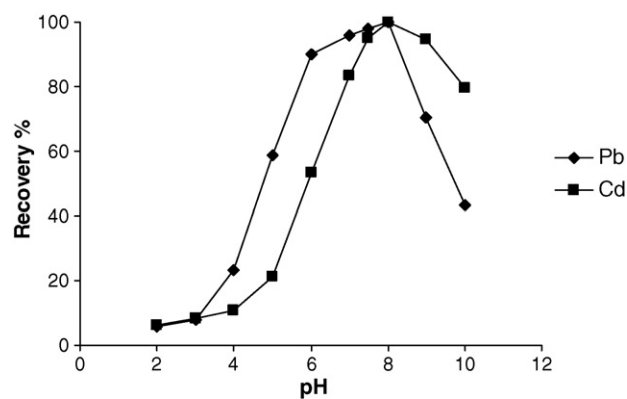


Fig. 1. Effect of pH on the recovery of $5\ \mu\text{g}$ of lead and $2\ \mu\text{g}$ of cadmium. Conditions—sample volume: 100 mL; flow rate: 3 mL min^{-1} ; amount of adsorbent: 2.5 g.

higher than 8, lead and cadmium ions form complexes and precipitates with OH^- [35] and their retention is changed and the recovery of the method is decreased.

3.2. Effect of flow rate of sample solution and eluent

The retention of the metal ions on sulfur adsorbent depends on the flow rate of the sample solution. Thus influence of this factor was investigated by passing sample solutions through the column with flow rates in the range of $1\text{--}10\text{ mL min}^{-1}$. The flow rates of the sample solutions were controlled by stopcock and application of vacuum. At flow rates greater than 4 mL min^{-1} , there was a decrease in the recovery of the metal ions. At higher flow rates the sample solution passes through the column faster and there is not enough time for equilibration between the analyte and the adsorbent surface and the recovery of the analytes decreases. Therefore a flow rate of 3 mL min^{-1} was applied for analytes.

The flow rate of eluent solution was examined in the range of $1\text{--}5\text{ mL min}^{-1}$. Maximum recoveries for metal ions were obtained in the range of $1\text{--}2\text{ mL min}^{-1}$. The flow rate of 1 mL min^{-1} was chosen as optimum value.

3.3. Effect of the adsorbent amount

The amount of adsorbent is another important parameter to obtain quantitative recovery. For this reason the amounts of sulfur was optimized. The influence of the adsorbent amount was tested in

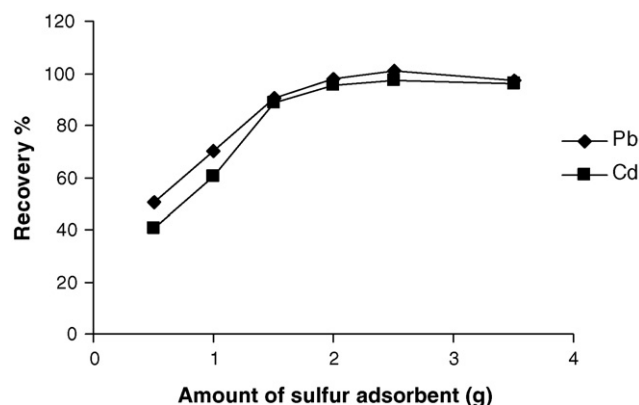


Fig. 2. Effect of amount of adsorbent on recovery of $5\ \mu\text{g}$ of lead and $2\ \mu\text{g}$ of cadmium. Conditions—pH 8; sample volume: 100 mL; flow rate: 3 mL min^{-1} .

the range of 0.5–3.5 g. As presented in Fig. 2 quantitative recoveries were obtained when sulfur amount was above 2.5 g. Accordingly, 2.5 g of sulfur was used in all experiments.

3.4. Effect of the type, concentration and volume of the eluent

Various inorganic acids and organic solvents were used to identify the best eluent for the adsorbed metal ions on sulfur. The results are shown in Table 1. Among different eluents used, 1 mol L⁻¹ of HNO₃ in methanol provided higher recovery and reproducibility. Therefore, this solution was chosen as an eluent for the metal ions from sulfur adsorbent. Then the concentration of the HNO₃ in methanol as an eluent was optimized. The results given in Fig. 3 indicate that highest recoveries are obtained for both analytes at 1 mol L⁻¹ concentration of HNO₃ in methanol. Thus this concentration was selected as optimum.

Subsequent experiments showed that even 0.5 mL of the eluent solution was enough for elution of metal ions, however, in all experiments metal ions were eluted by 2 mL of 1 mol L⁻¹ of HNO₃ in methanol solution because this volume was necessary for reading absorption signal of lead and cadmium by FAAS.

3.5. Effect of the sample volume

Due to the low concentrations of trace metals in real samples, these analytes should be taken into smaller volumes for high preconcentration factor by using sample solutions with large volumes. Therefore the maximum applicable sample volume was determined by increasing the dilution of metal ion solution, while keeping the total amount of loaded metal ion fixed at 5 µg for Pb and 2 µg for Cd. Different feed volumes varied between 100 and 750 mL. The results are given in Fig. 4. As can be seen the recoveries of metal ions were quantitative up to 500 mL of sample volume.

Table 1
Effect of eluting solution (3 mL) on lead and cadmium recovery

Eluent	Recovery (%)	
	Pb	Cd
1 mol L ⁻¹ HCl	67.6 ± 1.6	100.0 ± 3.0
1 mol L ⁻¹ HNO ₃	67.5 ± 1.6	93.2 ± 2.0
1 mol L ⁻¹ CH ₃ COOH	56.3 ± 1.5	88.1 ± 1.9
1 mol L ⁻¹ HCl in methanol	22.5 ± 0.5	90.7 ± 1.9
1 mol L ⁻¹ HNO ₃ in methanol	100.0 ± 3.2	98.4 ± 2.0
1 mol L ⁻¹ CH ₃ COOH in methanol	67.6 ± 1.6	93.2 ± 2.0
1 mol L ⁻¹ HCl in acetone	21.1 ± 0.6	68.4 ± 1.7
1 mol L ⁻¹ HNO ₃ in acetone	87.3 ± 2.0	67.4 ± 1.7
1 mol L ⁻¹ CH ₃ COOH in acetone	42.3 ± 1.3	51.8 ± 1.1

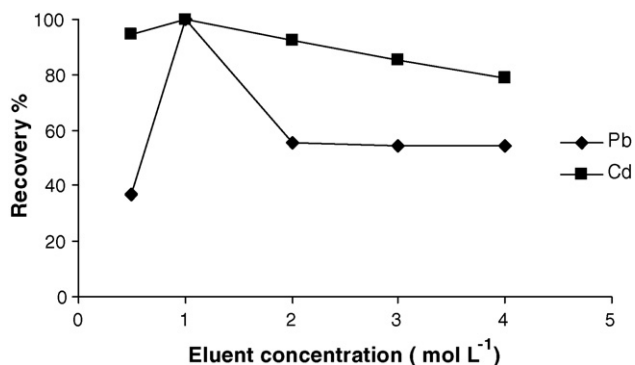


Fig. 3. Effect of eluent concentration on the recovery of 5 µg of lead and 2 µg of cadmium. Conditions—pH 8; sample volume: 100 mL; flow rate: 3 mL min⁻¹; amount of adsorbent: 2.5 g.

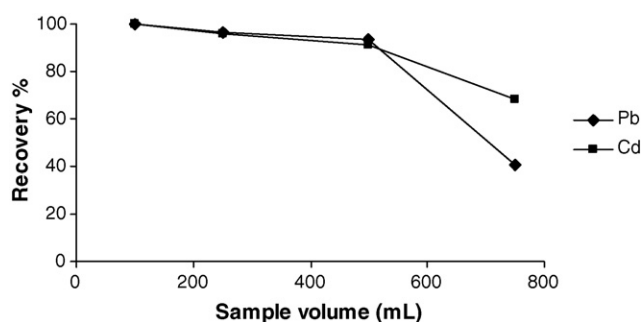


Fig. 4. Effect of sample volume on the recovery of 5 µg of lead and 2 µg of cadmium. Conditions—pH 8; flow rate: 3 mL min⁻¹; amount of adsorbent: 2.5 g.

At volumes higher than 500 mL probably the analyte ions are not retained effectively because of passing excess water through the column. As stated previously, the final solution volume, after eluting the metal ions, was 2 mL, therefore the preconcentration factors of 250 was obtained for both analytes.

3.6. Effect of interfering ions on recovery

For application of recommended solid phase extraction to real samples, effects of some interfering ions on the recovery of metal ions were investigated with the optimized procedure. The tolerance limit was defined as the amount of foreign ion causing a change of less than ±5% in the absorbance reading. The tolerable limits of interfering ions are given in Table 2. The results show that some of the metal ions are tolerable up to 10-fold excess for Pb and 50-fold for Cd.

3.7. Loading capacity

The loading capacity of sulfur was determined by batch method. The adsorbent was added to a solution containing 4 mg L⁻¹ of Pb and 2 mg L⁻¹ of Cd ion and stirred on a stirrer for 1 h, and after filtration lead and cadmium in the filtrate were determined by FAAS. The loading capacity was 15.6 µg g⁻¹ for Pb and 3.4 µg g⁻¹ for Cd.

3.8. Analytical performance

The analytical features of the presented method such as linear range of the calibration curve, limit of detection and precision were also examined. The calibration graph was linear in the range of 10–300 and 1–20 ng mL⁻¹ of lead and cadmium, respectively. The equations for the lines were $A = 0.0012C_x + 0.0029$ ($r = 0.9987$) and $A = 0.0133C_x - 0.0029$ ($r = 0.9971$) for lead and cadmium, respectively. The limits of detection (LOD) based on three times the standard deviation of the blank ($3S_b$) [36] under optimal experimental conditions was 3.2 and 0.2 ng mL⁻¹ ($n = 10$) for lead and cadmium, respectively. The relative standard deviation (R.S.D.) for 50 ng mL⁻¹ of lead and 20 ng mL⁻¹ of cadmium ($n = 10$) was 5.1 and 4.7, respectively. The sulfur adsorbent can be reused at least five times.

Table 2
The effect of foreign ions on determination of 100 ng mL⁻¹ of Pb and 20 ng mL⁻¹ of Cd

Ion	Tolerance limit (mg L ⁻¹)
Na ⁺ , K ⁺ , Cl ⁻ , SO ₄ ²⁻	1000
Ca ²⁺ , Mg ²⁺	500
Cu ²⁺ , Co ²⁺ , Ni ²⁺ , Cr ³⁺	1
Hg ²⁺ , Fe ²⁺ , Fe ³⁺	1

Table 3

Determination of lead and cadmium in tap and river water samples (100 mL) with the proposed method

Analyte	Added (μg)	Tap water		River water	
		Found ^a (μg)	Recovery (%)	Found ^a (μg)	Recovery (%)
Pb	–	ND ^b	–	ND ^b	–
	5.00	4.69 \pm 0.08	93.80	4.84 \pm 0.09	96.80
	10.00	10.17 \pm 0.09	101.70	9.93 \pm 0.08	99.30
Cd	–	ND ^b	–	ND ^b	–
	1.00	1.02 \pm 0.02	102.00	1.01 \pm 0.02	101.40
	2.00	1.92 \pm 0.02	95.80	1.90 \pm 0.02	95.10

^a $x \pm s$ ($n=5$).

^b Not detected.

Table 4

Determination of lead and cadmium in wastewater sample (100 mL) with the proposed and ICP methods

Analyte	Added (μg)	Wastewater	
		Found ^a by present method (μg)	Found ^a by ICP (μg)
Pb	–	2.51 \pm 0.10	2.62 \pm 0.12
	5.00	7.42 \pm 0.10	7.55 \pm 0.13
	10.00	12.52 \pm 0.09	12.60 \pm 0.10
Cd	–	ND ^b	ND
	1.00	0.90 \pm 0.02	0.95 \pm 0.03
	2.00	1.79 \pm 0.02	1.86 \pm 0.08

^a $x \pm s$ ($n=5$).

^b Not detected.

Table 5

Comparison of the proposed method with some of the methods reported in literature

System	Preconcentration factor	DL (ng mL^{-1})		Ref.
		Cd	Pb	
Chelating resin	75	4.2	16.0	[7]
Coprecipitation	250	6.0	16.0	[11]
Liquid–liquid extraction	80	0.30	4.2	[14]
Cloud point extraction	43	0.74	4.6	[23]
Modified silica gel	27	1.10	22.5	[25]
Sulfur adsorbent	250	0.20	3.2	Present work

3.9. Application to real samples

The proposed SPE method was applied to determination of lead and cadmium in various water samples. To examine the reliability and accuracy of the method, different amounts of the investigated metal ions were spiked into 100 mL of the water samples at optimum conditions. The results are given in Tables 3 and 4. The recoveries of analyte ions were evaluated and the results showed the capability of the method to real samples. The wastewater sample was also analyzed by inductively coupled plasma (ICP) emission spectrometry and the results presented in Table 4 show that there was no significant difference between two methods.

4. Conclusion

We have introduced sulfur as a new non-toxic and cheap adsorbent. The use of sulfur as the adsorbent for lead and cadmium preconcentration possessed several advantages such as simplicity, high preconcentration factor and low cost. The sulfur adsorbent can be reused at least five times. The LOD and preconcentration factor of the method is comparable or better than some of the previously reported preconcentration methods (Table 5). The proposed procedure was successfully applied for simultaneous determination of lead and cadmium at low concentrations in water samples.

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