Magnetic Solid Phase Extraction of Lead, Cadmium, and Cobalt on Magnetic Carboxyl-Modified Nanodiamonds (MCNDs) from Natural Water Samples and Their Determination by Flame Atomic Absorption Spectrometry

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INTRODUCTION

The excessive discharge of Pb, Cd, and Co into the natural water body from many industrial, natural, and anthropogenic sources causes serious environmental pollution. These heavy metals are toxic to various organs of humans and animals such as the central nervous, reproductive, immune, and gastro-intestinal systems even at trace levels (1-4). Therefore, the determination of these heavy metals at trace and ultra-trace levels is of immense interest. The analytical technique of flame and graphite furnace atomic absorption spectrometry (FAAS/GFAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), including electroanalytical techniques have been employed excessively in the recent past (5). However, due to the low levels of these heavy metals in the environment, the direct determination even by using sensitive analytical techniques is not possible. A proper pre-concentration step is required prior to their determination by flame atomic absorption spectrometry (FAAS) to increase the detection limit in environmental samples (6-8).

The analytical extraction and preconcentration methods of dispersive liquid-liquid extraction (DLLE) (9), head space liquid phase extraction (HSLPE) (10), cloud

ABSTRACT

A magnetic carboxyl-modified nanodiamond (MCND) was used for the magnetic solid phase extraction of Pb(II), Cd(II), and Co(II) prior to their quantification by flame atomic absorption spectrometry. The external magnetic field was used to separate the magnetic solid phase from the analyte solution in order to avoid sample loss during filtration and centrifugation. Various factors affecting the extraction efficiency of the adsorbent such as solution pH, adsorbent dose, sample volume, temperature, matrix effect, and desorption condition were optimized. The analytical parameters of the limit of detection (Pb: $0.99 \mu\text{g L}^{-1}$, Co: $1.73 \mu\text{g L}^{-1}$, Cd: $0.15 \mu\text{g L}^{-1}$), preconcentration factor of 20 for the analytes, and percent relative standard deviation (Pb: 0.5%, Cd: 0.6%, Co: 0.6%) were calculated under optimized experimental condition. The kinetic data show that this adsorption process follows pseudo-second order kinetics. The thermodynamic data show that this adsorption process was feasible and exothermic in nature. The method was validated by applying the method to certified reference materials TMDA 64.2 and SPS-WW2 and natural water samples with satisfactory recovery results.

point extraction (CPE) (11), *in situ* solvent formation extraction (ISFE) (12), ultrasound ionic liquid-based dispersive liquid extraction (UILB-DLE) (13), co-precipitation (14), and switchable solvent-based liquid extraction (SSLE) (15) have been

employed over the last few years. However, high amounts of toxic organic reagents discharged into the waste make these techniques environmentally unfriendly and expensive. These limitations can be eliminated by using solid phase extraction (SPE), which is a promising technique for the removal of heavy metals from environmental samples (16-18).

Magnetic nanoparticles and magnetically modified materials such as carbon nanotubes (19), magnetic nanoparticles (20, 21), magnetic graphene (22), magnetically impregnated biosorbents (23), and mesoporous materials have been used as SPE adsorbents (24). Due to the smaller particle size (1 nm to 200 nm) (25), large surface area, and magnetic property, the magnetic nanoparticle can be used as an effective SPE adsorbent for heavy metals in water samples and is an excellent method for the preconcentration of heavy metals from aqueous solutions (26, 27).

Due to the unique properties of hardness, thermal conductivity, and optical transparency over a wide spectral range, diamonds have become a focus of interest and are used for electronic and electrochemical devices, sensors, protective coatings, and optical windows. Diamond nanowires and nanopillars for photonic devices are the recent application of single crystalline nanodiamonds. A new kind of carbon material called nanodiamond was found to have properties close to diamonds and is considered a key material in quantum engineer-

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ing, has widespread biological and electronic application, as well as for composite materials (28, 29). Due to their high surface reactivity, nanodiamonds can be used as an excellent adsorbent for heavy metals determination from environmental water samples.

The aim of the present work was to use magnetic carboxyl-modified nanodiamonds (MCNDs) as adsorbents for Pb, Cd, and Co separation-concentration and determination in various water samples. Adsorption kinetics, thermodynamics, and equilibrium of constants were also studied.

EXPERIMENTAL

Instrumentation

A flame atomic absorption spectrometer Model A300 (PerkinElmer, Inc., Shelton, CT, USA) with an air-acetylene flame on a 10 cm long slot burner head was used for the metal determinations. A hollow cathode lamp was the excitation source. A continuous injection system was used to inject 100 μ L of the eluent to the nebulizer of the FAAS. All instrumental settings used were as recommended by the manufacturer and are listed in Table I.

The measurements were performed with the continuous aspiration mode of the FAAS. The pH of the solution was measured with a Nel-pH-900 meter with a glass electrode (Ankara, Turkey). The solid phase was separated by using a Nd magnet. A vortex mixer (Wiggen

Hauser, Malaysia) was used for the homogenous mixing of the solutions.

Chemicals and Reagents

High purity analytical grade reagents were used for preparation of the Pb, Cd, and Co stock solutions (E. Merck Co., Germany). In order to prepare the magnetic iron oxide nanoparticle (Fe_3O_4); ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) salts were used (E. Merck Co., Germany). Ammonia solution (35 %), hydrochloric acid (37%), acetone, and ethanol were purchased from Riedel-deHaen (Sleeze, Germany) and Sigma-Aldrich (St. Louis, MO, USA).

Nanodiamonds (Sigma-Aldrich No: 636428-1G) were purchased from Sigma Aldrich (St. Louis, MO, USA). Synthesis and characterization of the magnetic carboxyl-modified nanodiamonds (MCNDs) were performed according to the literature (30).

To obtain the appropriate pH of the sample solutions, different combinations of acids and salts were used: Phosphate buffer solution (pH 2-4, sodium dihydrogen phosphate/phosphoric acid), acetate buffer solution (pH 5.0-7.0 acetic acid and ammonium acetate),

ammonia buffer solution (pH 8.0, ammonia/ammonium chloride), and phosphate buffer solution (pH 9.0 and pH 10 sodium phosphate).

Batch Adsorption Studies

A 10-mL sample solution containing 8 μ g Pb, 4 μ g Co, and 2 μ g Cd was taken into a 50-mL centrifuge tube at pH 7. The solution was then added to another tube having 0.1 g of magnetic carboxyl-modified nanodiamonds (MCNDs). The adsorption was allowed for 4 minutes using a vortex revolution speed of 40 $\times$ 100 per minute. After complete adsorption, the solid phase was separated by using the external magnetic field, and the liquid phase was carefully decanted to waste. For desorption, 2 mL of 2 M HCl in acetone was added to the tube with the adsorbent, again subjected to vortex revolution for 4 minutes, and separated from the liquid phase using the external magnetic field. A 1.9 mL amount of acetone was separated by using a boiling waterbath for half an hour. An amount of 100 μ L of eluent was injected into the nebulizer of the FAAS by using the micro-injection system for measurement of the analytes. The schematic of the presented procedure is summarized in Figure 1.

TABLE I
Instrumental and Operating Conditions for Cd, Pb, and Co

Elements	Wave length (nm)	Slit Width (nm)	Lamp Current (mA)
Cd	228.8	0.7	4
Pb	283.3	0.7	10
Co	240.7	0.7	23

Fig. 1. Schematic presentation of present procedure.

The adsorption capacity (q) was calculated by using the following equation:

$$q = (C_i - C_f) m/v \quad (\text{Eq. 1})$$

where C_i is the initial concentration of the analyte, C_f is the final concentration, m is the amount of adsorbent, and V is the sample volume.

Application

Two certified reference materials of TMDA 64.2 Environmental Water (The National Water Research Institute, Environment Canada, Burlington, Canada) and SPS-WW2 Wastewater (Spectrapure Standards AS, Oslo, Norway) were used for the trace metal determination of Pb, Cd, and Co. Three environmental water samples (underground water, seawater, and wastewater obtained from various cities in Turkey) were used for validation of the method. The certified reference materials were used directly without further purification, while the environmental water samples were passed through a cellulose membrane filter having 0.45 μm pore size (Millipore Corporation, USA) prior to use to remove the waste particles. Then the procedure given above (see Batch Adsorption Studies) was applied.

RESULTS AND DISCUSSION

The analytical variables of pH, adsorbent dose, vortex time, sample volume, matrix effect, type, and volume of the eluent were optimized for the quantitative percent recovery of Pb(II), Co(II), and Cd(II) on magnetic carboxyl-modified nanodiamonds (MCNDs). The following equation was used to calculate the percent recovery values (31):

$$(\text{Eq. 2})$$

$$\text{Recovery}(\%) = (w_o/w_f) \times 100$$

where w_o (μg) and w_f (μg) are the amount of analyte in the final and the sample solutions, respectively.

Effect of pH

The pH of a solution greatly influences the surface charge of the adsorbent and the hydronium (H_3O^+) ion concentration in the sample solution greatly affects the adsorption efficiency of the adsorbent (32–36). Therefore, for a suitable pH, adsorption studies of Pb(II), Co(II), and Cd(II) on magnetic carboxyl-modified nanodiamonds (MCNDs) were carried out at a different pH ranging from 3.0 to 9.0 (see Figure 2). The quantitative recoveries of the analyte ions were obtained at pH 7.0 and 7.5.

Thus, pH 7.0 was used for all optimization studies.

Effect of Adsorbent Dose

The smallest amount of adsorbent required to obtain quantitative percent recoveries of the analyte ions was determined by using different adsorbent doses (20 mg to 140 mg). Figure 3 shows that a 100-mg amount of magnetic carboxyl-modified nanodiamonds (MCNDs) was sufficient to obtain quantitative percent recoveries of Pb, Cd, and Co, and was used in further optimization studies.

Effect of Sample Volume

The highest preconcentration factor of the method can be calculated after determining the highest sample volume to which the method is successfully applicable. For this purpose, the proposed solid phase extraction method was applied to sample volumes ranging from 5 mL to 50 mL. Figure 4 shows that 40 mL is the highest volume at which quantitative percent recoveries of the analyte metals are achieved. Therefore, a preconcentration factor of 20 was achieved using a 40-mL sample volume and 2 mL of final volume.

(F)ig. 2. Effect of pH on recovery (%) of Pb(II), Cd(II) and Co(II) using MCNDs as adsorbent.

(F)ig. 3. Effect of adsorbent dose on recovery (%) of Pb(II), Cd(II) and Co(II) using MCNDs as adsorbent.

Desorption Studies

The selection of type, concentration, and volume of the best eluent is of enormous importance in solid phase extraction and preconcentration studies. Various types of eluting agents with different concentrations were used for desorption of Pb(II), Cd(II), and Co(II) from the surface magnetic carboxyl-modified nanodiamonds (MCNDs). Table II shows that 2 M HCl in acetone is the best eluting agent for desorption of the analytes from the surface of magnetic carboxyl-modified nanodiamonds (MCNDs).

To investigate the smallest volume of eluent, different volumes (1 to 6 mL) of 2M HCl in acetone were used. Figure 5 shows that 2 mL of eluent was enough for the complete desorption of the metal ions from the surface of the adsorbent.

Matrix Effect

The interfering influences of the cations of the IA and IIA group elements and some transition elements, as well as some anions on the instrumental detection of metals at trace levels are known as matrix effects (37–42). The effects of different interfering ions on the percent recovery of analyte ions

were investigated and the results are listed in Table III. No significant interferences were obtained even at high concentrations of the interfering ions. It can, therefore, be concluded that the adsorption of Pb(II), Cd(II), and Co(II) on magnetic carboxyl-modified nanodiamonds (MCNDs) is highly selective.

Kinetic Studies

Kinetic data can be explained by using various kinetic models such as pseudo-first-order, pseudo-second-order kinetics, and intraparticle diffusion models for the adsorption

of Pb(II), Cd(II), and Co(II) on magnetic carboxyl-modified nanodiamonds (MCNDs). For pseudo-first-order kinetics, the following expression was used (43):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (\text{Eq. 3})$$

The values of adsorption at equilibrium q_e and k_1 pseudo-first-order constant were calculated from intercept and slope, respectively, and the values are listed in Table IV. The smaller coefficient values

TABLE II
Effect of Type and Concentration of Eluent on (%) Recovery of Pb(II), Cd(II), and Co(II) Magnetic Carboxyl Modified Nanodiamonds (MCNDs) (N=3)

Eluent Type	Pb	Cd	Co
1 M HCl	83±2 ^a	69±4	78±2
2 M HCl	84±1	84±2	84±2
3 M HCl	89±1	92±2	89±2
1 HNO ₃	68±2	62±2	61±3
2 HNO ₃	80±1	85±5	73±4
3 HNO ₃	89±3	91±4	75±1
1 M HCl in Acetone	99±4	95±3	93±2
2 M HCl in Acetone	102±2	99±3	97±3
3 M HCl in Acetone	104±4	100±3	96±4

^a Mean ± standard deviation.

Fig. 4. Effect of sample volume on recovery (%) of Pb(II), Cd(II) and Co(II) using MCNDs as adsorbent.

Fig. 5. Effect of eluent volume on recovery (%) of Pb(II), Cd(II) and Co(II) using MCNDs as adsorbent.

and the difference between experimental adsorption capacities and calculated adsorption capacities from pseudo-first-kinetics confirm that this adsorption study follows some other kinetic model.

The rate limiting step in chemisorption can be calculated by using the pseudo-first-order kinetics model which can be expressed by using the following equation (44):

Fig. 6. Pseudo-second order kinetics.

TABLE III
Effect of Coexisting Ions on (%) Recovery of Pb(II), Cd(II), and Co(II) Using (MCNDs), pH: 7, Adsorbent: 0.1 g, Sample Solution: 10 mL (N=3)

Interfering Ions	Added as	Concentration (mg L ⁻¹)	Recovery(%)		
			Pb(II)	Cd(II)	Co(II)
Na ⁺	NaCl	5000	95±5 ^a	99±3	99±4
K ⁺	KCl	5000	95±6	95±2	94±6
Ca ⁺⁺	Ca(NO ₃) ₂ ·4H ₂ O	500	98±4	100±4	95±4
Mg ⁺⁺	Mg(NO ₃) ₂ ·6H ₂ O	500	96±4	93±5	92±2
Al ⁺⁺⁺	Al(NO ₃) ₃ ·7H ₂ O	100	94±5	95±7	102±1
Zn ⁺⁺	Zn(NO ₃) ₂ ·6H ₂ O	100	100±3	98±1	98±5
Cu ⁺⁺	Cu(NO ₃) ₂ ·6H ₂ O	50	96±2	93±4	99±3
Ni ⁺⁺	Ni(NO ₃) ₂ ·6H ₂ O	100	96±3	97±7	97±3
Mn ⁺⁺	Mn(NO ₃) ₂ ·6H ₂ O	50	95±4	93±5	94±4
SO ₄ ⁻	Na ₂ SO ₄	500	96±2	95±3	99±2
CO ₃ ⁻	Na ₂ CO ₃	500	94±6	95±2	101±2
F ⁻	NaF	100	100±5	97±2	98±8

^a Mean ± standard deviation.

$$t/q_t = t/q_e + 1/k_2 q_e^2 \quad (\text{Eq. 4})$$

The value of equilibrium adsorption capacity q_e and rate constant for pseudo-second-order kinetics k_2 were calculated from slope and intercept and intercept of the linear plot, represented by Figure 6. The close agreement was found between the calculated adsorption capacities and high correlation coefficient (R^2) values. The calculated adsorption capacities confirm that these adsorption studies follow pseudo-second-order kinetics (Table IV).

The following equation was used in order evaluate intraparticle diffusion model (23):

$$q_t = k_{int} t^{1/2} + C \quad (\text{Eq. 5})$$

The value of boundary layer thickness C and intraparticle diffusion rate constant k_{int} ($\text{mg g}^{-1} \text{min}^{-1/2}$) were calculated directly from intercept and slope of the intraparticle diffusion model and are given in Table IV. The plot of q_t (mg g^{-1}) and $t^{1/2}$ shows that this adsorption process is a three-step process, mainly due to surface diffusion and intraparticle diffusion, while the positive value of C is mainly due to the boundary layer diffusion. The multistep adsorption process confirmed some other adsorption mechanism, such as ion exchange may control the rate of adsorption.

Thermodynamic Studies

In order to determine the values of enthalpy (ΔH°), Gibbs-free energy (ΔG°), and entropy (ΔS°),

TABLE IV
Kinetic Parameter of the Adsorption of Pb(II), Cd(II), and Co(II) Using MCNDs as Adsorbent

Metal Ion	Kinetic Models								
	Experimental	Pseudo First Order			Pseudo Second Order			Intra-particle Diffusion	
	$q_e \mu\text{g g}^{-1}$	$K_1 \text{ min}^{-1}$	$q_e \mu\text{g g}^{-1}$	R^2	$K_2 \text{ min}^{-1}$	$q_e \mu\text{g g}^{-1}$	R^2	$K_{int} \text{ min}^{-1}$	C
Pb(II)	0.809	1.08	2.88	0.917	0.74	0.96	0.981	0.461	0.421
Co(II)	0.149	0.78	0.229	0.902	0.55	0.217	0.997	0.085	0.124
Cd(II)	0.386	0.67	0.516	0.936	1.33	0.483	0.98	0.461	0.421

the adsorption studies were carried out at different temperatures ranging from 293 K to 373 K. The following equations were used to calculate the various parameters of the thermodynamic studies for this particular adsorption study (45, 46):

$$\Delta G^0 = -RT \ln K_D \quad (\text{Eq. 6})$$

$$\Delta H^0 = R \frac{T_2 T_1}{T_2 - T_1} \ln \frac{K_2}{K_1} \quad (\text{Eq. 7})$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (\text{Eq. 8})$$

where K_D is the equilibrium constant, q_e equilibrium concentration of the metal ion on the adsorbent (mg L^{-1}), and C_e is the concentration of the metal ion in the solution (mg L^{-1}), respectively. The values of

(ΔS^0), (ΔH^0), and (ΔG^0) were calculated, and the values are listed in the Table V. The negative values of all of these parameters show that this adsorption process is exothermic and highly feasible in nature.

Analytical Performance of Method

An analytical method can be performed by calculating various analytical parameters such as detection limit (LOD), limit of quantification (LOQ), enhancement factor (EF), preconcentration factor (PF), percent relative standard deviation, and correlation coefficient. All of these parameters were calculated as follows: The values of LOD were calculated as the ratio of three times standard deviation of 10 blank absorbances to the slope

of the regression equation, while the values of the LOQ were calculated as 10 times the standard deviation of 10 blank absorbances to the slope of the regression equation. The percent relative standard deviation of three repeated determinations having 2 ppm concentrations was determined and given in the Table VI. EF was calculated by using the ratio of the slopes with and without the preconcentration step (47). PF was calculated as the ratio of the model solution to the final volume and CIn is calculated as the ratio of sample volume (in milliliters) to enhancement factor. The values of these parameters are given in the Table VI.

TABLE V
Thermodynamics of Proposed Method for Adsorption of Pb(II), Cd(II), and Co(II) on magnetic carboxyl modified nanodiamonds MCNDs

Temp.	ΔG^0 KJmol^{-1}	Pb(II) ΔH^0 KJmol^{-1}	ΔS^0 KJmol^{-1}	ΔG^0 KJmol^{-1}	Cd(II) ΔH^0 KJmol^{-1}	ΔS^0 KJmol^{-1}	ΔG^0 KJmol^{-1}	Co(II) ΔH^0 KJmol^{-1}	ΔS^0 KJmol^{-1}
293	-18.26			-221.69			-213.80		
303	-15.42			-189.24			-182.66		
313	-14.93			-174.85			-174.98		
323	-14.27			-172.11			-158.37		
333	-14.19	-38.3	-0.07	-164.99	-42.7	-0.08	-151.17	-45.5	0.09
343	-12.87			-158.19			-148.94		
353	-12.34			-157.01			-146.13		
363	-11.99			-155.39			-137.54		
373	-12.18			-153.92			-141.78		

TABLE VI
Analytical Parameters of Method

Analytical Parameter	Pb(II)	Cd(II)	Co(II)
Limit of detection ($\mu\text{g L}^{-1}$)	0.99	0.15	1.73
Limit of quantification ($\mu\text{g L}^{-1}$)	3.3	4.95	5.8
Preconcentration factor (PF)	20	20	20
Enhancement factor (EF)	19.9	19	19
Relative standard deviation (%)	0.5	0.6	0.7
Correlation coefficient (r^2)	0.997	0.998	0.993

TABLE VII
Validation of Proposed Solid Phase Extraction Method of Pb(II), Cd(II), and Co(II) at Trace Level Using Certified Water Reference Material (pH: 7, Adsorbent: 0.1 g, Sample Volume: 15 mL, Final Volume: 2 mL)

CRM	Pb(II)			Cd(II)			Co(II)		
	Certified	Found	Recovery(%)	Certified	Found	Recovery(%)	Certified	Found	Recovery(%) ^b
TMDA 64.2	286	278±5 ^a	98	264	263±10	99	253	257±12	101
SPS-WW2	500	479±20	95	100	99±6	99	300	295±13	98

^a Mean of three determinations ± standard deviation.

^b (%)Recovery = (Observed Value/Expected Value) × 100.

TABLE VIII
Addition Recovery Results for Pb(II), Cd(II), and Co(II) Using Proposed Solid Phase Extraction Method (pH: 7, Adsorbent: 0.1 g, Sample Volume: 15 mL, Final Volume: 2 mL (N=3))

Sample	Added (µg)	Pb(II)		Cd(II)		Co(II)	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Underground Water	0	BDL ^a	–	0.04	–	0.03	–
	0.5	0.94	94	0.29	100	0.53	100
	1	1.87	94	0.52	94	1.02	99
Seawater	0	0.11	–	0.07	–	0.10	–
	0.5	0.36	95	0.38	101	0.58	97
	1	0.63	103	0.41	96	1.09	99
Wastewater	0	0.09	–	0.06	–	0.06	–
	0.5	0.57	97	0.44	95	0.55	97
	1	1.07	98	0.49	95	1.07	101

^a BDL = Below the detection limit.

Validation of the Method

For trace metal analysis, two certified reference materials TMDA 64.2 Environmental Water and SPS-WW2 Wastewater were used and the recovery results are listed in the Table VII. The quantitative recovery result shows that the method can successfully be used for trace metal analysis.

For addition recovery, the method was applied to underground water, seawater, and wastewater. The percent recovery results are given in Table VIII and show that the method is applicable to environmental water samples. The application of trace metal analysis and addition recovery shows that the proposed solid phase extrac-

tion is highly accurate and valid for the determination of the toxic heavy metals.

The proposed solid phase extraction was compared with other extraction methods in the literature with regard to the LOD values (Table IX). It can be concluded that the developed method is either superior or similar in extraction efficiency to other extraction studies given in the literature (52-59).

CONCLUSION

Magnetic carboxyl modified nanodiamonds were synthesized and characterized. The adsorbent was used as magnetic solid phase extractant of Pb(II), Cd(II), and

Co(II) prior to the determination by FAAS. The pH of 7.0 was optimum to obtain maximum percent recoveries. The kinetic data fit to pseudo-first order kinetics. The thermodynamic data show that adsorption of Pb(II), Cd(II) and Co(II) on magnetic carboxyl nanodiamonds is feasible and exothermic in nature. The developed method is sensitive with low values of detection limits, reproducible with low values of RSD, and useful with other analytical techniques such as ICP-MS with the added benefit of matrix removal. The method was also successfully applied to certified reference materials and natural water samples.

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TABLE IX
Comparison of Developed Method With Other Pre-concentration Methods for Pb(II), Cd(II), and Co(II)

Method	Analysis	PF/EF	Detection Limit ($\mu\text{g L}^{-1}$)	Sample	Reference
Solid phase extraction	Flame AAS	80	Pb(II): 0.6, Co(II): 0.4	Environment	(19)
Solid phase extraction	Flame AAS	200	Pb(II): 1.1	Water	(48)
Solid phase extraction	FlameAAS	–	Pb(II): 3.9, Co(II): 2.9	Environment	(49)
Solid phase extraction	Flame AAS	100	Pb: 0.86	Hair	(50)
Dispersive liquid-liquid extraction	X-Ray fluoresc. spectrometry	–	Pb(II): 2.6, Co(II): 0.7	Water	(51)
Ionic liquid dispersive liquid-liquid extraction	Flame AAS	–	Pb(II): 9.5	Environment	(52)
Dispersive liquid-liquid extraction	GFAAS	101	Co(II): 0.03	Rice and water	(53)
Solid phase extraction	Flame AAS	20	Pb(II): 0.99, Co(II): 1.73, Cd:0.148	Water	This work

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