

Enrichment/separation of cadmium(II) and lead(II) in environmental samples by solid phase extraction

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Abstract

A preconcentration/separation procedure is presented for the solid phase extraction of trace cadmium and lead ions as their 1-(2-pyridylazo) 2-naphthol (PAN) chelates in environmental samples on Chromosorb-106 resin, prior to cadmium and lead determinations by atomic absorption spectrometry. The preconcentration procedure was optimized by using model solutions containing cadmium and lead ions. The influences of pH of the model solutions, amounts of PAN, eluent type and volume etc. were investigated. Also the effects of the matrix constituents of the samples were also examined. Separation of cadmium and lead from real samples was achieved quantitatively. The procedure presented was checked with the analysis of microwave-digested standard reference materials (IAEA-336 Lichen and SRM 1515 Apple leaves). The preconcentration procedure was applied for the lead and cadmium contents of the natural water samples, some salts with satisfactory results (recoveries >95%, relative standard deviations <8%).

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1. Introduction

The transition metals including cadmium, chromium and lead etc. are an important risk for humans and animals [1–3]. Also heavy metals at trace levels are components of the natural biosphere. Because the main sources of heavy metals for humans and animals are water, food and atmosphere [1,4,5], reliable and sensitive analytical methods and procedures have an important role to evaluate the impacts of metal pollutants. The determination of traces metal ions in these samples are continuously performed in the analytical chemistry laboratories around the world by using various instrumental techniques including atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) etc. Although, atomic absorption spectrometry and atomic emission spectrometry are among the most widely

methods used for trace metal determination, their sensitivity is usually insufficient for monitoring the low level concentrations of metals in the environmental samples. The interfering effects of the matrix components of the samples are the one of the main problems in the determination of traces heavy metals by AAS and or ICP-AES. Also lower elements concentrations than the detection limits of the instrumental technique are another problem in the trace heavy metal determinations in environmental samples. Consequently, a preconcentration/separation process is usually required [6–10]. Coprecipitation [11–13], membrane filtration [14,15], electrodeposition [16], cloud point extraction [17] and solvent extraction [18–21] are the popular methods for the preconcentration and separation of the traces transition metal ions.

Solid phase extraction (SPE) of trace metal ions is also an important preconcentration/separation technique [1,22–25]. SPE has many advantages: it is a simple technique. Several analytes can be enriched and separated simultaneously. Furthermore, high preconcentration factors can be obtained by using solid phase extraction procedures. Main properties of

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the solid phases for solid phase extraction should be high surface area, their high purity and good sorption properties including porosity, durability, and uniform pore distribution. A large variety of efficient solid materials like Amberlite XAD resins [22,26], silica gel [27–30], chitosan [31], Diaion HP-2MG [32], benzophenone/naphthalene [33], Chelex 100 [34] etc. have been used for solid phase extraction of metal ions at trace levels by various researchers.

Chromosorb resins (Chromosorb-101, -102, -105, -108 etc.) are synthetic polymeric materials [35,36] and have been used for gas chromatography as stationary phases, because they have good physical and chemical properties such as porosity, high surface area, durability and purity and are resistant in concentrated mineral acid, concentrated bases and organic solvents for a long time. Chromosorb-106 is a member of the chromosorb resin family. It is a cross-linked polystyrene resin. It has been used on the gas chromatographic analysis of various organic compounds as stationary phase [35–39].

This paper describes a preconcentration/separation procedure based on solid phase extraction of lead and cadmium in some environmental samples and some salts. The analytical parameters relevant quantitative retentions of lead and cadmium on Chromosorb-106 as PAN chelates were investigated.

2. Experimental

2.1. Apparatus

A Perkin Elmer AAnalyst 700 atomic absorption spectrometer with deuterium background corrector was used in this study. A 10 cm long slot-burner head, a lamp and an air-acetylene flame were used. The operating conditions given in Table 1, adjusted in the spectrometer were carried out according to the standard guidelines of the manufacturers. The atomic absorption signal was measured as a peak height mode against an analytical curve.

A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used. Digestion conditions for the microwave system for the tobacco, river sediment and black tea samples were 6 min for 250 W, 6 min for 400 W, 6 min for 550 W, 6 min for 250 W, vent: 8 min [26,32]. For human hair and spice samples, digestion conditions for microwave system were applied as 2 min

for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min [26,32].

2.2. Reagents and solutions

Analytical reagent-grade chemicals from Merck, Darmstadt were employed for the preparation of all solutions. All aqueous solutions were prepared from distilled water (Milli-Q Millipore 18.2 M Ω cm⁻¹ resistivity). All the plastic and glassware were cleaned by soaking in dilute HNO₃ (1+9) and were rinsed with distilled water prior to use. Stock metal ion solutions, 1000 mg/L (Merck, Darmstadt) were diluted daily for obtaining reference and working solutions. Stock solutions of diverse elements supplied by Sigma Chem. Co., St. Louis, were prepared from high purity compounds.

The calibration curves for analyte ions were established using the standard solutions prepared in 1 M HNO₃ by dilution from stock solutions. The calibration standards were not submitted to the preconcentration procedure. The range of the calibration standards for cadmium and lead on flame atomic absorption spectrometric determinations were 0.02–2.0, and 1.0–10.0 mg/L, respectively. The correlation coefficient of the calibration curves were generally 0.999.

Chromosorb-106 (60–80 mesh fraction, surface area: 600–700 m²/g) (Sigma Chem. Co., St. Louis) was washed successively with methanol, water, 1 M HNO₃ in acetone, water, 1 M NaOH and water, sequentially, in order to eliminate trace metal ions and other inorganic and organic contaminants in the resin.

The glass column, having a stopcock and a porous disk, was 10 cm long, and 1.0 cm in diameter. The column contains about 600 mg resin (ca 2.0 cm bed). The column was prepared by aspirating water slurry of Chromosorb-106 into the glass column. It was conditioned with 10–15 mL of pH 9 buffer.

The ligand; 1-(2-pyridylazo) 2-naphtol (PAN) (Sigma Chem. Co., St. Louis) was dissolved in a water/ethanol (75/25, v/v) mixture. Ammonium acetate buffer solutions (0.1 M) were prepared by adding an appropriate amount of acetic acid (Merck, Darmstadt) to ammonium acetate (Merck, Darmstadt) solutions for pH 4–6 and ammonium chloride buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia (Merck, Darmstadt) to ammonium chloride solutions for pH 8–10.

2.3. Preconcentration procedure

The column method was tested with model solutions. Model solutions (containing 5 μ g of cadmium and 20 μ g of

Table 1
Conditions for flame atomic absorption spectrometric determinations

Element	Wavelength (nm)	Slit (nm)	Lamp current (mA)	Flow rate of oxidant and fuel	
				Air (L/min)	Acetylene (L/min)
Pb	283.3	0.7	30	2.0	17.0
Cd	228.8	0.7	4	2.0	17.0

lead in 40–60 mL) were adjusted to the desired pH. Then 1-(2-pyridylazo) 2-naphthol (PAN) was added to form the metal–PAN chelates. After 5–10 min, the solution was loaded into the column. The flow of sample solution through the column was gravitationally performed. After passage of the solution finished, the column was washed with a chelating agent solution adjusted to the working pH. The metals were recovered with the aid of 8–10 mL of 1 M HNO₃ in acetone at 5.0 mL/min of flow rate. The eluent was evaporated over a hot plate to near dryness at 35 °C in a hood and was diluted to 2 mL or 5 mL with 1 M HNO₃. The metal concentrations in the final solution were determined by AAS.

2.4. Procedure for standard reference materials

Lichen (IAEA-336) and apple leaves (SRM 1515) standard reference materials (100 mg) were digested with 6 mL of HNO₃ (65%), 2 mL of H₂O₂ (30%) in microwave digestion system for 31 min and diluted to 50 mL with deionized water. A blank digest was carried out in the same way. Final volume was 2 mL. Then the preconcentration procedure given above was applied to the final solutions.

2.5. Analysis of real samples

2.5.1. Analysis of the water samples

The water samples analyzed were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 9. Then PAN solution was added. The sample was passed through the column. The PAN chelates adsorbed on column were eluted with 1 M HNO₃ in acetone. The effluent was evaporated to near dryness and made up to 2.0 mL with 1 M HNO₃. The levels of the investigated analyte ions in the samples were determined by AAS.

2.5.2. Determination of cadmium and lead ions in salt samples

For the determination of analyte ions in alkaline salt samples, 3.0 g of each salt sample was dissolved in 3 mL of distilled water and diluted to 100.0 mL with distilled water. The procedure given above was applied to these solutions. The analyte ions in the final solution were determined by atomic absorption spectrometry.

2.5.3. Procedures for tobacco, black tea, human hair, spice and river sediment

0.25 g of tobacco sample was digested with 4 mL of concentrated HNO₃ and 2 mL of concentrated H₂O₂ in microwave system. Blank digestions were also performed at the same conditions. After digestion, the volume was made up to 25 mL with distilled water. The enrichment procedure given above was applied to the samples. The final volume was 2 mL. The metal concentrations in the final solutions were determined by flame AAS.

For the digestion of black tea samples, 0.25 g of tea was mixed with 6 mL of HNO₃:H₂SO₄:H₂O₂ (1:1:1) in microwave system. After digestion, the volume was made up to 25 mL with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples. The final volume was 2 mL.

For the microwave digestion of human hair and a spice sample, 1.0 g of samples were digested with 4 mL of concentrated HNO₃ and 2 mL of concentrated H₂O₂ in microwave system. After digestion, the volume was made up to 25.0 mL with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples. The final volume was 2 mL.

0.25 g of river sediment was digested with HCl:HNO₃:H₂SO₄ (4:2:2) in microwave system. After digestion, the volume was made up to 25 mL with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples. The final volume was 5 mL.

3. Results and discussions

3.1. Influences of pH of aqueous solutions on the retentions of cadmium and lead ions on Chromosorb-106

The effects of the pH of the aqueous solution on the recoveries of the PAN complexes of lead and cadmium were investigated in the pH range of 6–10 by using buffered model solutions containing 5 μg of cadmium(II) and 20 μg of lead(II). The results are depicted in Fig. 1. The recovery values for lead and cadmium ions were not quantitative at the pH values below 8. The recoveries increase with increasing pH and reach quantitative values at the pH range of 8–9 for both ions. All further studies were performed at pH 9 with ammonia/ammonium chloride buffer.

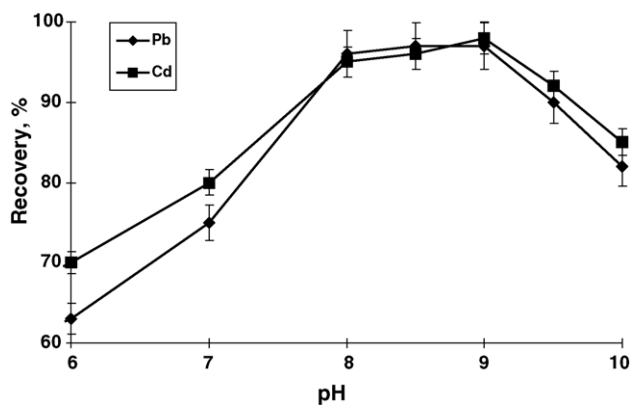


Fig. 1. Recoveries of cadmium and lead as a function of pH (eluent: 1 M HNO₃ in acetone, amount of resin: 600 mg, *N* = 3).

3.2. Ligand amounts

Prior to adsorption of traces heavy metal ions on a solid phase for preconcentration, generally metal ions were converted to a suitable form including metal chelates or metal inorganic complexes. Because of this point, 1-(2-pyridylazo) 2-naphthol (PAN) was selected as chelating agent for lead and cadmium ions. Different volumes of 1×10^{-2} M of PAN solutions were added to model solutions containing $5 \mu\text{g}$ of cadmium(II) and $20 \mu\text{g}$ of lead(II). Then this solution passed through Chromosorb-106 resin column. Quantitative recoveries were obtained for lead and cadmium ions in the 2.0–4.0 mL of 1×10^{-2} M PAN solution. Because of insufficient ligand amounts in the solutions, the recoveries of analytes were not quantitative when less than 2.0 mL PAN solution was used. After 4.0 mL of PAN solution, the recoveries were below 95%, due to competition on the adsorption between PAN–metal chelates and excess PAN in the solution. In all further work, 3.0 mL of 1×10^{-2} M PAN solution was added to the solutions.

3.3. Eluent type and eluent volume

Various elution solutions at 5 mL/min flow rate were examined to obtain quantitative recovery values for lead–PAN and cadmium–PAN chelates from Chromosorb-106 column. The recoveries of analytes were quantitative only with 1 M HNO_3 in acetone. The recoveries were not quantitative when 1 and 2 M HNO_3 , 1 and 2 M HCl and 1 M HCl in acetone were used as eluent. 1 M HNO_3 in acetone was used as the eluent all further work for quantitative recovery of metal ions from Chromosorb-106.

The volume of eluent (1 M HNO_3 in acetone) that can completely strip the retained analytes from the solid phase is an important parameter for obtaining the maximum preconcentration factor. Thus some experiments were carried out in order to choose a proper eluent volume for the retained analyte ions on Chromosorb-106. The recovery values for lead and cadmium ions from the Chromosorb-106 column were greater than 95%, in the eluent volume range of 5.0–10.0 mL. In the eluent volume lower than 5.0 mL, because of insufficient eluent volume, the recoveries of the analyte ions were not quantitative.

3.4. Effect of sample volume

The solid phase extraction technique is a common procedure for extraction and separation of metal ions from large sample volumes to obtain high preconcentration factor in the solid phase extraction studies. The recovery values as a function of sample volume were shown in Fig. 2. It was found that the recoveries were constant when up to 500 mL of the sample solution was used. At the higher volumes the recoveries for analytes decreased. Therefore a preconcentration factor of 250 can be achieved when using 500 mL of the sample and 2.0 mL of final volume.

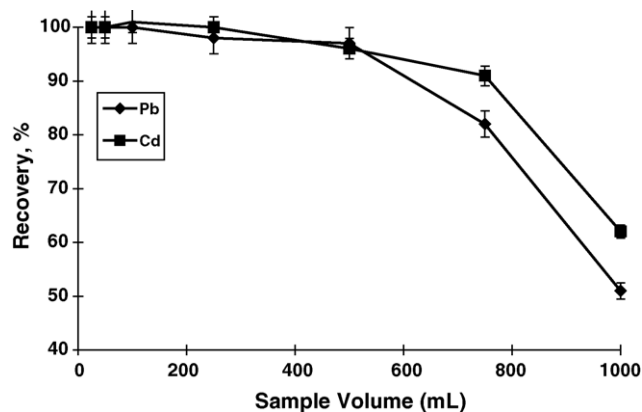


Fig. 2. Effects of sample volume on the recoveries of lead and cadmium ions on Chromosorb-106 ($N=3$).

3.5. Amount of Chromosorb-106

Due to the amounts of solid phase extractor is the one of the important factor for the quantitative retention of heavy metals at traces levels in the preconcentration studies based on solid phase extraction, the influences of the amount of Chromosorb-106 resin on the retention of cadmium and lead ions were examined by using the model solution containing analytes. The results are depicted in Fig. 3. Cadmium and lead ions were quantitatively retained in the range of 500–700 mg of Chromosorb-106 resin. The short glass column was filled with 600 mg of Chromosorb-106 for all further studies.

3.6. Influences of flow rates of sample and eluent solutions on the recoveries

The influences of the flow rates of sample and eluent solutions on the recoveries of cadmium and lead ions were investigated in the range of 1–10 mL/min. In the examination

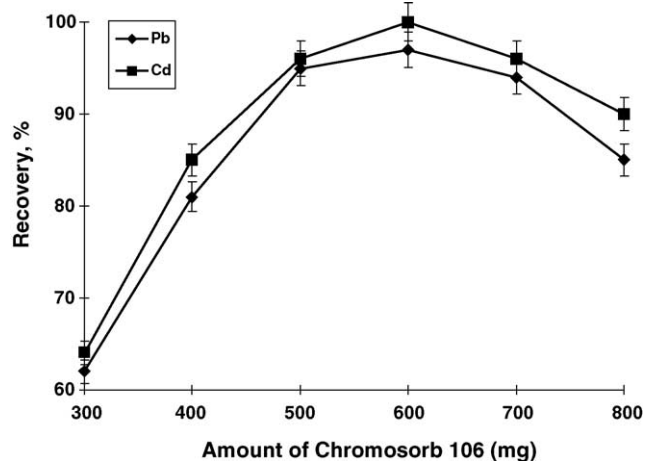


Fig. 3. Influences of amount of Chromosorb-106 resin on the retentions of cadmium and lead ions ($N=3$).

Table 2
Effect of the matrix ions on the recovery of metal ions (sample volume: 100 mL, $N=3$)

Ion	Added as	Concentration (mg/L)	Pb	Cd
Na ⁺	NaCl	10,000	99 ± 3	98 ± 3
		30,000	96 ± 3	95 ± 2
K ⁺	KCl	10,000	100 ± 1	99 ± 3
		20,000	95 ± 4	96 ± 3
Ca ²⁺	CaCl ₂	10,000	98 ± 3	96 ± 4
		15,000	97 ± 2	95 ± 3
Mg ²⁺	MgCl ₂	5000	98 ± 3	96 ± 3
		10,000	96 ± 2	95 ± 2
Cl ⁻	NaCl	10,000	100 ± 2	99 ± 3
		30,000	96 ± 3	97 ± 2
SO ₄ ²⁻	Na ₂ SO ₄	5000	98 ± 3	99 ± 3
		10,000	96 ± 2	95 ± 3
PO ₄ ³⁻	Na ₃ PO ₄	1000	96 ± 3	97 ± 3
		3000	95 ± 3	95 ± 2
F ⁻	NaF	1000	97 ± 3	98 ± 3
		3000	96 ± 3	97 ± 4
NO ₃ ⁻	KNO ₃	5000	98 ± 2	96 ± 3
		10,000	97 ± 3	95 ± 2
Fe ³⁺	FeCl ₃	25	97 ± 3	97 ± 2
		50	98 ± 3	95 ± 3
Al ³⁺	Al ₂ (SO ₄) ₃	25	99 ± 3	98 ± 1
		50	98 ± 2	96 ± 3
Mn ²⁺	MnSO ₄	25	97 ± 3	96 ± 3
		50	96 ± 2	95 ± 3
Zn ²⁺	ZnSO ₄	25	97 ± 3	98 ± 2
		50	96 ± 2	95 ± 3
Cu ²⁺	CuSO ₄	25	99 ± 3	97 ± 2
		50	100 ± 2	97 ± 3
Cr ³⁺	Cr(NO ₃) ₃	25	98 ± 3	99 ± 2
		50	97 ± 2	97 ± 3
Co ²⁺	CoSO ₄	25	97 ± 3	98 ± 3
		50	96 ± 2	97 ± 3
Ni ²⁺	NiSO ₄	25	96 ± 3	97 ± 2
		50	96 ± 2	96 ± 4

of the effects of sample and eluent solutions, 1 M HNO₃ in acetone was used as eluent. The quantitative recovery values were obtained in the flow rate range of 1–8 mL/min for sample and eluent solution. After 8 mL/min of eluent solution, the recovery values of cadmium and lead ions were below 95%. Five milliliter per minute was selected as the flow rate for

the all experiments for both flow rates of sample and eluent solutions.

3.7. Matrix effects

Because of the determination of the levels of traces metal ions of the highly saline samples were the goal, the influences of possible matrix ions in the environmental samples and some transition metals were also examined. The effect of potential interfering ions on the determination of lead and cadmium were investigated by adding known concentrations of each ion in a solution containing analytes and then determining the latter. The results were summarized in Table 2. The tolerated amounts of each ion were the concentration values tested that caused less than 5% the absorbance alteration. The ions normally present in water do not interfere under the experimental conditions used. Also, some of the transition metals at mg/L levels did not interfere with the recoveries of the analyte ions. This results show that the proposed preconcentration/separation method could be applied to the highly saline samples and the samples that contains some transition metals including Ni²⁺, Co²⁺, Cr³⁺, Zn²⁺, Cu²⁺, Fe³⁺, Al³⁺ and Mn²⁺ at mg/L levels.

3.8. Figure of merits

The accuracy of the results was verified by analyzing the concentration after addition of known amounts of cadmium and lead into seawater, tap water, unrefined table salt and a refined salt sample. The results were given in Table 3. For all four samples, good agreements were obtained between the recoveries of analyte for spiked and control samples using the experimental procedure for analytes. The recoveries calculated for the additions were quantitative, thus confirming the accuracy of the present procedure and the absence of matrix effects.

The analytical performance of the procedure can be calculated for the results from FAAS measurements. The reproducibility of the preconcentration and separation method was evaluated by passing 50 mL of solution containing analyte ions through the column and repeating this procedure

Table 3
Analysis of various samples spiked analyte ions (sample volume: 100 mL, final volume: 10 mL, $N=4$)

Analyte	Added (μg)	Tap water		Seawater		Unrefined table salt (3% (w/V))		Refined table salt (3% (w/V))	
		Found (μg), $x \pm S.D.^a$	Recovery (%)	Found (μg), $x \pm S.D.^a$	Recovery (%)	Found (μg), $x \pm S.D.^a$	Recovery (%)	Found (μg), $x \pm S.D.^a$	Recovery (%)
Pb	0	N.D.	–	N.D.	–	N.D.	–	N.D.	–
	10	9.9 ± 0.4	99 ± 3	9.8 ± 0.5	98 ± 2	9.7 ± 0.4	97 ± 3	9.8 ± 0.4	98 ± 3
	20	19.8 ± 0.3	99 ± 3	20.2 ± 0.4	101 ± 3	19.5 ± 0.6	98 ± 2	19.7 ± 0.5	99 ± 3
	40	40.2 ± 0.3	101 ± 3	39.6 ± 0.3	99 ± 3	39.2 ± 0.4	98 ± 3	39.5 ± 0.4	99 ± 3
Cd	0	N.D.	–	N.D.	–	N.D.	–	N.D.	–
	2.5	2.5 ± 0.2	100 ± 3	2.4 ± 0.3	96 ± 2	2.4 ± 0.3	96 ± 3	2.4 ± 0.3	96 ± 3
	5	5.1 ± 0.3	102 ± 3	4.9 ± 0.4	98 ± 2	4.8 ± 0.4	96 ± 2	4.9 ± 0.3	98 ± 2
	10	10.1 ± 0.4	101 ± 3	9.8 ± 0.5	98 ± 3	9.7 ± 0.4	97 ± 3	9.6 ± 0.4	96 ± 3

^a S.D.: standard deviation, N.D.: not detected.

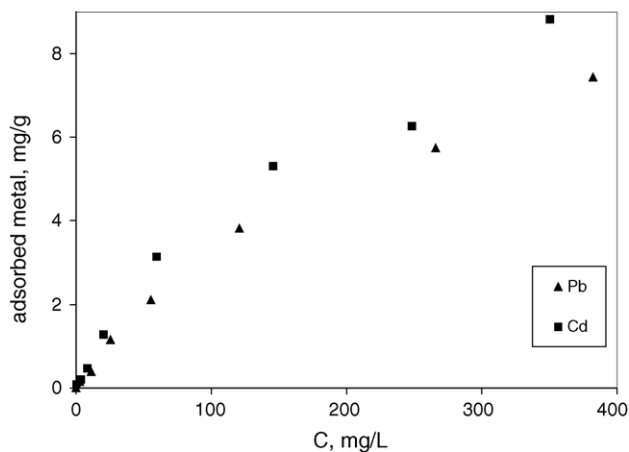


Fig. 4. Langmuir isotherm adsorption plots of lead(II) and cadmium(II) ions on Chromosorb-106.

ten times. The relative standard deviations (R.S.D.) were below 7%.

The detection limits of the investigated elements based on three times the standard deviations of the blank ($k = 3$, $N = 20$) on a sample volume 500 mL for cadmium and lead were 0.19 and 0.32 $\mu\text{g/L}$, respectively.

3.9. Adsorption isotherms and adsorption capacity

The adsorption behavior of Chromosorb-106 was determined by studying the amount of adsorbed cadmium and lead as a function of cadmium and lead concentrations; 50 mL of solutions containing cadmium and lead at concentrations in the range 0.35–385 and 0.24–350 mg/L, respectively, were maintained under the optimum conditions determined before. The analytes in the eluents was determined by FAAS and the adsorption capacities of resin for cadmium and lead were calculated from Langmuir plots. The concentration of adsorbed cadmium(II) and lead(II) in mg/g (n) on to Chromosorb-106 as a function of its concentration in solution in mg/L (C) was investigated. The adsorption isotherms for cadmium and lead were shown in Fig. 4. The maximum adsorption capacity were obtained by using a model Langmuir adsorption isotherm [40,41], based on following equation:

$$\frac{C}{n} = \frac{1}{n_m K} + \frac{1}{n_m} C \quad (1)$$

Table 4

The levels of lead(II) and cadmium(II) as $\mu\text{g/g}$ in reference standard materials (final volume: 2 mL, $N = 4$)

Element	SRM (IAEA-336 Lichen)		SRM 1515 Apple leaves	
	Certified value	Observed value	Certified value	Observed value
Pb	5	4.9 \pm 0.2	0.47	0.51 \pm 0.05
Cd	0.117	0.115 \pm 0.01	(0.013) ^a	0.015 \pm 0.001

^a The value in the parenthesis is not certified. Mean expressed as 95 % tolerance limit.

Table 5

Concentration of analyte ions in natural water samples as $\mu\text{g/L}$ ($N = 4$, sample volume: 500 mL, final volume: 2 mL)

	Pb	Cd
Tab water from GOP university	4.7 \pm 0.4	1.8 \pm 1.8
River water from Yesilirmak	2.4 \pm 0.2	1.2 \pm 0.1
Bottled mineral water	2.9 \pm 0.2	1.5 \pm 0.2

Mean expressed as 95% tolerance limit.

Table 6

Application of presented method for the levels of cadmium and lead in some salt samples (final volume: 2 mL, $N = 4$)

	Concentration ($\mu\text{g/g}$)	
	Pb	Cd
Refined table salt	1.3 \pm 0.1	0.12 \pm 0.01
Unrefined table salt	1.9 \pm 0.1	0.25 \pm 0.02
Ammonium chloride (technical grade)	7.6 \pm 0.3	0.40 \pm 0.03
Sodium chloride (technical grade)	6.5 \pm 0.5	0.32 \pm 0.03

Mean expressed as 95% tolerance limit.

The maximum adsorption capacities (n_m) of Chromosorb-106 for cadmium and lead were found to be 2.70 and 4.56 mg/g, respectively. The binding constants (K) were 0.211 l/mg for cadmium and 0.12 l/mg for lead.

3.10. Cadmium and lead contents of SRM samples

The method presented was checked to two different reference materials (IAEA-336 Lichen and SRM 1515 Apple leaves) for the determination of cadmium(II) and lead(II) ions. The certified and observed values for IAEA-336 Lichen and SRM 1515 Apple leaves were given in Table 4. The results found were in good agreement with the certified values of SRMs. If the concentration levels of the most common matrix constituents of reference standard materials analyzed and the accuracy of the presented method are considered together, it can be concluded that the proposed method is free from interferences of the various constituents.

3.11. Application to real samples

The PAN/Chromosorb-106 solid phase extraction procedure for lead and cadmium ions was applied to various environmental samples. The results for natural water and some salt samples were given in Tables 5 and 6, respectively.

Table 7

The application of presented method in microwave-digested samples for cadmium and lead contents ($\mu\text{g/g}$, $N = 4$)

	Pb	Cd
Human hair	1.41 \pm 0.12	0.25 \pm 0.03
Tobacco	2.63 \pm 0.16	2.85 \pm 0.21
Black tea	1.35 \pm 0.11	0.74 \pm 0.10
Spice	0.80 \pm 0.10	0.21 \pm 0.04
River sediment	16.5 \pm 1.2	3.50 \pm 0.23

Mean expressed as 95 % tolerance limit.

Table 8
Comparative data from recent papers on 1-(2-pyridylazo) 2-naphthol (PAN) used chelating agent on preconcentration studies

Analytes	Method and instrumental detection	PF	Detection limit ($\mu\text{g/L}$)	R.S.D. (%)	References
In(III)	SPE on naphthalene/DDP	25–50	200	0.96	[44]
Co(II)	SPE on surfactant-coated alumina/AAS	100	–	1.4–4.0	[45]
Ir(III)	SPE on naphthalene/spectrophotometry	40	20	1.1	[46]
Ni(II)	SPE on surfactant-coated alumina/AAS	300	40	2.4	[47]
Cd(II)	SPE on naphthalene/DDP	40	70	0.98	[48]
Co	CPE/AAS	115	0.38	<10	[49]
Cu(II), Cd(II), Pb(II)	SPE on Amberlite XAD-2/AAS	50	0.8–23.2	<5	[50]
Ni(II)	SPE on aminocarboxylic amphoteric resin/DRS	–	50	<5	[51]
Cd(II)	SPE on surfactant-coated alumina/AAS	100	0.024	1.6	[52]
Cu(II), Co(II)	CPE/CE	15.9–16.3	0.12–0.26	0.74–1.8	[53]
Pb(II)	Electroanalytical/voltammetry	–	15	<10	[54]
Hg(II)	SPE on chloromethylated polystyrene/AAS	100	0.4	2.1–3.0	[55]
Pb(II), Cd(II)	SPE on Chromosorb-106/AAS	250	0.19–0.32	5–7	Present work

PF: preconcentration factor, CPE: cloud point extraction, SPE: solid phase extraction, CE: capillary electrophoresis, AAS: atomic absorption spectrometry, DDP: differential pulse polarography, DRS: diffuse reflection spectroscopy.

The proposed method has been combined with the microwave assisted digested samples including a human hair, a tobacco, a black tea, a spice and a river sediment. For this purpose, these samples were digested by closed microwave system, and then Chromosorb-106/PAN preconcentration/separation procedure given in Section 2 was applied. The results are given in Table 7. Concentrations of the investigated ions in our samples were $\mu\text{g/g}$ level.

3.12. Comparison with other preconcentration studies used 1-(2-pyridylazo) 2-naphthol (PAN)

1-(2-Pyridylazo) 2-naphthol (PAN) is a reagent for the spectrophotometric determination of lots of transition metal ions [42,43]. PAN acts as a terdentate ligand complexing with metals through the hydroxyl oxygen atom, pyridine nitrogen atom and one of the azo group nitrogen atoms. PAN has been also used for the separation and preconcentration of traces heavy metals as chelating agent from various media. Comparative data from some recent papers on preconcentration studies used 1-(2-pyridylazo) 2-naphthol (PAN) for traces metal ions for the figure of the merits are summarized in Table 8.

The Chromosorb-106/PAN method presented in this study is most promising for the analyte ions as the preconcentration factor is 250. The preconcentration factor achieved with presented procedure is superior to solid phase extraction method given in Table 8 and some preconcentration/separation procedures including cloud point extraction, solid phase extraction, electroanalytical techniques [44–55]. The detection limits of investigated elements are superior to those of some preconcentration/separation techniques for analyses [44–56]. The matrix effects with the method were reasonably tolerable. The elution of the analytes from the Chromosorb-106 column was easily performed with 1 M HNO_3 in acetone. The good features of the proposed method showed that its convenient and low cost. Also the method is relatively rapid as compared with previously reported procedures for the

enrichment of lead and cadmium ions. The Chromosorb-106 resin in the column can be used at least 200 times.

4. Conclusion

The reusability of Chromosorb-106 was as high as greater than 200 cycles without any loss in its sorption behavior. The system was also successful in preconcentrating metal ions from large sample volumes. In addition to validating the developed method by successfully analyzing standard reference materials (lichen (IAEA-336) and apple leaves (SRM 1515)), lead(II) and cadmium(II) content was established in natural waters, some salts, human hair, river sediment, spice, tobacco and black tea samples by the developed preconcentration method.

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