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Determination of Cadmium(II) in Water and Soil Samples after Preconcentration with a New Solid Phase Extractor

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Abstract: A new simple and reliable method has been developed to separate and preconcentrate trace cadmium ion from water and soil samples for subsequent measurement by flame atomic absorption spectrometry (FAAS). Cadmium ions adsorbed quantitatively on Amberlyst 36 cation exchange resin were eluted with a 5 mL of 3 mol/L hydrochloric acid solution. Different factors and matrix effects for the preconcentration step were examined. The analytical figures of merit for the determination of cadmium are as follows: analytical detection limit, 0.51 μg/L; precision (RSD), 2.9%; enrichment factor, 200; capacity of resin 192 mg/g. The method was applied for cadmium determination in tap water, natural drinking water, soil, and roadside dust samples. The accuracy of the method is confirmed by analyzing standard reference material (Montana Soil, SRM 2711).

Keywords: Cadmium determination, water analysis, soil analysis, preconcentration, Amberlyst 36

INTRODUCTION

Cadmium is a highly toxic element. It is now widely accepted that this metal is among the most dangerous of all the metal contaminants of food, not only because of its high level of toxicity, but also because of its wide distribution and its many important applications. Therefore, it has been described as one of the most dangerous trace metals in the food and environment of human beings

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(1). The FAO/WHO Joint Expert Committee on Food Additives recommended provisional maximum tolerable daily intake of cadmium from all sources (water, food, and air) of 1.0–1.2 μg/kg body mass (2). National and international regulations on food quality are lowering the maximum permissible levels of toxic metals in human food; thus, the maximum permissible level of cadmium in drinking water is 5.0 μg/L (3). Therefore, it is very important to determine this element in the environment such as drinking water and soil.

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the separation and preconcentration of trace cadmium from the matrix prior to its determination, due to its frequently low concentrations in environmental samples. Several methods, such as coprecipitation (4), cloud point extraction (5), liquid-liquid extraction (6), and solid phase extraction (7–14) etc. have been used for the enrichment of trace cadmium from environmental samples. In the last two decades, the SPE approach has gained rapid acceptance because it offers a number of important benefits, such as reduced solvent usage and exposure, the availability of a wide variety of sorbent phases, suitability to automation, reduced disposal costs, and shorter extraction times for sample preparation (15, 16).

Recently, Tarley and Arruda described a new sensitive and low cost method for flame atomic absorption spectrometry. In this method, cadmium is preconcentrated from an acidic medium by forming a complex with ammonium O·O-diethyldithiophosphate, which is then adsorbed onto polyurethane foam. The elution step was performed by using 80% (v/v) ethanol (12). Alonso et al. proposed an automatic separation-preconcentration system coupled to an electrothermal atomic absorption spectrometer. The preconcentration step is performed on a chelating resin microcolumn [silica gel functionalized with 1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide] placed in the autosampler arm. The system is applied to the determination of cadmium in sea water (13). Pourreza and Mousavi described a sensitive and simple solid-phase preconcentration procedure for enrichment of cadmium prior to determination of cadmium after enrichment as CdI_4^{2-} on naphthalene-methyltrioctylammonium chloride adsorbent, elution by nitric acid, and subsequent determination by FAAS (14). In many separation/preconcentration methods, such as those described above, either a known amount of chelating agent is added to the solution to form the metal chelate or a chelating agent is immobilized on a support material of column prior to enrichment procedure. However, in this study, any chelating agent was not used for obtaining metal chelates or immobilization. Cadmium(II) ions retained on resin without chelating agent. This resin was used in catalyst reactions of some organic components (17, 18). Yadav and Joshi (17) examined the synthesis of tert-amyl methyl ether from tert-amyl alcohol and methanol in the presence of a variety of solid acid catalysts. Amberlyst 36 was found to be very effective in comparison with other solid acids. Yadav and Rahuman (18) discuss the use of acid treated clays such as K-10 and Filtrol-24 and cation exchange resins such as Amberlyst 36, Amberlyst 15, and Indion 130 as catalysts at 25°C which have different acid strengths and pore size distributions. Amberlyst 36 was the most active of the catalysts.

In this work, Amberlyst 36 was used first for trace cadmium as a solid-phase extractor. The resin has been used first before for the preconcentration of copper from various matrices in our previous study (19). In this method, any chelating agent has not been used for the preconcentration procedure. Various parameters such as pH, amount of resin and influences of interfering ions, etc. have been evaluated.

EXPERIMENTAL

Apparatus

A Philips PU 9285 model atomic absorption spectrometer, equipped with a deuterium-lamp background corrector, a cadmium hollow cathode lamp (Philips), and an air-acetylene flame as the atomizer was used for the determination of cadmium. The wavelength, lamp current, slit width, and acetylene flow rate were 228.8 nm, 6 mA, 0.5 nm and 1.2 L/min, respectively. pH measurements were made with a Jenway 3010 model pH meter and a combination glass electrode.

Reagents and Solutions

Triple-distilled water was used to prepare all solutions. All reagents were of analytical grade, unless otherwise stated. Laboratory glassware was kept overnight in a 5% nitric acid solution. A stock solution of cadmium (1000 mg/L) was prepared by dissolving 0.2744 g $Cd(NO_3)_2 \cdot 4H_2O$ (Merck) in 100 mL of water. A working aqueous solution of cadmium(II) (10 mg/L) was also prepared from cadmium stock solution. Sodium fluoride, hydrochloric acid (37%), and nitric acid (65%) were from Merck. Amberlyst 36 (Aldrich) was used after washing with methanol, 1 mol/L HCl solution and water, respectively and dried for 4 h at 60°C.

Collection and Preparation of Samples

A tap water sample was collected from our laboratory and a commercial natural drinking water was collected from local market in Ankara, Turkey. These water samples were filtered through a Millipore cellulose nitrate membrane of pore size 0.45 μm. The samples, 20 L of every one, were stored in polythene bottles and then acidified with 1.0 mL of concentrated hydrochloric acid per liter of sample. A soil sample, collected from

Kılıçözü Industrial Estate, Kırşehir, Turkey, a roadside dust sample, collected from Ankara-Kayseri Main Road in the city of Kırşehir, Turkey, and one certified reference material (Montana Soil, SRM 2711) were analyzed. The soil sample (seven different sample points) was collected from industrial estate, which includes mainly automotive services. The roadside dust sample (six different sample points) was collected from the left and right side of the road. Samples were collected from the top of the soil and roadside and stored in plastic bags. In the laboratory, other particles in samples, such as pieces of wood, grass, etc. were manually removed. Equal amount of samples collected from different sample points have been mixed manually. Samples were dried in an oven at 100°C for 24 h. Dried samples were ground in a ball mill (steel balls). These ground samples sieved through a 0.5 mm stainless steel sieve in order to obtain homogenous samples, approximately 0.8 kg for each sample, and to dissolve easily. The soil sample, roadside dust sample, and certified reference material were digested with aqua regia extraction procedure recommended by the International Organization for Standardization (ISO) (20). Samples were digested at room temperature with 37% HCl/70% HNO_3 (3 : 1) mixture (10 mL per 200 mg of sample) for 16 h. After this, the suspension was evaporated to dryness. The residue was treated with 10 mL 2 mol/L HNO_3 instead of 0.5 mol/L HNO_3 recommended by ISO 11466. The suspension was filtered through a fine porosity filter paper, and the insoluble part was washed with distilled water. The resulting solution was diluted with distilled water to 100 mL in a volumetric flask.

Column Preparation

The glass column, having a stopcock and a tank of 250 mL, was 15 cm length and 0.8 cm internal diameter. A small amount of glass wool was placed at one end of the column in order to hold the resin. 0.5 g dried resin was placed. Then, another small glass wool plug was inserted onto the tap of the resin. The bed height of the resin in the column was approximately 1.5 cm. It was washed successively with water, methanol and 1 mol/L hydrochloric acid, respectively. After each use, the resin in the column was washed with 2 mL of 3 mol/L hydrochloric acid solution and triply distilled water and stored in water for the next experiment.

Preconcentration and Determination Procedure

Proposed preconcentration procedure was tested with model solutions prior to the determination of trace cadmium in samples. An aliquot of a solution (50 mL) containing 5 μg of the cadmium(II) was placed in a beaker and pH of the solution was adjusted to 2 by using HCl solution. The column was preconditioned by passing the solution of pH 2 through the column and then, the model solution was passed through the column at a flow rate of 5 mL/min. The adsorbed cadmium(II) ions on the column was eluted into a 5 mL volumetric flask by using 5 mL of 3 mol/L hydrochloric acid solution. The eluent was analyzed for the determination of cadmium concentration by FAAS. The Amberlyst 36 column has been used repeatedly after washing with 2 mL of 3 mol/L hydrochloric acid solution and triply distilled water, respectively. Using the procedure described above, the recovery of the cadmium was calculated from the ratio of the concentration found by FAAS and the concentration calculated theoretically as follows:

$$\text{Recovery (\%)} = \frac{\begin{array}{c}\text{analyte concentration in eluent (found by AAS)}\\ \times \text{ volume of eluent}\end{array}}{\begin{array}{c}\text{analyte concentration in sample solution (known)}\\ \times \text{ volume of sample solution}\end{array}} \times 100$$

RESULTS AND DISCUSSION

Adsorption Isotherm and Adsorption Capacity

The adsorption capacity of the resin for cadmium(II) was determined by the batch technique. The effect of contact (shaking) time on the adsorption of the cadmium was evaluated at room temperature ($25 \pm 1°C$). For this purpose, an aliquot of the model solution 0.1 μg/mL cadmium(II) and 100 mg of the resin were placed in a flask. The pH of the solution was adjusted to 2 and the flask was shaken at different time intervals at 200 rpm. The amount of residual cadmium(II) in the solution was determined by FAAS after filtration. The data obtained from the adsorption of cadmium on the solution showed that a contact time of 60 min was sufficient to achieve equilibrium and the adsorption did not change with further increase in contact time.

The adsorption behavior of Amberlyst 36 was determined by studying the amount of adsorbed cadmium as a function of cadmium concentration. Therefore, 50 mL of sample solutions having a cadmium concentration in the range of 20 to 500 mg/L at pH 2 were shaken for 60 min with a constant mass (100 mg) of the resin. The profile of the adsorption isotherm of the resin for cadmium is shown in Fig. 1, representing the amounts of adsorbed cadmium versus the cadmium concentration of the supernatant under equilibrium conditions. The analysis of the isotherm data is important in order to develop an equation that accurately represents the results. When the adsorption profile reaches a plateau, a monolayer adsorption is supposed to be established. The data of the isotherm reveal that the adsorption

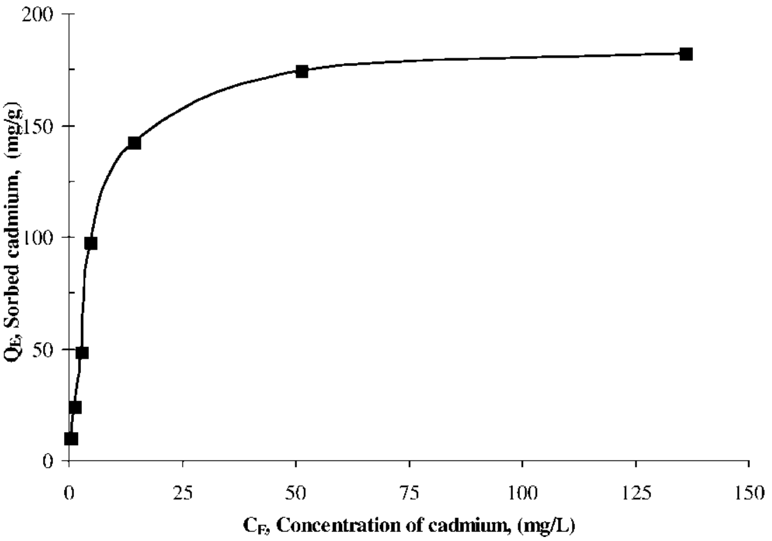

Figure 1. Adsorption isotherm of Amberlyst 36 for cadmium(II) in batch procedure.

process conforms to the Langmuir model. In Fig 1, the graph shows an excellent fit to the data in the concentration interval studied in all cases for the Langmuir model. A modified Langmiur equation conformed to this kind of adsorption isotherm as represented below:

$$\frac{C_E}{Q_E} = \frac{C_E}{Q_0} + \frac{1}{Q_0 b}$$

Where, C_E is the concentration of cadmium(II) in the solution at equilibrium (mg/L), Q_E is the amount of sorbed cadmium per gram of resin at equilibrium (mg/g), b is the "affinity" parameter or Langmuir constant (L/mg) and is the "capacity" parameter (mg/g). Based on the linearized form of the adsorption isotherm derived from plots of C_E/Q_E vs. C_E, the constant Q_0 values were calculated from the slope of the graph (Fig. 2). The value of Q_0 is found to be 192 mg/g. The adsorption capacity of this adsorbent for cadmium is much higher than the adsorbents already reported in the literature (21–23). The Langmuir constant is 0.160 L/mg.

Optimization of Chemical and Flow Parameters

In order to obtain the maximum recoveries, a lot of parameters such as pH of sample solution, the type and concentration of elution solution and flow rates of sample solution have been optimized. Interfering affects have also been studied. The first variable optimized was the pH of the sample solution. Because the pH is one of the most important environmental factors influencing

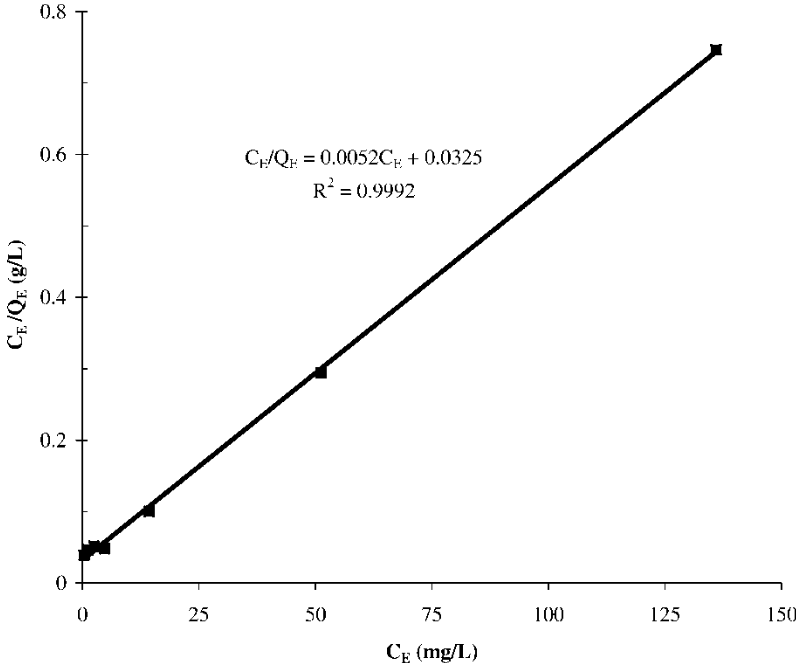

Figure 2. Linearized Langmuir isotherm obtained from the cadmium(II) adsorption on Amberlyst 36.

not only site dissociation, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation are strongly influenced by pH, and on the other side, strongly influence the speciation and the sorption availability of the heavy metals.

The recovery was determined by applying the general sorption procedure by changing the pH of sample solution in the range of 1–8. The sample solutions were adjusted to the desired pH with diluted hydrochloric acid and/or a diluted ammonia solution and passed through the resin. The column was eluted with 3 mol/L HCl solution and then the eluent was analyzed by FAAS. The results for the recovery of cadmium(II) as the mean of three measurements are shown in Fig. 3. Quantitative recoveries (>95%) were obtained at pH range of 1.5–8. pH 2 was selected for subsequent studies. Lower pH values are generally preferred for analyzing real samples, because real samples (geological, biological, etc.) are dissolved generally with acids and there is no precipitation risk of sample components.

In order to choose a proper eluent for the retained cadmium ions, after the extraction of 0.1 μg/mL cadmium from the model solution, the cadmium ions were stripped with varying concentrations of different eluting agents, such as,

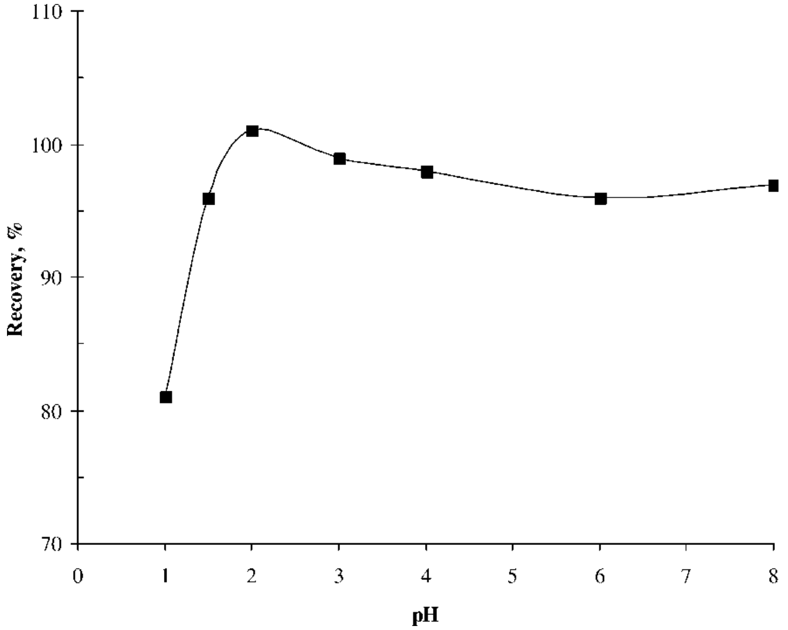

Figure 3. The effect of pH on the recovery of cadmium on a column of Amberlyst 36 (sample volume: 50 mL, amount of cadmium(II): 5 μg, eluent: 5 mL of 3 mol/L hydrochloric acid, flow rate of sample: 5 mL/min).

HCl, $HClO_4$, HNO_3, ethanol and acetone. As can be seen in the Table 1, the performance of the inorganic acids was much better than that observed with organic eluents. Thus, in subsequent experiments, 5 mL of 3 mol/L hydrochloric acid solution was chosen as eluent to desorb the cadmium on the column.

The amount of resin is another important parameter that affects the recovery. A quantitative recovery is not obtained when the amount of resin is less. On the other hand, an excess amount of resin may prevent the elution of the retained analyte by a small volume of eluent quantitatively. For this reason, the amount of resin was optimized. For this purpose, different amounts of Amberlyst 36 (50–800 mg) were examined. Quantitative recoveries of the cadmium were obtained above 200 mg of resin. Therefore, 500 mg of resin has been used for subsequent experiments because of easy elution and for obtaining sufficient recovery in real samples.

The retention of the analyte also depends upon the flow rate of the sample solution. Thus the effect of flow rate was examined by applying the recommended procedure. The model solution (50 mL, 0.1 μg/mL Cd, pH 2) was passed through the column with the flow rate adjusted by gravity action in the range of 0.5–5 mL/min. The cadmium(II) ion was desorbed with 5 mL 3 mol/L HCl solution from the resin and determined as mentioned in

Table 1. The effect of type, concentration and volume of elution solution on the recovery of cadmium (pH, 2; flow rate of sample, 5 mL/min; sample volume, 50 mL; amount of the cadmium, 5 μg)

Type, concentration and volume of eluent	Recovery[a], %
10 mL 1 mol/L HCl	55
5 mL 2 mol/L HCl	89
10 mL 2 mol/L HCl	93
5 mL 3 mol/L HCl	99
10 ml 1 mol/L HNO_3	43
5 mL 3 mol/L HNO_3	93
5 mL 3 mol/L $HClO_4$	88
10 mL metanol	2
10 mL ethanol	3
10 mL acetone	34

[a] Mean of three replicates.

the recommended procedure (Section titled preconcentration and determination procedure). According to the results, flow rate in the examined range had no significant effect on the recoveries of the cadmium. These results indicate that the sorption of cadmium(II) is very rapid. This fact is a useful feature of the proposed method, because it permits a higher sample throughout. Therefore, the flow rate of 5 mL/min was found to be suitable for optimum loading of the analyte and was used for further studies.

In order to determine the maximum applicable sample solution (or minimum analyte concentration), the effect of the volume of sample solution on the recovery of cadmium was investigated. For this purpose, cadmium was preconcentrated from volumes of 50, 100, 250, 500, 750, and 1000 mL sample solutions containing 5 μg of cadmium by applying the general procedure mentioned above. The recovery of cadmium was quantitative (>95%) at all of sample volumes tested. By using 5 mL of eluent and 1000 mL of sample solution, the highest preconcentration factor of 200 was obtained.

Influence of Foreign Ions on the Preconcentration of the Cadmium

The effects of foreign ions usually found in drinking water and soil were examined using cadmium(II) (5 μg in 50 mL of solution) and excess matrix ions. The ions were added to model solution as their nitrate or chloride salts. The experimental results were given in Table 2. Results show that the most serious interference arises from iron(III). Interference from this ion is probably that it retains strongly on the resin than cadmium. In order to eliminate the iron interference, sodium fluoride was added to model solutions having iron. However, the concentration of iron in drinking water is normally lower than

Table 2. The effect of some ions on the recovery of cadmium (II) (pH: 2, eluent: 5 mL of 3 mol/L hydrochloric acid, flow rate of sample: 5 mL/min, sample volume: 50 mL, concentration of the cadmium(II): 0.1 mg/L)

Interfering ions	Concentration (mg/L)	R[a] (%)	Interfering ions	Concentration (mg/L)	R[a] (%)
Na^+	1	100 ± 1	K^+	1	98 ± 3
	5	96 ± 2		5	100 ± 2
	25	98 ± 2		25	98 ± 1
	100	96 ± 2		100	97 ± 2
Mg^{2+}	1	98 ± 2	Ca^{2+}	1	98 ± 2
	5	98 ± 3		5	96 ± 2
	25	96 ± 2		25	94 ± 3
	100	95 ± 3		100	97 ± 2
Al^{3+}	1	102 ± 3	Fe^{3+}	1	96 ± 2
	5	98 ± 1		5	95 ± 3
	25	99 ± 1		25	97 ± 3
Zn^{2+}	1	97 ± 1	Fe^{3+}, [b]	1	97 ± 2
	5	99 ± 2		5	78 ± 4
	25	99 ± 1		25	32 ± 4
Cu^{2+}	1	97 ± 2	Co^{2+}	1	98 ± 3
	5	97 ± 1		5	101 ± 2
	25	97 ± 2		25	99 ± 1
Mn^{2+}	1	98 ± 1	Ni^{2+}	1	98 ± 1
	5	100 ± 2		5	99 ± 2
	25	96 ± 1		25	97 ± 3

[a] Mean ± standard deviation for three determinations.
[b] Without masking agent (0.01 mol/L NaF).

5 mg/L (24), the concentration of iron in soil, such as standard reference material (Montana Soil SRM 2711) used in this study, is higher than 5 mg/L. Therefore, prior to preconcentration procedure, sodium fluoride was added to solution of soil, roadside dust and standard reference material samples in order to prevent the iron interference. But, sodium fluoride was not added to tap and natural drinking water samples. Because, there is no interference of iron at below tenfold of the concentration of cadmium. As can be seen in Table 2, among the tested other cations none had serious interference. Therefore, cadmium in tap water, natural drinking water, soil and roadside dust samples can be recovered quantitatively and determined accurately by using the proposed procedure.

Analytical Features

By using direct aspiration in FAAS without applying the preconcentration system the linear range for cadmium determination was between

0.1–4.0 μg/mL. The calibration equation was $A = 0.0116 + 0.1274\,C$, where C is the cadmium concentration in μg/mL, and A is the absorbance. Calibration equation calculations are based on the average of triplicate readings for each standard solution.

The recovery of spiked cadmium and the precision of the procedure for seven determination, as the relative standard deviation of recovery at the optimum conditions given above (amount of cadmium, 5 μg; volume of solution, 50 mL; pH, 2; elution solution, 5 mL of 3 mol/L hydrochloric acid solution; flow rate, 5 mL/min), were 98 ± 3% and 2.9%, respectively.

In order to determine the instrumental detection limit, 50 mL of blank solution was adjusted to pH 2 and then, this solution was passed through the column. Blank solution was prepared by adding a minimum amount of cadmium to the tap water in order to obtain readable cadmium signal. The column was washed by 50 mL of 3 mol/L hydrochloric acid solution (there is no preconcentration). The instrumental detection limit based on mean of blank values plus three-times the standard deviation of the blank values was found to be 102 μg/L for cadmium ($N = 20$). The analytical detection limit calculated by dividing the instrumental detection limit by the preconcentration factor (200) was 0.51 μg/L (25). Analytical characteristics of the proposed method are resumed in Table 3.

Accuracy and Application of the Proposed Method

In order to evaluate the accuracy of the developed procedure, cadmium was determined in the standard reference material (Montana Soil, SRM 2711). Cadmium concentration found as the mean of five determinations at 95% confidence level was 42.25 ± 2.20 μg/g with a relative error of %1.3. It was found that there is no significant difference between the result found by the proposed method and the certified value (41.70 ± 0.25 μg/g) according

Table 3. Analytical characteristics of the proposed method for cadmium

Enrichment factor	200
Adsorption capacity	192 mg/g
Recovery ($n = 7$, at 5 μg/L)	98 ± 3%
Precision ($n = 7$, at 5 μg/L, %RSD)	2.9%
Instrumental detection limit ($N = 20$)	102 μg/L
Analytical detection limit ($N = 20$)	0.51 μg/L
Linear range	0.1–4.0 μg/mL
Calibration equation	$A = 0.0116 + 0.1274\ C$

A: absorbance, C: cadmium concentration in μg/mL.

Table 4. Determination of cadmium(II) in various samples (volume of water samples: 1000 mL, amount of soil and roadside dust: 0.2 g)

Sample	Added	Found[a] $\bar{x} \pm ts/\sqrt{N}$	Relative error (%)
Tap water	—	N.D	—
	5.0 μg/L	5.1 ± 0.6 μg/L	+2.0
Drinking water	—	N.D	—
	5.0 μg/L	4.8 ± 0.5 μg/L	−4.2
Soil	—	11.4 ± 1.0 μg/g	—
	12.5 μg/g	22.0 ± 1.2 μg/g	−7.9
Roadside dust	—	7.1 ± 0.8 μg/g	—
	12.5 μg/g	19.4 ± 1.3 μg/g	−1.0

[a] Mean of seven determinations at 95% confidence level.
N.D.: Not detected.

to the t-test. It can be concluded that there is no systematic error in the determination at 95% confidence level.

Since it was found that the proposed preconcentration method was useful for the preconcentration of trace cadmium in the presence of other metal ions in order to show the applicability of the method, the method was applied to the determination of cadmium in tap water, natural drinking waters, soil and roadside dust samples, under optimal experimental conditions. The accuracy of the method was also checked by measuring the recovery of spiked samples. The results obtained are given in Table 4. Relative errors, below 8%, demonstrate the applicability of the method and indicate that the proposed method is essentially free from interferences when applied to the analysis of drinking waters, soil and roadside dust samples.

Table 5. Comparison of adsorption capacities and preconcentration factors for cadmium

Resin	Adsorption capacity, mg/g	Preconcentration factor	Ref.
Amberlyst 36	192	200	This work
Ambersorb 572	19.6	200	(22)
Polyurethane foam	40.5	—	(23)
Thioacetamide immobilized on silica gel	16.4	200	(24)
Escherica coli immobilized on sepiolite	9.9	50	(8)
Naphthalene-methyltrioctylammonium chloride	—	40	(14)

CONCLUSION

A proposed procedure provides a simple, selective, accurate, economical, rapid, and precise method for the preconcentration and determination of cadmium in large volumes of various sample solution. The main advantages of the method over the many other solid-phase preconcentration methods are permitting to study in a wide range of pH, that is, no necessity buffer to control the pH values precisely, higher sample volume, and not requiring the chelating agent. The enrichment factor (200) and the adsorption capacity of this resin (192 mg/g) for cadmium are higher than the adsorbent already reported in the literature (Table 5). The detection limit achieved is satisfactory for the samples studied, and can be improved by using more sensitive detectors such as ICP-AES and ICP-MS. The methodology proposed has shown adequate accuracy.

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