



## Analytical Methods

# A solid phase extraction procedure for the determination of Cd(II) and Pb(II) ions in food and water samples by flame atomic absorption spectrometry



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## ABSTRACT

A relatively rapid, accurate and precise solid phase extraction method is presented for the determination of cadmium(II) and lead(II) in various food and water samples. Quantitation is carried out by flame atomic absorption spectrometry (FAAS). The method is based on the retention of the trace metal ions on Dowex Marathon C, a strong acid cation exchange resin. Some important parameters affecting the analytical performance of the method such as pH, flow rate and volume of the sample solution; type, concentration, volume, flow rate of the eluent; and matrix effects on the retention of the metal ions were investigated. Common coexisting ions did not interfere on the separation and determination of the analytes. The detection limits ( $3\sigma_b$ ) for Cd(II) and Pb(II) were found as 0.13 and 0.18  $\mu\text{g L}^{-1}$ , respectively, while the limit of quantification values ( $10\sigma_b$ ) were computed as 0.43 and 0.60  $\mu\text{g L}^{-1}$  for the same sequence of the analytes. The precision (as relative standard deviation was lower than 4% at 5  $\mu\text{g L}^{-1}$  Cd(II) and 10  $\mu\text{g L}^{-1}$  Pb(II) levels, and the preconcentration factor was found to be 250. The accuracy of the proposed procedure was verified by analysing the certified reference materials, SPS-WW2 Batch 108 wastewater level 2 and INCT-TL-1 tea leaves, with the satisfactory results. In addition, for the accuracy of the method the recovery studies ( $\geq 95\%$ ) were carried out. The method was applied to the determination of the analytes in the various natural waters (lake water, tap water, waste water with boric acid, waste water with  $\text{H}_2\text{SO}_4$ ) and food samples (pomegranate flower, organic pear, radish leaf, lamb meat, etc.), and good results were obtained. While the food samples almost do not contain cadmium, they have included lead at low levels of 0.13–1.12  $\mu\text{g g}^{-1}$ .

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## 1. Introduction

The increase in industrial activities has intensified environmental pollution problems and the deterioration of several ecosystems with the accumulation of toxic metals (Baytak, Kendüzler, Türker, & Gök, 2008). The potential risks of heavy metal pollution on the bio-environment have evoked intensive investigations over the past decades (Illuminati, Annibaldi, Truzzi, & Scarponi, 2014; Srijaranai et al., 2011; Xie, Lin, Wu, & Xie, 2008; Zhang, Li, Shi, & Kong, 2006). Some metals are essential for living organisms at very low concentrations (i.e., copper), but some metals such as cadmium and lead are toxic even at low levels and have a direct and adverse influence on various biological processes (Behbahani et al., 2014; Debelius, Forja, DelValls, & Lubián, 2009; Junior,

Silva, Leao, & Ferreira, 2014; Liu et al., 2011). Cadmium has a biological half-life in the range of 10–30 years, and is known to damage organs such as kidneys, liver and lungs (Xiang et al., 2012). The heavy use of toxic metals has caused local and global contamination of air, dust, and soil (Hsu & Guo, 2002). There is limited data on lead toxicity in marine microalgae (Debelius et al., 2009).

There are more than 20 heavy metals, but four are of particular concern to human health: lead (Pb), cadmium (Cd), mercury (Hg), and inorganic arsenic (As). According to the U.S. agency for toxic substances and disease registry ([http://tuberoose.com/Heavy\\_Metal\\_Toxicity.html](http://tuberoose.com/Heavy_Metal_Toxicity.html); <http://www.ctahr.hawaii.edu/oc/freepubs/pdf/tea>), they are highly toxic and can cause damaging effects even at very low concentrations (Longas, Arrona, Ostra, & Millan, 2009).

Food and cigarette smoke are the largest potential sources of cadmium exposure for members of the general population (Lemos et al., 2008). Prolonged intake, even of very small amounts, leads to severe dysfunction of the kidneys. At high doses it is also

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known to produce health effects on the respiratory system and has been associated with bone disease. More recently, the possible role of cadmium in human carcinogenesis has been also studied. In human body, cadmium acts by binding to the –SH group of cysteine residues in proteins and so inhibits –SH enzymes. It can also inhibit the action of the zinc enzymes by displacing the zinc (Custódio, Pessanha, Pereira, Carvalho, & Nunes, 2011; Ferreira et al., 2007).

For a long time, it is known that lead is toxic for brain, kidney and reproductive system and can also cause impairment in intellectual functioning, infertility, miscarriage and hypertension. Due to its malleability, low melting point, and ability to form compounds, Pb has been used in hundreds of products such as pipes, solder, brass fixtures, crystal, paint, cable, ceramics, and batteries (Srijaranai et al., 2011). As a result, populations in, at least, 100 countries are still exposed to air pollution with lead in spite of banning the usage of lead in gasoline (Kaya & Yaman, 2008; Mashhadizadeh, Amoli-Diva, Shapouri, & Afruzi, 2014). Children are exposed to lead right from their birth, as children in the embryonic stage receive lead from their mothers through the blood ([http://ec.europa.eu/environment/waste/studies/pdf/heavy\\_metalsreport.pdf](http://ec.europa.eu/environment/waste/studies/pdf/heavy_metalsreport.pdf)). The world health organization (WHO) established provisional tolerable weekly intakes of Cd and Pb of 7 and 25  $\mu\text{g kg}^{-1}$  body weight, respectively, for all human groups (WHO, 2000). Therefore, analytical techniques with high sensitivity are required for detection of such low concentrations of these two metals (Acar, 2011).

Growing attention is being given to health hazards presented by the existence of heavy metals in the environment; their accumulation in living tissues throughout the food chain, poses a serious health problem (Zouboulis, Loukidou, & Matis, 2004). Controlling heavy metal discharges and removing toxic heavy metals from aqueous solutions have become a challenge for the 21st century (Volesky, 2001). The determination of trace elements and contaminants in complex matrices such as food, often requires extensive sample preparation and/or extraction regimes prior to instrumental analysis (Korn et al., 2008). The monitoring and control of these trace elements in food sources require processing a lot of samples to accurately characterise their abundance and to reach reliable conclusions (Saçmacı, Kartal, & Saçmacı, 2011).

The determination of trace metals in food samples has routinely been done by inductively coupled plasma optical emission spectrometry (ICP-OES) (He, Chang, Huang, & Hu, 2008), inductively coupled plasma-mass spectrometry (ICP-MS) (Hammer, Nicolas, & Andrey, 2005), graphite furnace atomic absorption spectrometry (GFAAS) (Manjusha, Dash, & Karunasagar, 2007), and flame atomic absorption spectrometry (FAAS) (Karadaş, Turhan, & Kara, 2013; Liu, Ding, Qi, Han, & Zhang, 2007; Neves et al., 2009).

Preconcentration of traces of heavy metals is often required prior to the instrumental determination to lower the detection limits and to improve the precision and accuracy of analytical results (Hiraide, Hommi, & Kawaguchi, 1991). Solid phase extraction is an extraction method that uses a solid phase and a liquid phase to isolate one, or one type, of analyte from a solution. Also, this method has the advantages of being more sensitive, simple environment friendly, faster and sampler saving. It has known as a powerful tool for separation and preconcentration of various inorganic and also organic analytes (Saçmacı, Kartal, Saçmacı, & Soykan, 2011).

In this study, a simple and rapid solid phase extraction procedure by using Dowex Marathon C (DMC) resin was developed in order to preconcentrate Cd(II) and Pb(II) ions in water and various food samples (meat product, vegetable, fruit, herbal plant, spices, fruit, cereals and beverages) prior to their flame atomic absorption spectrometric (FAAS) determinations. The determinations of the Cd(II) and Pb(II) contents in representative food samples in Turkey were done. To the best of our knowledge, there is no any study for

separation/preconcentration of the analytes by using this resin. We here report the usefulness of the resin to separate and concentrate the metal ions in food and various water samples.

## 2. Experimental

### 2.1. Instrument

A PerkinElmer model AAnalyst 800 flame atomic absorption spectrometer (Norwalk, CT, USA) equipped with a deuterium background correction system and an air-acetylene burner was used for the determination of all the metal ions. The operating conditions adjusted in the spectrometer were carried out according to the standard guidelines of the manufacturer. For measuring pH values in the aqueous phase, a Consort model C533 pH meter combined with a glass-electrode.

### 2.2. Reagents and standard solutions

All reagents used were of the highest available purity and at least analytical reagent grade (Merck, Darmstadt, Germany). Deionised ultra pure water was used for the preparation of the aqueous solutions. Standard stock solutions of the analytes ( $1000 \text{ mg L}^{-1}$ ) were prepared by dissolving appropriate amounts of their nitrate salts in 2% (w/v) nitric acid solution. Working standard solutions were prepared fresh daily by stepwise dilution of the stock solutions with deionised water. The calibration curve was established using the standard solutions prepared in  $1 \text{ mol L}^{-1}$   $\text{HNO}_3$  by dilution of the stock solutions. 1-g of the DMC resin was used as solid phase extractant. The glassware used was cleaned by soaking overnight in dilute  $\text{HNO}_3$  (1:5) and then rinsed with deionised water several times.

The following buffer solutions were used for the presented preconcentration procedure: HCl/KCl buffer for pH 1.0–2.0;  $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$  buffer for pH 3.0–5.0;  $\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$  buffer for pH 6.0–7.0;  $\text{NH}_4\text{Cl}/\text{NH}_3$  buffer for pH 8–10. All the buffer solutions have been prepared from the relevant components for which are in  $0.1 \text{ mol L}^{-1}$  concentration.

### 2.3. Sampling

The bean ( $n = 2$ ), fruit and vegetable ( $n = 7$ ), herb ( $n = 6$ ), meat ( $n = 8$ ), spices ( $n = 16$ ), organic flour ( $n = 1$ ) and beverage ( $n = 5$ ) samples were purchased from local markets in Kayseri. The cereal, vegetable, fruit and herb samples were washed thoroughly with tap water and deionised ultra pure water. The shells of vegetable and fruit samples were grinded when necessary. Then, the samples were dried at  $70 \text{ }^\circ\text{C}$  for 24 h and meat samples were dried at  $110 \text{ }^\circ\text{C}$  for 48 h.

### 2.4. Solid phase extraction procedure

The proposed solid phase extraction method was tested with model solutions prior to its application to real samples. Twenty-five milliliter portions of aqueous solutions containing  $10 \mu\text{g L}^{-1}$  of Pb(II) and  $5 \mu\text{g L}^{-1}$  of Cd(II) were used. The pH of the solutions was adjusted to 3.5 with 10 mL of  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer solution. The flow of the sample and eluent solution through the column was gravitationally performed at a flow rate of  $2.0 \text{ mL min}^{-1}$ . The flow rate of the sample solution was controlled by using the stopcock of the column. After being completed the passing of the sample solution, the column was washed with a small amount of deionised water. Then, the retained metal ions were eluted from the column by the aid of 25 mL of  $3 \text{ mol L}^{-1}$   $\text{HNO}_3$ . After the evaporation was continued almost to dryness

and the final volume of moisty residue was completed to 2 mL with  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ . The metal ion concentrations in the eluate solution were determined by (FAAS).

### 2.5. Preparation of samples and application of the proposed method

A 1.0-g portion of the standard reference material (INCT-TL-1 tea leaves) was dissolved in the mixture of 10 mL of concentrated  $\text{HNO}_3$  and 3 mL of concentrated  $\text{H}_2\text{O}_2$  on a hot plate. After completing the dissolution process, all the sample solutions were clear. The volume of the samples was diluted to 25 mL with deionised water by adjusting the pH to 3.5 ( $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer). These sample solutions were analyzed by using the proposed preconcentration procedure described above. The final measurement volume of the sample solutions was 2 mL.

The second certified reference material was the SPS-WW2 Batch 108 waste water sample (10 mL). The pH values of the samples were adjusted to 3.5 with  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer solution. Then the separation/preconcentration procedure given above was applied to these sample solutions. The concentration of the investigated analyte ions in the final measurement solution was determined by FAAS.

A 1.0-g aliquot from each of the food samples was treated with 10 mL of concentrated  $\text{HNO}_3$  and then heated until obtaining a clear solution. The evaporation was continued almost to dryness, and to the moisty residue 10 mL of concentrated  $\text{HNO}_3$  was added once more. Afterwards the mixture was evaporated near to dryness and then 2 mL of concentrated  $\text{H}_2\text{O}_2$  was added to it. After completing the dissolution process, the sample solution was filtered through a cellulose filter paper. The filter paper was washed with 1–2 mL of  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ . The filtrate was diluted to 25 mL with deionised water by adjusting the pH to 3.5 ( $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer). These sample solutions were treated by the proposed procedure described above. The final measurement volume of the sample solutions was 2 mL. A blank digest was carried out in the same way. Analyte elements in the final solution were determined with FAAS.

The proposed method was applied to various water samples. First, the pHs of the water samples were adjusted to 3.5 and then the preconcentration procedure was applied. The analyte concentrations in the final solution were determined by FAAS.

## 3. Results and discussion

### 3.1. Effect of pH

The pH of the working solutions in the solid phase extraction is one of the critical parameters for quantitative recoveries of the analytes. The effect of pH on the recoveries of Cd(II) and Pb(II) was investigated on the pH range of 1.0–10.0. The buffer solutions used in this range were: HCl/KCl buffer for pH 1.0–2.0;  $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$  buffer for pH 3.0–5.0;  $\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$  buffer for pH 6.0–7.0; and  $\text{NH}_4\text{Cl}/\text{NH}_3$  buffer for pH 8–10. In the pH range of 2.5–4, the analyte ions were simultaneously and quantitatively (>95%) recovered. All further works were performed at pH 3.5 (Fig. 1).

### 3.2. Effect of type, concentration and volume of eluent

For the elution of the trace metals adsorbed on the resin, dilute acid solutions having different concentrations and volumes were investigated. For this reason, various elution solutions were used for desorption of the trace metals from the resin. It was found that 25 mL of  $3 \text{ mol L}^{-1} \text{ HNO}_3$  was sufficient for complete elution of the metal ions studied. Therefore, 25 mL of  $3 \text{ mol L}^{-1} \text{ HNO}_3$  solution was used as eluent in further experiments (Table 1).

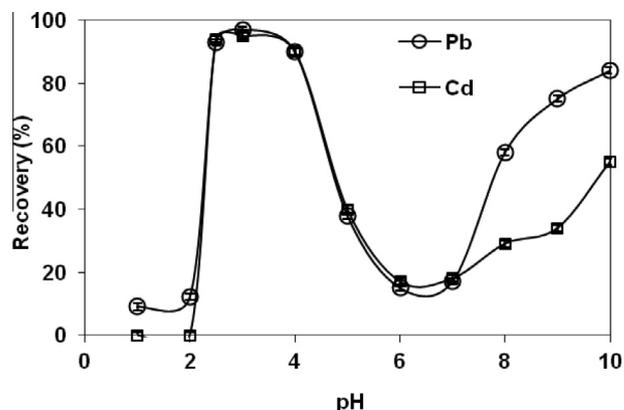


Fig. 1. Effect of pH on the recoveries of the analyte ions ( $n = 3$ ).

### 3.3. Effect of flow rates of sample and eluent solutions

The effect of the flow rate of sample solution and eluent was examined under the optimum conditions (pH 3.5, eluent: 25 mL of  $3 \text{ mol L}^{-1} \text{ HNO}_3$ ). The influences of the flow rates of both the sample and the eluent solutions on the recoveries of the metal ions were investigated in the range of  $1.0$ – $10.0 \text{ mL min}^{-1}$ . The flow rates for the both solutions were adjusted with the aid of the stop-cock of the column. For the flow rates higher than  $2 \text{ mL min}^{-1}$ , the recovery of the metal ions were not quantitative and so a flow rate of  $2 \text{ mL min}^{-1}$  was chosen for the subsequent experiments for both the sample and elution solutions (Figs. 2 and 3).

### 3.4. Effect of the amount of the resin

The effect of the amount of the resin on adsorption of the metals were investigated under the optimised conditions (pH 3.5, eluent: 25 mL of  $3 \text{ mol L}^{-1} \text{ HNO}_3$ , sample and eluent flow rates:  $2 \text{ mL min}^{-1}$ ). The recovery values increased with the increasing amount of the resin and reached to quantitative value (recovery about 100%) for the resin amount of 1 g. The recovery of the metal ions decreased with increasing amounts of the resin beyond 1 g due to the insufficient eluent volume. If the eluent volume was higher than 25 mL, the recoveries were quantitative. In all subsequent studies, the glass column was filled with 1 g of the resin.

### 3.5. Effect of sample volume

In order to deal with real samples, especially water samples, containing very low concentrations of the metal ions, the maximum applicable sample volume must be determined. For this purpose, 25–1000 mL volumes of the model solutions containing  $5 \mu\text{g L}^{-1}$  of Cd(II) and  $10 \mu\text{g L}^{-1}$  of Pb(II) were passed through the

Table 1

Effect of kind, volume and concentration of HCl and  $\text{HNO}_3$  solutions on the recovery of the analytes (sample volume: 25 mL, pH 3.5,  $n = 3$ ).

Concentration and type of eluent	Volume (mL)	Recovery (%) <sup>a</sup>	
		Cd(II)	Pb(II)
$3 \text{ mol L}^{-1} \text{ HNO}_3$	25	99 ± 1	102 ± 1
$3 \text{ mol L}^{-1} \text{ HNO}_3$	10	93 ± 1	102 ± 1
$2 \text{ mol L}^{-1} \text{ HNO}_3$	25	82 ± 2	85 ± 1
$2 \text{ mol L}^{-1} \text{ HNO}_3$	10	60 ± 2	65 ± 1
$1 \text{ mol L}^{-1} \text{ HNO}_3$	25	42 ± 1	28 ± 1
$1 \text{ mol L}^{-1} \text{ HNO}_3$	10	34 ± 1	36 ± 1
$3 \text{ mol L}^{-1} \text{ HCl}$	25	93 ± 2	95 ± 2
$2 \text{ mol L}^{-1} \text{ HCl}$	25	85 ± 2	82 ± 2
$1 \text{ mol L}^{-1} \text{ HCl}$	10	36 ± 2	37 ± 2

<sup>a</sup> Average ± standard deviation.

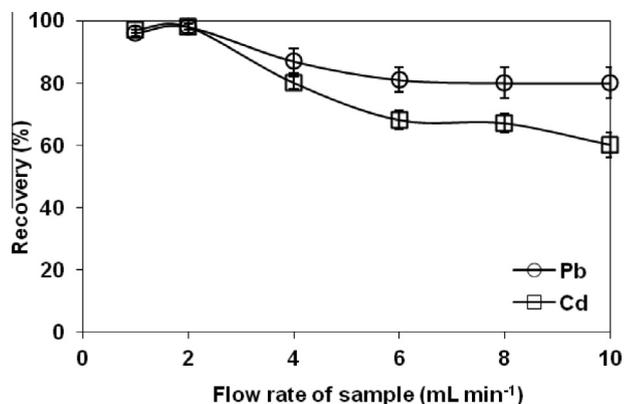


Fig. 2. Effect of the flow rate of sample on the recoveries ( $n = 3$ ).

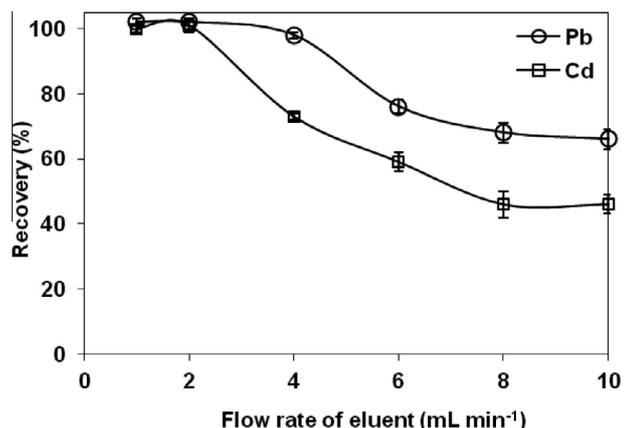


Fig. 3. Effect of the flow rate of eluent on the recoveries ( $n = 3$ ).

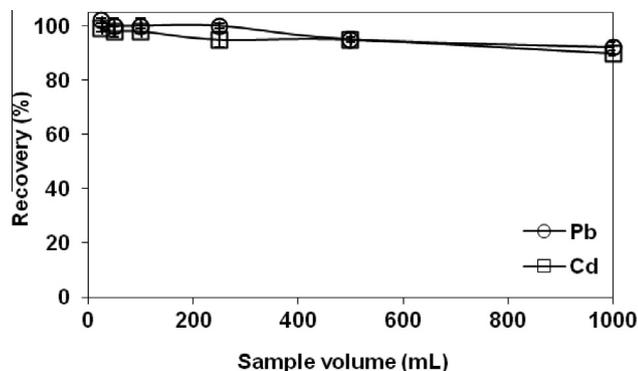


Fig. 4. Effect of the sample volume on the recoveries of the analyte ions ( $n = 3$ ).

column under the optimum conditions (pH 3.5, eluent: 25 mL of 3 mol L<sup>-1</sup> HNO<sub>3</sub>, sample and eluent flow rates: 2 mL min<sup>-1</sup>, resin amount: 1 g). The recovery values as a function of sample volume are shown in Fig. 4. The recoveries were quantitative and constant up to 500 mL of the sample solution. The preconcentration factor was calculated as the ratio of the highest sample volume (500 mL) to the final volume (2 mL) and found to be 250 for the metal ions.

### 3.6. Effect of matrix ions

The effects of possible matrix ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) present in water and food samples on the recoveries of the studied elements were also exam-

ined by adding the known concentration of each matrix ion to the model solution. The results are summarised in Table 2. The ions normally present in this samples did not interfere under the experimental conditions used (recoveries ≥ 95%). The tolerated amounts of each ion were the concentration values tested that caused less than 5% of the absorbance alteration. These results indicate that the proposed separation/preconcentration method could be applied to various water and food samples for the determination of Cd(II) and Pb(II).

### 3.7. Adsorption capacity of the resin

The adsorption isotherm of the resin for Cd(II) and Pb(II) were studied by the column method. The adsorption capacity of the chelating resin was obtained by using the Langmuir equation (Saçmacı, Saçmacı, Soykan, & Kartal, 2010) given below:

$$\frac{C}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m}\right) \times C$$

where  $C$  (mg L<sup>-1</sup>) is the concentration of Cd(II) and Pb(II) in solution at equilibrium and  $n$  (mg g<sup>-1</sup>) is the amount of adsorbed Cd(II) per gram of the resin at equilibrium (mg g<sup>-1</sup>).

The adsorption capacity of the chelating resin for Cd(II) and Pb(II) was found to be 61.4 and 20.3 μmol g<sup>-1</sup>, respectively. And binding equilibrium constant was calculated to be 0.002 L mg<sup>-1</sup> and 0.087 L mg<sup>-1</sup> for Cd(II) and Pb(II), respectively. The results showed that the sorbent has a high adsorption capacity for this analytes.

### 3.8. Analytical performance

In order to determine the detection limit (DL) of the proposed method, the pH of the blank solutions (25 mL,  $n = 20$ ) was adjusted to pH 3.5 using CH<sub>3</sub>COOH/CH<sub>3</sub>COONa buffer solution and then the preconcentration method was applied. The detection limits, calculated as the amount of analyte required to yield a net peak equal to three times the standard deviation of the blank solution, 3s<sub>b</sub>, were found to be 0.13 for Cd(II) and 0.18 μg L<sup>-1</sup> for Pb(II). The limit of quantification values for the method, according to the criteria of 10 s<sub>b</sub>, were computed as 0.43 and 0.60 μg L<sup>-1</sup> for Cd(II) and Pb(II), respectively (Mocák, Janiga, & Rábarová, 2009). In the calculation of the DLs of the method, the 250-fold preconcentration factor was taken into consideration. The preconcentration factor was calculated as ratio of the highest sample volume (500 mL) to the final measurement volume (2 mL) and found to be 250 for the metal ions studied.

The precision of the method under the optimum conditions was determined by performing successive 20 retention and elution cycles at 10 μg L<sup>-1</sup> Pb(II) and 5 μg L<sup>-1</sup> Cd(II) concentration levels followed by FAAS. The relative standard deviations for the metals studied were lower than 4%.

For purpose of quantitative analysis, the calibration curves were constructed under the optimum conditions. Primarily, the standard solutions were prepared in the range of 0.002–0.01 mg L<sup>-1</sup> for Pb(II) ions and of 0.001–0.01 mg L<sup>-1</sup> for Cd(II) ions. After applying the proposed method to these standard solutions, the measurements for Pb(II) and Cd(II) ions have been carried out by FAAS. The calibration curves were linear for Pb(II) concentrations in 0.5–2.5 mg L<sup>-1</sup> range, with a determination coefficient of 0.9989, and for Cd(II) concentrations in 0.1–2.5 mg L<sup>-1</sup> range, with a determination coefficient of 0.9996 after employing the proposed procedure.

**Table 2**Effect of foreign ions on the recovery of Cd(II) and Pb(II) (pH 3.5, eluent: 25 mL of 3 mol L<sup>-1</sup> HNO<sub>3</sub>, sample volume: 25 mL, n = 3).

Ions	Added as	Concentration (mg L <sup>-1</sup> )	Recovery Pb(II)	Recovery Cd(II)
Na <sup>+</sup>	NaNO <sub>3</sub>	20,000	95 ± 1 <sup>a</sup>	90 ± 2 <sup>a</sup>
K <sup>+</sup>	KNO <sub>3</sub>	10000	96 ± 2	87 ± 1
Ca <sup>2+</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	1000	95 ± 1	96 ± 1
Mg <sup>2+</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	1000	95 ± 1	98 ± 1
Cl <sup>-</sup>	NaCl	1000	99 ± 1	99 ± 1
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	1000	100 ± 1	98 ± 1
PO <sub>4</sub> <sup>3-</sup>	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	1000	99 ± 2	100 ± 2
Ni <sup>2+</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	10	95 ± 1	95 ± 1
Cu <sup>2+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	10	103 ± 2	100 ± 2
Zn <sup>2+</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	10	96 ± 1	95 ± 2
Co <sup>2+</sup>	Co(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	10	95 ± 1	97 ± 1
Fe <sup>3+</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	10	102 ± 3	98 ± 1

<sup>a</sup> Average ± standard deviation.

### 3.9. Accuracy and application of the method

In order to investigate the accuracy of the proposed procedure, the first work made was the recovery study. For this reason, the known amounts of the analyte ions were added to various water and various food samples and then the proposed method has been applied. The results are shown in Table 3. A good agreement was obtained between the added and the measured amounts of the metals. The recovery values calculated were always higher than 95%, thus confirming the accuracy of the proposed procedure and its independence from the matrix effects. These results confirm the accuracy of the proposed separation/preconcentration method.

To verify the accuracy of the solid phase extraction procedure, the second work made was to analyze the certified reference materials, SPS-WW2 Batch 108 wastewater level 2 and INCT-TL-1 tea leaves. The results are given in Table 4. The found values of the analytes in the certified reference materials were in good agreement with their certified values.

The method was also extended for the separation and preconcentration of the trace elements in various food samples. The final measurement volume was 2 mL for all the samples. Based on the above findings, the presented procedure was applied to the deter-

**Table 4**

The determination of Cd(II) and Pb(II) in the standard reference materials by using the presented preconcentration procedure (n = 3).

Sample	Cd(II)	Pb(II)
<i>SPS-WW2 Batch 108</i>		
Certified value (µg L <sup>-1</sup> )	1000 ± 0.5 <sup>a</sup>	500 ± 3
Found	990 ± 2	502 ± 1
Recovery	99 ± 1	100 ± 1
<i>INCT-TL-1 tea</i>		
Certified value (µg g <sup>-1</sup> )	30.2 ± 4.0	1.78 ± 0.24
Found	29.7 ± 2.0	1.71 ± 0.30
Recovery	98 ± 5	96 ± 1

<sup>a</sup> Average ± standard deviation.

mination of the analytes in some food and herbal plant samples. The results are shown in Table 5.

The highest Pb(II) concentrations in the meat product were found as 0.21 µg g<sup>-1</sup> in wurst, and Cd(II) and Pb(II) in spices samples were found in cumin as 0.11, 0.33 µg g<sup>-1</sup>, respectively. The maximum concentrations in herbal plant were found in mate as 1.12 µg g<sup>-1</sup> and island tea as 0.49 for Pb(II).

**Table 3**

The results of accuracy test for samples (n = 3).

Sample (mg L <sup>-1</sup> )	Added	Found	Recovery (%)	Found	Recovery (%)
		Tap water		Waste water with H <sub>2</sub> SO <sub>4</sub>	
Cd	–	– <sup>a</sup>	–	0.24 ± 0.02 <sup>b</sup>	–
	0.2	0.19 ± 0.01	95 ± 5	0.42 ± 0.01	95 ± 2
Pb	–	–	–	2.02 ± 0.02	–
	1	0.98 ± 0.02	98 ± 2	2.97 ± 0.03	98 ± 5
		Lake water		Waste water with boric acid	
Cd	–	0.20 ± 0.01	–	–	–
	0.2	0.38 ± 0.01	95 ± 3	0.19 ± 0.02	95 ± 5
Pb	–	1.70 ± 0.02	–	–	–
	1	2.67 ± 0.01	99 ± 1	0.97 ± 0.02	97 ± 2
		Radish leaf		Lamb meat	
Cd	–	–	–	–	–
	0.5	0.49 ± 0.01	98 ± 2	0.49 ± 0.01	98 ± 2
Pb	–	–	–	–	–
	1	0.99 ± 0.01	99 ± 1	0.99 ± 0.03	99 ± 3
		Organic pear		Pomegranate flower	
Cd	–	–	–	–	–
	0.5	0.51 ± 0.01	102 ± 2	0.48 ± 0.01	96 ± 2
Pb	–	–	–	–	–
	1	0.99 ± 0.01	99 ± 1	0.98 ± 0.01	98 ± 1

<sup>a</sup> Below detection limit.<sup>b</sup> Average ± standard deviation.

**Table 5**

Determination of the analytes in some food samples after application of the proposed solid phase extraction procedure ( $n = 3 \mu\text{g g}^{-1}$ ). Samples which have cadmium and lead contents below the detection limits: carry handle, chicken, chili pepper, cinnamon, fish, flour, ginger, lamb meat, linden tree, parsley, pomegranate flower, radish leaf, thyme, turmeric, veal, wild plum, and Organics: apple, apricot, basil, bean, chickpea, cress, eggplant, grape, heartburn, lettuce, mint, pear, rocket, and squash.

Sample	Cd(II)	Pb(II)
Sausage	– <sup>a</sup>	$0.19 \pm 0.02^b$
Salami	–	$0.19 \pm 0.03$
Wurst	–	$0.210 \pm 0.002$
Pastrami	–	$0.13 \pm 0.01$
Sweet basil	–	$0.35 \pm 0.01$
Rosemary	–	$0.30 \pm 0.05$
Cumin	$0.11 \pm 0.06$	$0.33 \pm 0.03$
Heath	–	$0.250 \pm 0.004$
Linseed	–	$0.37 \pm 0.01$
Carnation	–	$0.28 \pm 0.01$
Mate	–	$1.12 \pm 0.20$
Black tea	–	$0.360 \pm 0.006$
Green tea	–	$0.19 \pm 0.02$
Island tea	–	$0.49 \pm 0.02$

<sup>a</sup> Below detection limit.

<sup>b</sup> Average  $\pm$  standard deviation.

#### 4. Conclusions

In this work, the solid phase extraction method was used for determining of the Cd(II) and Pb(II) levels in representative food samples, in Turkey. The proposed solid phase extraction method is simple, fast and accurate for the flame atomic absorption spectrometric determination of traces of cadmium and lead in various water and food samples from Kayseri – Turkey. The possible interference of alkaline and earth alkaline ions to the analysis were investigated and an important interference was not encountered. The accuracy of the results was verified by analysing the spiked water and food samples and certified reference materials. The good features of the proposed method showed that it is a convenient and low cost one. Also the presented solid phase extraction procedure is relatively rapid as compared with previously reported procedures for the enrichment–separation of cadmium and lead.

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