

Technical paper

# Solid-Phase Extractor with Ram Horn Powder for Lead and Cadmium Determination in Environmental Samples by Flame Atomic Absorption Spectrometry

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## Abstract

In the present paper, a separation/preconcentration procedure is presented for the solid phase extraction of Pb and Cd from environmental samples on a natural adsorbent (ram horn powder, RHP), prior to their determination by flame atomic absorption spectrometry (FAAS). The procedure is based on the adsorption of the bivalent ions of these metals as their 1-nitroso-2-naphthol-3,6-disulphonic acid chelate on the mini column packed with (RHP) followed by elution with 10 mL 1 M HCl and determination by flame atomic absorption spectrometry (FAAS). The influences of pH, amounts of chelating agent, eluent type, flow rate and sample volume were optimized and the analytical figures of merit were determined. Considering analytical figures of merits for the two elements, in the order of Pb and Cd recoveries of  $97 \pm 2\%$  and  $100 \pm 2\%$ , limit of detection of  $5.62 \text{ ng mL}^{-1}$  and  $1.74 \text{ ng mL}^{-1}$  (with enrichment factor of 50), sorbent capacity of  $4.55 \text{ mg g}^{-1}$  and  $2.69 \text{ mg g}^{-1}$  ( $0.022 \text{ mmol g}^{-1}$  and  $0.024 \text{ mmol g}^{-1}$ ) were found, respectively. The enrichments were made at concentration  $0.02$  to  $0.2 \mu\text{g mL}^{-1}$  of the two metals from 500 mL original water samples, at pH 4–8. Diverse ions of Mn(II), Co(II), Fe(III), Zn(II), Ni(II), Mg(II) and Cu(II) up to  $10 \mu\text{g L}^{-1}$  level, did not interfere with Pb and Cd. The accuracy of the method was checked by using standard reference materials (tea leaves GBW-07605 and fish tissue IAEA-407). Results demonstrated good agreement with the certified values. This procedure was applied for the determination of Pb and Cd in various waters, tap water, Ataturk Dam water and thermal water samples and in carrot and lettuce samples (recoveries  $>95\%$ , relative standard deviations  $<8\%$ ).

**Keywords:** Lead, cadmium, preconcentration, ram horn, solid-phase extraction, atomic absorption spectrometry.

## 1. Introduction

Separation/preconcentration of lead and cadmium in various samples such as water, vegetable, seafood and the other biological samples is of great importance for environmental chemistry. The concentration of these metals in water, carrot, lettuce and fishes can serve as base for to characterize the level of pollution of certain area. Some toxic metal ions such as Pb(II), Cd(II), Cr(VI), Hg(II) etc. are an important risk for humans and animals.<sup>1</sup> Contamination of water, soil, vegetable and the other biological samples with toxic metals such as Pb and Cd etc. has become a global environmental problem. Pollution by lead and cadmium usually come from several industrial processes such as electroplating, plastics manufacturing, nickel-cadmium batteries, fertilizers, pigments, mining and metallurgical processes.<sup>2</sup> Lead and cadmium contamination of foodstuffs and water caused harmful effects on

human health. It decreased enzymatic activities and kidneys functions and also causes neuromuscular difficulties.<sup>3</sup> Pb and Cd is both vital and toxic for many biological systems, and at higher levels it affects the central nervous system. Therefore, trace lead and cadmium content in water and foods must be controlled periodically. Therefore, to develop simple, sensitive and selective analytical methods that do not require expensive equipment and complicated procedure is of great importance, and this demand is well satisfied by the FAAS technique.<sup>4–6</sup> However, the application of an analyte preconcentration step is usually necessary before FAAS determination.<sup>6,7</sup> For this purpose solvent extraction,<sup>8</sup> coprecipitation,<sup>9</sup> electroanalytical techniques,<sup>10</sup> ion-change,<sup>11</sup> cloud-point extraction<sup>4</sup> and solid-phase extraction (SPE)<sup>12–16</sup> have been used in the literature. From these methods, SPE provided the highest enrichment factors and it was suitable for developing a continuous flow system.

A large variety of efficient solid materials like synthetic polymers<sup>13</sup> and natural fibers<sup>17</sup> have been used for solid phase extraction of trace metals. Recently, the use of natural fibers (cellulose, silk, wool, hair etc.) as a sorbent in the preconcentration of metal ions has attracted significant interest because of their advantages over synthetic materials (fibers, polymers etc.).<sup>17</sup>

Two ways are known for the preparation of SPE columns. In the first method, chelates of trace metals are formed by a specific reagent and passed onto the column to retain the chelates.<sup>18</sup> In the second method microorganisms are immobilized first on the solid phase and then trace metal solution is passed through the column.<sup>14</sup> The first method was selected to the present work.

The ram horn powder is a natural material and consists of keratin as major tissue component. Keratin acts as an interface between the internal and external environment of a living organism, which is durable with high strength and low density. It is rich in cysteine, which forms disulfide bonds that cross-link adjacent polypeptide chains. In addition, they contain most of the other common amino acids. Trace metals may accumulate by binding with polypeptides through the available amino and carboxylate groups of the constituent amino acids. Keratins are classified as hard or soft variants according to their sulfur content. Hard keratins, such as hair, horn or nail are less pliable than soft keratins, such as those of skin and callus, because the disulfide bonds resist deformation. These donor atoms such as sulfur, oxygen and nitrogen present in keratins are capable of selective binding with certain metal ions. Therefore, some natural materials containing such sulfur groups have been used for bioaccumulation of trace metals.<sup>19</sup> Baytak and Türker, have reported first on using ram horn powder (RHP) as an adsorbent for the preconcentration of copper in various samples that was followed by FAAS determination.<sup>18</sup>

The purpose of this study was to investigate the analytical potential of RHP as a sorbent material for the preconcentration of Pb and Cd in acidic aqueous solution that seems to be a first attempt for such purpose. The procedure developed and optimized has been successfully employed to the analysis of various water samples and vegetable samples, as described in the subsequent sections.

## 2. Experimental

### 2.1. Apparatus

A Varian GTA-97 SpectrAA 250 Plus atomic absorption spectrometer equipped with deuterium lamp background corrector was used under the operating conditions suggested by the manufacturer. The Pb 217.0 nm and Cd 228.8 nm lines were used with spectral band pass values of 1.0 nm, 0.2 nm and hollow cathode lamp cur-

rents of 5 mA and 6 mA, respectively. Acetylene-air flame was used as the atomization source, the flow rates of the fuel were 2.0 and 2.1 L min<sup>-1</sup>, for lead and cadmium, respectively.

All pH measurements were performed with a glass electrode applying a CRISON 20 model digital pH meter. Before using, the laboratory glassware was kept overnight in a 5% nitric acid solution, and afterwards it was rinsed thoroughly with deionized water and dried in a clean environment.

### 2.2. Reagents

Unless otherwise specified, all reagents were analytical reagent grade. Double distilled water was used in all experiments. Two components stock solution of lead and cadmium (1000 mg L<sup>-1</sup> each metal) was prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub> (Merck) and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Merck) in 250 mL of water. Working standard solution of 100 mg L<sup>-1</sup> of each Pb and Cd was prepared by dilution. Reagent solution (0.01 M) was prepared by dissolving 0.9433 g sodium salt of 1-nitroso-2-naphthol-3,6-disulphonic acid (Aldrich) in 250 mL of water, to be called “NNDA-reagent solution” in the followings. Diluted hydrochloric acid and nitric acid solutions (0.5, 1 and 2 M) were prepared from concentrated hydrochloric acid and nitric acid solution by dilution.

### 2.2. Preparation of the Adsorbent (Ram Horn Powder)

Ram horns were obtained from the slaughterhouse of Şanlıurfa, Turkey. For this “technical purpose”, after sacrificing the animal, the horn was cleaned mechanically to remove residual soft tissues, and then washed with tap water and distilled water and dried in oven at 80 °C until a constant weight was attained. After that, it was cut in pieces, grounded and sieved to 60–80 mesh. The powdered ram horn was washed 1 M HCl and finally in double distilled water. It was then dried at 40 °C in an oven for 24 h. The RHP prepared accordingly is resistant against dissolution in acid up to 6 M HCl or 3 M H<sub>2</sub>SO<sub>4</sub>.<sup>20</sup>

### 2.2. Column Preparation

A funnel-shaped glass tube (150 mm length and 8 mm i.d.) with a glass wool plug over its stopcock was used for housing the adsorption column. It was filled 300 mg RHP in the form of slurry, which took about 1 cm height. The adsorbent was slightly compressed with flat glass rod and another plug of glass wool was placed on its top. The latter glass wool plug prevented the adsorbent from dispersion in the sample solution that was passed through the column. Finally, the column thus prepared was washed out with 10 mL of 1 M HCl solution, and finished with water.

## 2. 3. General Procedure for Separation/Preconcentration

The operation of the column was tested with model solutions containing 20 µg of each Pb and Cd in 50–60 mL solutions, as follows. The pH of the solution was adjusted to 4–6 by adding 0.5 M HCl solution and the total volume was completed to 50–60 mL with water. The column was conditioned also by passing a few milliliters of pH 4–6 HCl solution. Then, 1 mL of NNDA-reagent solution was filled onto the column and after 5–10 min prepared model solution was passed through the column at a flow rate of about 3 mL min<sup>-1</sup>. The Pb and Cd chelates retained on the column were eluted into a 10 mL calibrated flask by using 10 mL of 1 M HCl solution. A blank solution was run under the same conditions without adding the analytes into the test solution.

## 2. 4. Dissolution of Tea Leaves and Fish Tissue Reference Materials

Masses of 100 mg and 200 mg of tea leaves and fish tissue (GBW-07605 and IAEA-407) were transferred into separate 250 mL beakers and 5 mL 0.5 M nitric acid was added to moisten the samples thoroughly. This was followed by adding 10 mL of concentrated nitric acid and heating on a hot plate (~130 °C) for 3 hours. After cooling to room temperature, 5 mL concentrated perchloric acid was added drop wise. The beaker was heated gently until completion of sample decomposition resulting in a clear solution. This was left to cool down and then was transferred into a 100 mL volumetric flask by rinsing the interior of the beaker with small portions of 0.1 M nitric acid and the solution was filled to the mark with the same acid.

## 2. 5. Dissolution of Carrot and Lettuce Samples

Carrot and lettuce samples were collected in a vegetables market in Şanlıurfa. First, the samples were cleaned with tap water and double distilled water. Then, the samples were dried at 110 °C. Vegetable samples (0.3 g) were dissolved according to the procedure given above for tea leaves and fish tissue reference materials.

## 2. 6. Preparation of Water Samples

Water samples were collected in Şanlıurfa city of Turkey: tap water (city pipe), dam water (Atatürk Dam), thermal water (Karaali), waste water (city garden). The water samples were acidified with 1.0 mL of concentrated hydrochloric acid per liter of sample, and then filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size to remove the particulate matters.

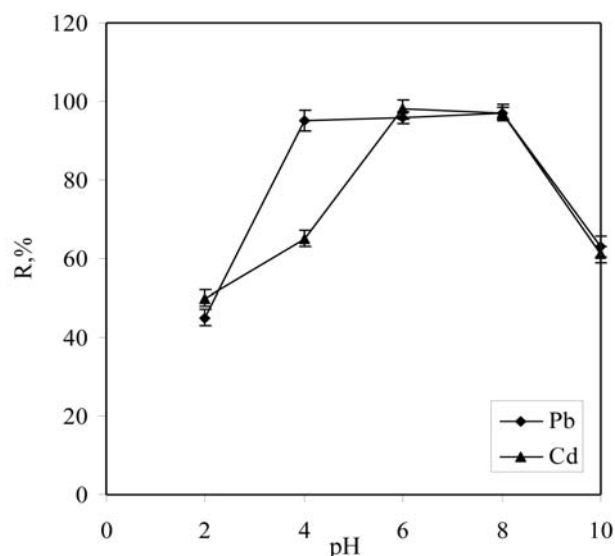
## 3. Results and Discussion

### 3. 1. Effect of the Amount of Chelating Agent

Preliminary studies indicated that the recovery for Pb and Cd was less than 10% on horn powder without a chelating agent. The effect of chelating agent was examined by adding 0.5, 1.0 and 2 mL volumes of NNDA reagent solution (0.01 M concentration) to a tap water sample and it was found that the recovery leveled off at about 70% with 1 mL reagent. When the column was pre-conditioned with few mL-s of chelating agent before sample loading, the recovery increased to 95% or above. Therefore, in the followings, the column was pre-conditioned in this manner and 1 mL of NNDA reagent solution was added to the sample solution.

### 3. 2. Influences of Ph on Recovery

The dependence of the recovery on the pH of solutions was determined in the 2–10 pH range. The results are shown in Fig. 1. Accordingly, the optimum ranges of pH for the near quantitative recovery (>95%) for Pb and Cd are 4–8 and 6–8, respectively. For subsequent works, pH values of 4 (Pb) and 6 (Cd) were selected as the working pH. Lower pH values are generally preferred for analyzing real samples (biological and geological) which are dissolved generally with acids. Moreover, there is no risk for the precipitation of metal ions in acidic solutions.



**Figure 1.** The effect of pH on the recovery of Pb and Cd on a column of RHP (amount of adsorbent, 300 mg; volume of sample solution, 100 mL; amount of Pb and Cd, 20 µg; chelating agent, 1 mL 0.01 M 1-nitroso-2-naphthol-3,6-disulphonic acid; eluent, 10 mL 1 M HCl; flow rate of sample, 1 mL min<sup>-1</sup>)

### 3. 3. Conditions of Elution

Various concentrations and volumes of HCl and HNO<sub>3</sub> solutions as eluents were applied in the recovery

test for the two elements, and results are listed in Table 1. As it can be seen the volume 10 mL was sufficient from both of 1 M HCl and HNO<sub>3</sub> solutions to the two elements (recovery >97%). Minimization of the eluent volume enables us to obtain larger enrichment factor. Therefore, concentration factor of 50 could be readily obtained with the use 10 mL eluent solution to 500 mL of sample solution in the present preconcentration procedure.

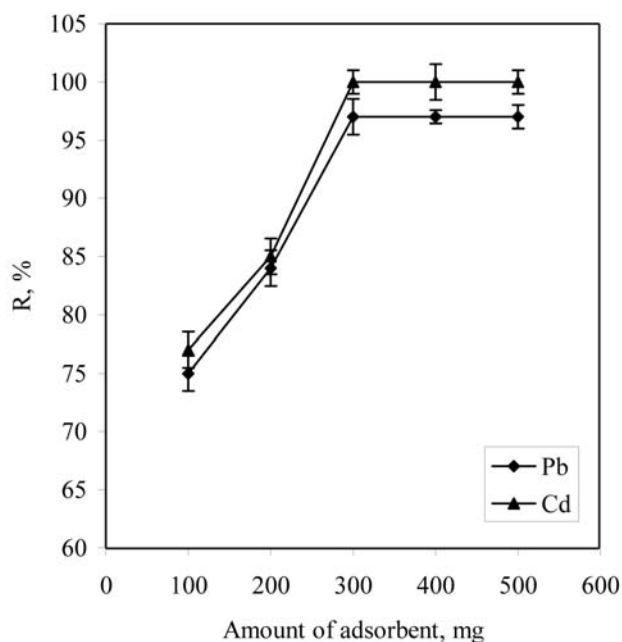
**Table 1:** Conditions of elution the recovery of Pb and Cd

Element	Type of elution solution	Volume (mL)	Concentration (M)	Recovery <sup>a</sup> (%)
Pb	HCl	5	1	70
		10	1	97
		10	2	98
	HNO <sub>3</sub>	5	1	60
		10	1	92
		10	2	95
Cd	HCl	5	1	75
		10	1	100
		10	2	100
	HNO <sub>3</sub>	5	1	86
		10	1	91
		10	2	97

<sup>a</sup> Mean of three determinations

### 3. 4. The effect of the Amount of Ram Horn Powder (RHP)

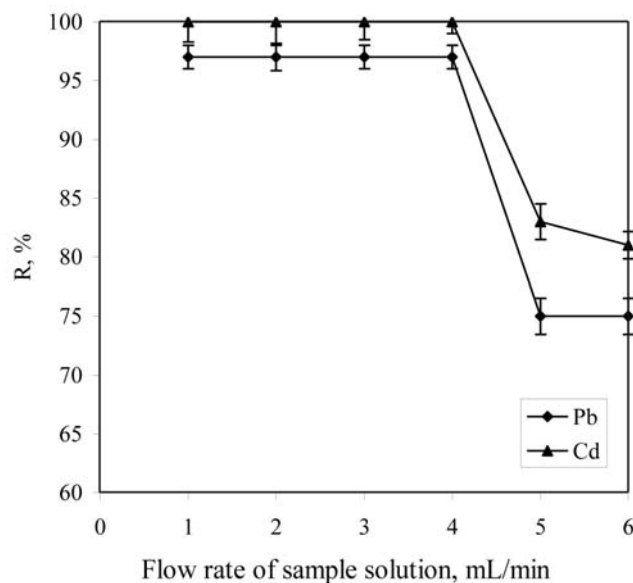
The effect of the amount of RHP on the sorption of Pb at pH 4 and of Cd at pH 6 was examined in the range of



100–500 mg, and the results are depicted in Fig. 2. It can be estimated from the curves that near quantitative recoveries were obtained in the range of 300–500 mg mass of RHP, and 300 mg of RHP was considered as optimum to the analytical work.

### 3. 5. Role of the Flow Rate of the Sample Solution

The sample flow was powered by the gravity effect and was controlled by applying restriction device in the flow out stream from column tube. The flow rate was varied in seven steps from 0.5 to 6 mL min<sup>-1</sup> using a 50–60 mL sample solution, and the results are shown in Fig. 3. It can be seen that the recovery was constant almost above 95% up to 4 mL min<sup>-1</sup> and above this rate value the recovery decreased steeply, due to the short residence time of the sample in the column. For that reason, 4 mL min<sup>-1</sup> flow rate was chosen as the optimum to the subsequent experiments. In such way the time of pre-concentration procedure could be reduced to about 15 min for 50–60 mL of sample solution.



**Figure 3.** The effect of flow rate on the recovery of Pb and Cd on a column of RHP (pH 4 for Pb and 6 for Cd; amount of adsorbent, 300 mg; volume of sample solution, 100 mL; amount of Pb and Cd, 20 µg; chelating agent, 1 mL 0.01 M 1-nitroso-2-naphthol-3,6-disulphonic acid; eluent, 10 mL 1 M HCl)

**Figure 2.** The effect of amount of adsorbent on the recovery of Pb and Cd on a column of RHP (pH 4 for Pb and 6 for Cd; volume of sample solution, 100 mL; amount of Pb and Cd, 20 µg; chelating agent, 1 mL 0.01 M 1-nitroso-2-naphthol-3,6-disulphonic acid; eluent, 10 mL 1 M HCl; flow rate of sample, 1 mL min<sup>-1</sup>)

### 3. 6. Limitations to Applicable Sample Volume

When dealing with real samples containing with very low concentrations of Pb and Cd, the maximum applicable sample volume must be determined. In order to determine the maximum volume of an applicable sample solution, lead and cadmium were preconcentrated from volumes 50, 100, 250, 500, 750 and 1000 mL synthetic sample solutions containing 20 µg Pb and Cd which corresponds 0.4, 0.2, 0.08, 0.04, 0.0267 and 0.02 µg mL<sup>-1</sup>, concentrations of each element. The recovery was approximately quantitative up to 500 mL of sample volume and decreased stepwise above 500 mL. Accordingly, by using 10 mL of elution solution, a 50-fold enrichment could be obtained.

### 3. 7. Sorption Capacity

The calculation method of sorption capacity was adapted from Maquieira et al.<sup>21</sup> Sample solution of 25 mL of solution containing Pb and Cd with concentrations in the range of 5–70 mg L<sup>-1</sup> was treated. Under optimum conditions, applying the same volume of elution solution in this capacity studied. The capacity C (µg analyte adsorbed/g sorbet) is calculated from the following equation:

$$C = cV/m \quad (1)$$

Where, c (µg/mL) analyte concentration in the eluent solution, V (mL) is the volume of the eluted solution and m (g) is the mass of adsorbent.

The breakthrough curve was obtained by plotting the Pb or Cd concentration (µg mL<sup>-1</sup>) in solution versus the amount of Pb and Cd adsorbed per gram of sorbent (µg g<sup>-1</sup>).

The breakthrough capacity of Pb and Cd evaluated from the breakthrough plot was 4.55 mg g<sup>-1</sup> and 2.69 mg g<sup>-1</sup> (0.022 mmol g<sup>-1</sup> and 0.024 mmol g<sup>-1</sup>), respectively.

### 3. 8. Precision and Limit of Detection

The precision of the method was investigated at optimum conditions mentioned above (pH: 4 for Pb and pH: 6 for Cd, chelating agent: 1 mL of 0.01 M 1-nitroso-2-naphthol-3,6-disulphonic acid, elution solution: 10 mL 1 M HCl, flow rate of sample: 4 mL min<sup>-1</sup>, volume of sample, 50 mL for both metal ions). For this reason, the general procedure was performed successively and Pb and Cd were determined in the elution solution by FAAS. The means of both ions recovery for five determinations at the 95% confidence level was 97.2% and 100.2%, respectively. As can be seen, the precision of the method is very good and the relative standard deviation for recovery was about 2%.

The limit of detection (LOD) was also studied. First, 50 mL of blank solution was passed through the column

**Table 2:** Recovery data for Pb and Cd (pH, 4 for Pb and pH, 6 for Cd; eluent, 10 mL 1 M HCl; flow rate of sample, 4 mL min<sup>-1</sup>; sample volume, 50 mL for both metals; amount of the Pb and Cd, 20 µg)

Interfering ions	Concentration (mg L <sup>-1</sup> )	R (%) <sup>a</sup>		Interfering ions	Concentration (mg L <sup>-1</sup> )	R (%) <sup>a</sup>	
		Pb	Cd			Pb	Cd
Na <sup>+</sup>	–	97	100	K <sup>+</sup>	–	97	100
	50	97	99		25	97	99
	100	96	98		50	96	98
	1000	96	97		100	96	98
Mg <sup>2+</sup>	–	97	100	Ca <sup>2+</sup>	–	97	100
	2.5	97	99		5	97	99
	5	97	98		10	96	98
	10	96	97		50	96	97
Cu <sup>2+</sup>	–	97	100	Fe <sup>2+</sup>	–	98	100
	2.5	97	99		2.5	99	99
	5	96	99		5	98	97
	10	96	98		10	97	97
Zn <sup>2+</sup>	–	97	100	Co <sup>2+</sup>	–	97	100
	2.5	97	98		2.5	97	99
	5	96	97		5	96	98
	10	96	97		10	95	98
Mn <sup>2+</sup>	–	97	100	Ni <sup>2+</sup>	–	97	100
	2.5	97	99		2.5	97	99
	5	97	98		5	96	98
	10	96	98		10	96	97

<sup>a</sup> Mean of three determinations

and retained Pb and Cd was eluted by 50 mL of 1 M HCl. This solution was used for the determination of LOD. The detection limit based on three times the standard deviation of the blank was for Pb 281  $\mu\text{g L}^{-1}$  and for Cd 87  $\mu\text{g L}^{-1}$  ( $N = 20$ ). It may be concluded that by applying a preconcentration factor of 50, a 5.62  $\mu\text{g L}^{-1}$  1.74  $\mu\text{g L}^{-1}$  of detection limit for Pb and Cd can be obtained. Because the method involves a 50-fold preconcentration, division by 50 is necessary to obtain the LOD.<sup>22</sup>

### 3. 9. Effect of Diverse Ions

In order to determine the selectivity of the method, the effect of diverse ions commonly present in water samples and in biologic samples studied, on the recovery of Pb and Cd was studied by using solutions (50–60 mL) containing 20  $\mu\text{g}$  of Pb and Cd and higher amount of other ions and applying general preconcentration procedure (Table 2). The diverse ions were added to the model solution as their nitrate or chloride salts. It can be seen from Table 2, the recovery of Pb and Cd is not compromised to any significant extent by any of the studied ions likely to present in water and biological samples.

### 3. 10. Accuracy

Accuracy of the developed procedure was estimated from the deviations found and certified concentrations in standard reference materials. Tea leaves (GBW-07605) and fish tissue (IAEA-407)]. The results were given in Table 3. It was found that there is no significant difference between the results obtained by the proposed method and certified results.

**Table 3:** Comparison of certified and determined concentration in tea leaves and fish tissue (GBW-07605 and IAEA-407)

Sample	Element	Concentration, ( $\mu\text{g g}^{-1}$ )		
		Certified	Found <sup>d)</sup> $\bar{x} \pm ts/\sqrt{N}$	Relative error, %
GBW-07605 <sup>a)</sup>	Pb	4.4	4.1 $\pm$ 0.2	-7
	Cd <sup>c)</sup>	2.0	1.9 $\pm$ 0.2	-5
IAEA-407 <sup>b)</sup>	Pb	0.12	0.11 $\pm$ 0.02	-8
	Cd	0.189	0.176 $\pm$ 0.004	-7

<sup>a)</sup> The composition of the tea leaf powder (GBW-07605) was As 0.28, Fe 264, Ni 4.6, Cu 17.3, Pb 4.4, Zn 26.3, Sb 0.056, Bi 0.063 Cd 0.057 and Co 0.18 ( $\mu\text{g g}^{-1}$ ).

<sup>b)</sup> The composition of the fish tissue (IAEA-407) was Cu 3.28, Ni 0.60, Fe 146, Pb 0.12, Zn 67.1, Cr 0.73, Al 13.8, Ca 27.0, Mg 2.72, Mn 3.52, Cd 0.189 and Co 0.1 ( $\mu\text{g g}^{-1}$ ).

<sup>c)</sup> Cd was added to the solution of tea leaf powder (GBW-07605)

<sup>d)</sup> Mean of five determinations at 95 % confidence level.

### 3. 11. Determination of Pb and Cd in Various Matrices

Determination of Pb and Cd in water (tap, dam, thermal and waste water) samples, carrot and lettuce samples was performed by applying the proposed method. For

the separation/preconcentration of Pb and Cd, carrot and lettuce dissolved in 100 mL solution and 500 mL of water samples were taken and the general procedure was applied. The results are indicated in Table 4 and Table 5.

**Table 4:** Determination of Pb and Cd in carrot and lettuce samples (amount of sample, 300 mg)

Sample	Element	Added ( $\mu\text{g g}^{-1}$ )	Found ( $\mu\text{g g}^{-1}$ ) <sup>a)</sup> $\bar{x} \pm ts/\sqrt{N}$	Relative error, %
Carrot	Pb	–	8.3 $\pm$ 0.2	–
		50	54.2 $\pm$ 0.5	-7
	Cd	–	N.D	–
		50	47.2 $\pm$ 0.1	-6
Lettuce	Pb	–	9.2 $\pm$ 0.4	–
		50	56.7 $\pm$ 0.2	-4
	Cd	–	N.D	–
		50	47.4 $\pm$ 0.3	-5

<sup>a)</sup> Mean of five determination at 95% confidence level.

**Table 5:** Determination of Pb and Cd in waste water, thermal water, tap water, and Atatürk Dam water (sample volume, 500 mL)

Sample	Element	Added ( $\mu\text{g g}^{-1}$ )	Found ( $\mu\text{g g}^{-1}$ ) <sup>a)</sup> $\bar{x} \pm ts/\sqrt{N}$	Relative error, %
Waste water	Pb	–	21 $\pm$ 1	–
		20	39 $\pm$ 2	-5
	Cd	–	N.D	–
		20	18.6 $\pm$ 0.4	-7
Thermal water	Pb	–	11 $\pm$ 2	–
		20	29 $\pm$ 2	-6
	Cd	–	N.D	–
		20	19 $\pm$ 2	-5
Tap water	Pb	–	14 $\pm$ 2	–
		20	32 $\pm$ 2	-6
	Cd	–	N.D	–
		20	19 $\pm$ 4	-5
Atatürk Dam water	Pb	–	13 2	–
		20	31 $\pm$ 2	-6
	Cd	–	N.D	–
		20	19.3 $\pm$ 0.2	-4

<sup>a)</sup> Mean of five determination at 95% confidence level.

These results proved also that the procedure is not affected by matrix interferences and can be applied satisfactorily for Pb and Cd determination in carrot and lettuce and various water samples.

## 4. Conclusion

The extraction process may depend on the formation of ion association complex between the Pb and Cd chelate

and horn powder constituent. The proposed procedure provides an established method for the separation/preconcentration of Pb and Cd in large volumes of various samples. Pb and Cd can be determined successfully by using the proposed procedure in the presence of high concentrations of interfere cations of Cu(II), Mn(II), Co(II), Fe(III), Ni(II), Zn(II), Na(I), K(I), Mg(II) and Ca(II) from an acidic medium. The two analyses can be preconcentrated quantitatively over a wide pH range (4–8 for Pb and 6–8 for Cd), no buffer is required to control the pH values precisely, which minimizes contamination. The duration of preconcentration step is about 40 min including regeneration of sorbent for 100 mL of sample solution. The RHP is environment friendly material. The elaborated separation method can be combined with other methods of element specific detection, such as GFAAS, ICP-AES, ICP-MS and electroanalytical methods, and used as an on-line preconcentration system.

## 5. Acknowledgment

The author thanks Prof. Dr. A. Rehber TÜRKER for help in preparing the manuscript and grateful for the financial support of the Unit of the Scientific Research Projects of Harran University.

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## Povzetek

Predstavljen je separacijsko-predkoncentracijski postopek za ekstrakcijo svinca in kadmija na trdni fazi z naravnim adsorbentom (roževina v prahu, RHP). Postopek je osnovan na adsorpciji kelatov dvovalentnih ionov svinca in cinka in 1-nitrozo-2-naftol-3,6 disulfonske kisline na miniaturni koloni, napoljeni z RHP. Po spiranju kolone z 10 mL 1 M HCl sta bila svinec in kadmij določena s plamensko atomsko absorpcijsko spektrometrijo FAAS. Optimizirani so bili vplivi pH, količine liganda, vrste eluenta, pretok in volumen vzorca. Za svinec so bili doseženi izkoristek postopka  $97 \pm 2\%$ , spodnja meja zaznavnosti  $5,62 \text{ ng mL}^{-1}$  in kapaciteta adsorbenta  $4,55 \text{ mg g}^{-1}$  ( $0,022 \text{ mmol g}^{-1}$ ), za kadmij pa izkoristek postopka  $100 \pm 2\%$ , spodnja meja zaznavnosti  $1,74 \text{ ng mL}^{-1}$  in kapaciteta adsorbenta  $2,69 \text{ mg g}^{-1}$  ( $0,024 \text{ mmol g}^{-1}$ ). Navedeni podatki veljajo za koncentracijski faktor 50 in za koncentracije 0,02 do  $0,2 \mu\text{g mL}^{-1}$  obeh kovin v 500 mL vzorcih s pH od 4 do 8. Različni ioni Mn(II), Co(II), Fe(III), Zn(II), Ni(II), Mg(II) in Cu(II) v koncentracijah do  $10 \mu\text{g L}^{-1}$  niso motili določevanja svinca in kadmija. Pravilnost metode potrjujejo analize standardnih referenčnih materialov (listi čajevca GBW-07605 in ribje tkivo IAEA-407), ki so pokazale dobro ujemanje rezultatov s certificiranimi vrednostmi. Opisana metoda je bila uporabljena za analize različnih vzorcev naravnih in vodovodnih vod ter vzorcev korenja in solate pri katarih so bili doseženi izkoristki postopkov boljši od 95 % in relativni standardni odmiki meritev pod 8 %.