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A Novel Carrier Element-free Co-precipitation Method for Separation/Preconcentration of Lead and Cadmium Ions from Environmental Matrices

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A new separation and pre-concentration method was presented in this study for two trace heavy metal ions, lead (Pb^{2+}) and cadmium (Cd^{2+}) from aqueous solutions, based on a carrier element free co-precipitation (CEFC) method using a triazole derivate, 3-(4-tert-butylphenyl)-5-phenyl-4-(2-hydroxy-5-methoxybenzylamino)-4H-1,2,4-triazole as an organic co-precipitating agent. The method was optimized with some analytical parameters which affect the quantitative recoveries of study metals. According to the results, optimum pH of solution, quantity of co-precipitating agent, centrifugation and incubation time, and sample volume were determined as 6.0, 1.5 mg, 10 min, and 10 min, and 100 mL, respectively. In addition, no significant matrix interferences were observed over the recovery of the metal ions. For analytical figure of merit, RSD values of the method were found as 5.7 and 4.8 for Pb^{2+} and Cd^{2+}, respectively. LOD values were also calculated as 2.0 µg L^{-1} for Pb^{2+} and 0.2 µg L^{-1} for Cd^{2+}. The accuracy of method was checked with spiked/recovery tests and analysis of a standard reference material. The developed method was finally applied to the real liquid/solid samples under the optimum conditions. © 2016 American Institute of Chemical Engineers Environ Prog, 35: 1709–1715, 2016

Keywords: separation and preconcentration, carrier element-free coprecipitation, cadmium, lead, triazole, FAAS

INTRODUCTION

Heavy metals in environmental sources such as natural waters and foods are a great concern due to their toxicity for living organisms [1]. Lead, which is one of the heavy metals, is toxic at even very low exposure levels and causes acute and chronic effects on human and of course other living

organisms. It is a serious toxicant that affects several organs and can cause hematological, gastrointestinal, cardiovascular, renal, and reproductive effects. Another toxicant for living cells is cadmium. It is nonessential and affects adversely kidney and skeleton of human body. It is also known as a carcinogen by inhalation [2].

Therefore, the determination of heavy metals and other trace elements in water and food samples is a very significant issue in Analytical Chemistry. The precise and accurate determinations of metals require the advanced analytical measurement techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma—atomic emission spectrometry (ICP–AES) and inductively coupled plasma—mass spectrometry (ICP–MS). Although these techniques have relatively lower LOD values than other techniques, unfortunately they cannot overcome the matrix interferences enough [3]. Hence, a separation/preconcentration step is usually required prior to measurements. Many novel methods developed recently for this purpose have been reported in the literature, such as solid-phase microextraction [4–6], dispersive liquid–liquid microextraction [7–10], single drop microextraction [11–13], cloud point extraction, [14–16], coprecipitation microsample injection [17], and carrier element-free co-precipitation [18–20], etc.

Recently, carrier element-free coprecipitation (CEFC) method has been developed for quantitative separation/preconcentration of metal ions from interfering complex environmental and biological matrices. A water-insoluble organic ligand is used as a coprecipitating agent in CEFC method in order to precipitate the metal ions from aqueous solutions without needing any carrier element. CEFC method has a great advantage of not requiring use of any carrier element which causes a possible interference effect over quantitative separation/preconcentration of metal ions from aqueous solution [18,19]. A carrier element in large quantities must be
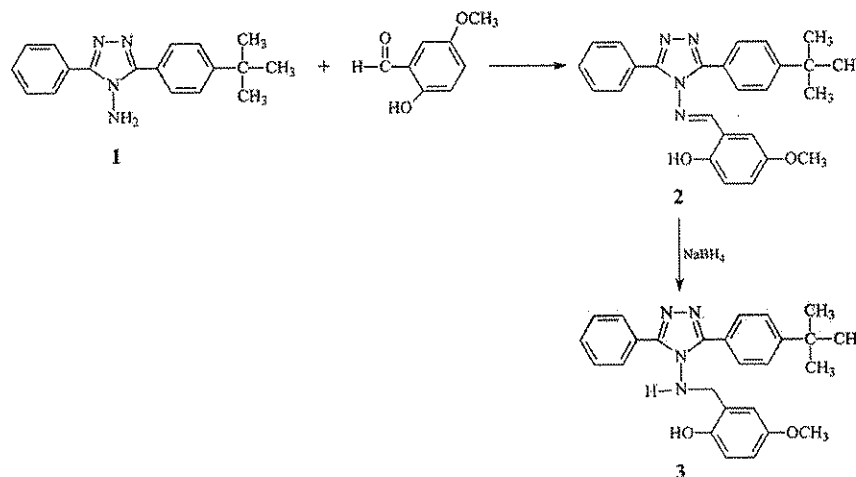
Figure 1. Synthesis of the ligand, used as a coprecipitating agent in this study.

used in conventional coprecipitation methods in order to form a precipitate which collects the metal ions on its own from aqueous solution. Therefore, the occurrence of interference is inevitable during the measurement of metal ions because of large quantities of a carrier element in the medium [18,19,21,22].

In this work, a separation/preconcentration method which is a simple, rapid and very sensitive has been developed to determine the levels of Pb^{2+} and Cd^{2+} in environmental samples. The present procedure is based on a combination of carrier element-free coprecipitation (CEFC) method and flame atomic absorption spectrometric (FAAS) determination. An organic water-insoluble ligand (coprecipitating agent), 3-(4-*tert*-butylphenyl)−5-phenyl-4-(2-hydroxy-5-methoxybenzylamino)−4H-1,2,4-triazole was used without adding any carrier element to co-precipitate the metal ions. The optimum conditions for the coprecipitation process were investigated on several commonly tested experimental parameters, such as pH of the solution, amount of coprecipitating agent, sample volume, incubation time, centrifugation rate, and time. The influences of some anions, cations, and transition metals on the recoveries of analyte ions were also investigated.

MATERIAL AND METHOD

Instrumentation

A Perkin-Elmer (USA) model AAnalyst 400 flame atomic absorption spectrometer (FAAS) with single element-hallow cathode lamp and air/acetylene-burner head was used in order to measure the concentration of two metal ions, Pb^{2+} and Cd^{2+}, from aqueous solutions. Melting points of the synthesized compounds (coprecipitating agent) were determined in capillaries on Büchi B-450 melting point apparatus (Switzerland). The IR spectra are recorded on a Perkin Elmer 1600 FT-IR spectrophotometer (USA) using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in DMSO-d_6 (USA). The elemental analyses were performed on Costech ECS 4010 instrument (USA).

A Hanna-211 model desktop pH-meter with glass electrode was used for adjusting the pH of the working solutions. MSE Mistral-2000 model centrifuge device was operated for settling the precipitate at the bottom of centrifugation tubes. A Milestone Ethos D with closed vessel

microwave irradiation system, providing 1500 psi and 300°C of maximum pressure and temperature, respectively, was run for obtaining limpid solutions of the solid samples.

Reagents and Solutions

Analytical reagent grade chemicals (Merck, Darmstadt/Germany) and distilled/deionized water were preferred at every stage of the work. The 1000 mg L^{-1} stock solutions of each metal ion from Merck Company (Darmstadt/Germany) were used all experiments after diluting the stock solutions with desired proportions.

To prepare 25 mL of 0.1% (*m/v*) coprecipitating agent, 0.025 g of coprecipitating agent was weighed into a beaker and dissolved in 5 mL of DMSO and 20 mL of ethyl alcohol (1:4) mixture.

Synthesis of the Organic Ligand, Coprecipitating Agent

The ligand, an organic coprecipitating agent was synthesized by the reaction given in Figure 1. The initial compound 1 was synthesized by the methods reported earlier in the literature [23].

Synthesis of Compound 2, 3-(4-tert-butylphenyl)−5-phenyl-4-(2-hydroxy-4-methoxybenzylidenamino)−4H-1,2,4-triazole

The 2-hydroxy-5-methoxybenzaldehyde (0.05 mole) was added to a solution of compound 1 (0.05) in 20 mL of glacial acetic acid and the mixture was refluxed for 4 h. After cooling, the mixture was poured into a beaker containing 100 mL of ice-water. The precipitate that formed was filtered. After drying in vacuum, the product was recrystallized from ethanol–water (1:1) to yield 87%, m.p. 178–179°C, IR (KBr) cm^{-1}: 1600, 1592 ($v_{C=N}$), 821, 769, 695 ($v_{arm.ring}$); ^{1}H NMR (DMSO-d_6) δ 1.30 (s, 9H, C(CH$_3$)$_3$), 3.76 (s, 3H, OCH$_3$), Ar-H: [6.85–6.87 (m, 1H), 7.09–7.12 (m, 1H), 7.40–7.56 (m, 6H), 7.81–7.84 (m, 4H)], 8.67 (s, 1H, N = CH), 9.98 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 31.39 (C(CH$_3$)$_3$), 35.06 (C(CH$_3$)$_3$), 55.96 (OCH$_3$), Ar-C: [110.2, 118.0, 118.4, 123.0, 124.2, 126.2 (2C), 127.0, 128.4 (2C), 128.8 (2C), 128.8 (2C), 130.2, 152.7, 153.0, 154.0], 150.4 (triazole C-5), 150.6 (triazole C-3), 166.7 (N = CH); Anal. Calcd. for (C$_{26}$H$_{26}$N$_4$O$_2$): C: 73.2, H: 6.1, N:13.1, Found: C: 73.4, H: 6.1, N: 13.0.
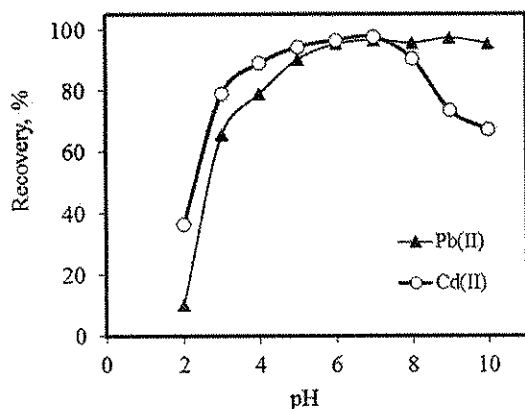
Figure 2. Effect of pH over the recovery yield (N: 3, quantity of analyte ions: 5.0 µg Pb^{2+} and 0.5 µg Cd^{2+}, sample volume: 50 mL, quantity of coprecipitating agent: 1.5 mg, final volume: 5.0 mL).

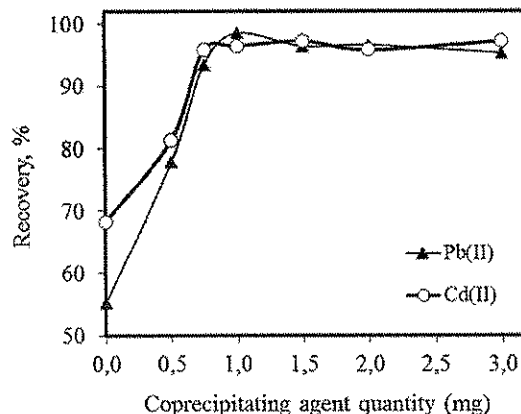**Figure 3.** Effect of ligand quantity over the recovery yield (N: 3, quantity of analyte ions: 5.0 µg Pb^{2+} and 0.5 µg Cd^{2+}, pH: 6.0, sample volume: 50 mL, final volume: 5.0 mL).

Synthesis of the Final Product; Compound 3 (coprecipitating agent), 3-(4-tert-butylphenyl)–5-phenyl-4-(2-hydroxy-5-methoxybenzylamino)–4H-1,2,4-triazole

Compound (2) (0.05 mole) was dissolved in 100 mL of dried methanol, and $NaBH_4$ (0.05) was added in small portions to this solution. The mixture was refluxed for 30 min and then allowed to cool. After evaporation under reduced pressure, the solid residue was washed with cold water. After drying in vacuum, the solid product was recrystallized from ethanol–water (1:1) to yield 92%, m.p. 178–179°C, IR (KBr) cm^{-1}: 1600, 1592 ($v_{C=N}$), 821, 769, 7 ($v_{arm.ring}$);^{1}H NMR (DMSO-d$_6$) δ 1.33 (s, 9H, C(CH$_3$)$_3$), 3.72 (s, 3H, OCH$_3$), 3.82 (d, 2H, NH-CH$_2$, J = 3.50 Hz), 7.45 (t, 1H, NH-CH$_2$, J = 3.50 Hz), Ar-H: [6.7 (m, 1H), 6.9 (m, 2H), 7 (d, 1H, J = 8.40 Hz), 7.5 (m, 4H), 7.8 (m, 4H)], 10.0 (s, 1H, OH); ^{13}C NMR (DMSO-d$_6$) δ 31.4 (C(CH$_3$)$_3$), 35.0 (C(CH$_3$)$_3$), 47.8 (NH-CH$_2$), 53.9 (OCH$_3$), Ar-C: [110.8, 118.7, 119.1, 122.6, 124.2, 126.2 (2C), 126.8, 128.4(2C), 128.8 (2C), 128.8 (2C), 130.3, 152.7, 152.9, 153.6], 153.6 (triazole C-5), 153.7 (triazole C-3); Anal. Calcd. for (C$_{26}$H$_{28}$N$_4$O$_2$): C: 72.9, H: 6.6, N:13.1, Found: C: 73.1, H: 6.6, N: 13.0.

Application of Developed CEFC Method

Before analysis of the real samples, the performance of the developed CEFC method was tested by using the model solutions: At first, pH of a solution (50 mL) containing 5.0 µg Pb^{2+} and 0.5 µg Cd^{2+} ions was adjusted to 6.0. After 1.5 mL of 0.1% (m/v) coprecipitating agent (1.5 mg) was added to the solution, the mixture was standed for 5 min to form a precipitate, and then the mixture was centrifuged at 2500 rpm for 10 min. After decantation procedure, the precipitate which formed in the aqueous medium was dissolved with 0.5 mL of conc.HNO$_3$. And then the final volume was made up 2.0 mL with distilled/deionized water. Finally, the solution was analyzed by FAAS in order to determine the levels of Pb^{2+} and Cd^{2+} ions.

Application of the CEFC Method to Real Samples

The novel CEFC method developed in this study was finally applied to the some real solid–liquid samples after optimization procedures. As the liquid samples, stream water was taken from Maçka district of Trabzon city (Turkey) and sea water from Trabzon city center. As the solid samples, tobacco and black tea samples were taken from local markets in Trabzon city center. The method was also applied to

a certified reference material, CRM-SA-C Sandy Soil C, in order to verify it.

The novel CEFC method was applied to 50 mL of the water samples after they were filtrated through a 0.45-µm pore sized nitrocellulose membrane. On the other hand, the method was applied to 50 mL of the limpid solutions which were obtained from the solid samples after digested with microwave irradiation. For this, 0.75 g tobacco and black tea, and 0.1 g CRM were weighed into Teflon beakers separately. 4.5 mL HCl, 1.5 mL conc.HNO$_3$, 1.0 mL conc. HF and 2.0 mL H$_2$O$_2$ for CRM, 6.0 mL HNO$_3$ and 2.0 mL H$_2$O$_2$ for tobacco and black tea were added to the beakers. The beakers were placed in a high pressure microwave oven and the mixtures were digested with the aid of microwave irradiation in order to obtain limpid solutions. After the digested samples were evaporated to near dryness, they were diluted to 50 mL with distilled/deionized water, and the method was finally applied to them.

RESULTS AND DISCUSSION

Effect of pH over the Recovery Yield

Effect of solution pH over the recovery yield is probably the most important experimental parameter in the separation/preconcentration procedures. Change of pH of the solution affects directly the sorption behavior of analytes on the solid phase. Different types of molecular metallic species with neutral, anionic or cationic character occur as a result of the increase in pH of the solution. These hydrolysis products which are formed in the solution help in choosing the best suitable pH value and/or determining the optimum working pH range [24,25].

In this study, the effect of pH over the recovery yield of Pb^{2+} and Cd^{2+} ions was studied in the pH range between 2 and 10. The percent recoveries of Pb^{2+} and Cd^{2+} as a function of solution pH are depicted in Figure 2. The recoveries for both metal ions increased sharply within the pH values between 2 and 4, indicating that the coprecipitation procedure was highly pH depended in these range. At low pH values, the functional groups of the ligand (coprecipitating agent) are more hydrogenated when compared to high pH values. Hence, the overall surface charge on the ligand becomes positive. In addition, the metal ions (Pb^{2+} and Cd^{2+}) show also a very strongly positive character within this pH range. Therefore, the convergences and interactions between metal cations and the ligand functional groups decrease due to the electrostatic repulsion, and thereby the
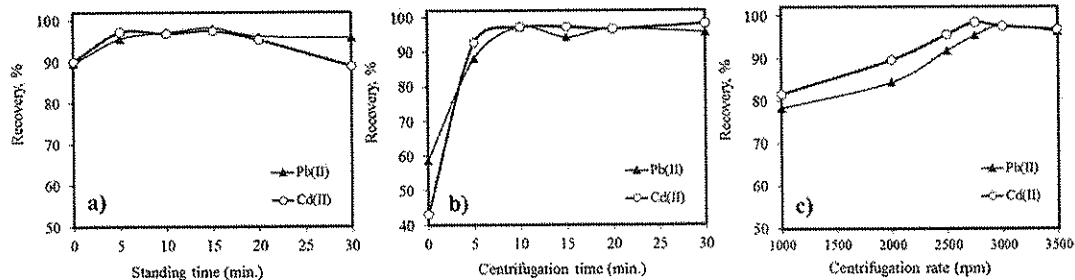
Figure 4. Effects of (a) incubation time, (b) centrifugation time and (c) centrifugation rate over the recovery yield (N: 3, quantity of analyte ions: 5.0 µg Pb^{2+} and 0.5 µg Cd^{2+}, pH: 6.0, sample volume: 50 mL, quantity of co-precipitating agent: 1.5 mg, final volume: 5.0 mL).
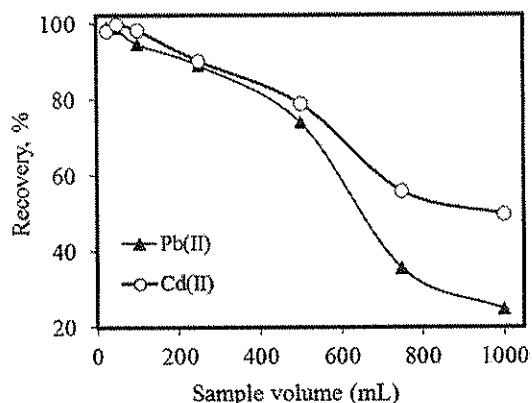

Figure 5. Effect of sample volume over the recovery yield (N: 3, quantity of analyte ions: 5.0 µg Pb^{2+} and 0.5 µg Cd^{2+}, pH: 6.0, quantity of coprecipitating agent: 1.5 mg, sample volume: 25–1000 mL, final volume: 2.0 mL).

recovery percent drops. The interactions will increase with increasing pH because the overall negative charge on the ligand surface until the relevant functional groups are deprotonated completely, and so the recovery yields of the metal ions rise (Figure 2). As can be seen from the Figure 2, the recovery percentages reach to the quantitative values of 95% approximately among the pH 5–7 for each metal. Therefore, optimum pH value was selected as 6.0 for all other working parameters of this study.

Effect of Coprecipitating Agent Quantity over the Recovery Yield

Another parameter used in the optimization of coprecipitation methods is the determination of the ligand quantity as a coprecipitating agent. In this study, effect of ligand quantity on the recovery yield was examined from 0 to 3.0 mg. The recoveries of Pb^{2+} and Cd^{2+} were 55.3 and 68.3%, respectively, without adding the coprecipitating agent at optimum pH 6.0 for each analyte. When the ligand quantity was increased, the percent recoveries also increased as seen Figure 3. Hence, the minimum coprecipitating agent quantity of 1.0 mg is sufficient for the quantitative recovery of both metals, 1.5 mg coprecipitating agent quantity were used as an optimized amount.

Effect of Incubation Time, Centrifugation Time, and Centrifugation Rate on the Recovery of Analytes

To complete the precipitate formation after adding the coprecipitating agent to the working solution containing the heavy metals, Pb^{2+} and Cd^{2+}, the mixture should be kept

for a while. Therefore, effect of incubation time was observed over the recovery yields of metal ions from working solution containing 1.5 mg coprecipitating agent at pH 6.0 in this study. The results showed that ~5.0 min was sufficient for the optimum incubation period (Figure 4a).

Centrifugation time is an optimization parameter that was studied after maturing the precipitate, and it's required to determine how much time the precipitate will be quantitatively settled towards to bottom of a centrifugation tube since the precipitate and the supernatant can be easily separated from each other. For this purpose, centrifugation time was studied in the range of time 0–30 min, and then 10 min centrifugation time was decided as optimized value (Figure 4b).

Centrifugation rate is also an important parameter in order to settle the precipitate to centrifugation tube bottom completely. Centrifugation rate was tested in the range of 1000–3500 rpm. Quantitative recovery for both metals was obtained after 2750 rpm, and then the optimum value was evaluated as 3000 rpm (Figure 4c).

Effect of Sample Volume over the Recovery Yield

Large sample volume is highly important in separation/preconcentration studies to have higher preconcentration factor and lower detection limit. On the other hand, large sample volume is not practical in analysis of real samples though it provides high preconcentration factor. Therefore, an optimization is required.

Sample volume was investigated in the range of 25–1000 mL by employing the model working solutions containing fixed quantity of the analyte ions in optimum conditions. The system was not resistant to the increased sample volume since the quantitative recoveries for both metals were up to only 100 mL. Therefore, this volume was selected for the analysis of the real water samples (Figure 5).

During the analysis of real water samples, the final sample volume was 2.0 mL at the end of the developed coprecipitation procedure while the initial volume is 100 mL. Because the analyte was concentrated 50-fold, preconcentration factor was 50. This factor can be considered satisfactory when comparing to the other methods in the literature [17,19,21].

Effect of Matrix Ions Over the Recovery Yield

Real samples contain various matrix components besides heavy metals. These components may cause interfering effects over the analyte recoveries. Therefore, Effect of matrix interference was examined by using the working solutions containing fixed quantity of Pb^{2+} and Cd^{2+} ions and known concentrations of different interfering ions given in Table 1. It can be concluded as shown in Table 1 that no significant interferences were observed over the recovery of both metal ions.

Table 1. Influences of some foreign ions on the recoveries of analyte ions (N: 3, quantity of analyte ions: 5.0 µg Pb^{2+} and 0.5 µg Cd^{2+}, pH: 6.0, sample volume: 50 mL, quantity of coprecipitating agent: 1.5 mg, final volume: 5.0 mL).

Ions	Added as	Concentration (mg L^{-1})	Recovery, % ($\bar{x} \pm s$)	
			Pb^{2+}	Cd^{2+}
Na^+	NaCl	10,000	93.4 ± 0.8	93.8 ± 3.6
K^+	KCl	1000	95.5 ± 2.8	97.8 ± 4.7
Ca^{2+}	$CaCl_2$	1000	96.3 ± 4.2	93.5 ± 1.8
Mg^{2+}	$Mg(NO_3)_2$	1000	93.7 ± 3.8	98.4 ± 3.5
NH_4^+	NH_4NO_3	350	98.3 ± 5.5	97.6 ± 4.8
NO_3^-	$NaNO_3$	5000	95.4 ± 3.8	99.3 ± 2.9
Cl^-	NaCl	15,000	95.3 ± 0.7	93.8 ± 3.4
CO_3^{2-}	Na_2CO_3	750	97.7 ± 2.8	94.3 ± 1.8
SO_4^{2-}	Na_2SO_4	750	92.9 ± 2.4	96.4 ± 4.8
PO_4^{3-}	Na_3PO_4	750	94.1 ± 4.6	102.4 ± 5.8
F^-	NaF	250	95.6 ± 1.7	98.7 ± 2.7
Fe^{3+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, $*V^{5+}$		50	92.1 ± 3.2	93.5 ± 0.8
Mixed**			93.0 ± 4.7	95.8 ± 2.6

$*V^{5+}$, added as V_2O_5, other ions added as their nitrate salts.
**10,000 mg L^{-1} Na^+, 15,000 mg L^{-1} Cl^-, 5000 mg L^{-1} NO_3^-, 250 mg L^{-1} K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, 50 mg L^{-1} F^-, NH_4^+, 10 mg L^{-1} Fe^{3+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, V^{5+}.

Table 2. Spiked/recovery test results for the real water samples (N: 3, pH: 6.0, sample volume: 50 mL, quantity of coprecipitating agent: 1.5 mg, final volume: 5.0 mL).

Analyte	Added (µg)	Stream water		Sea water	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Pb^{2+}	0	BDL*	—	BDL	—
	5.00	4.82 ± 0.32	96.4	5.08 ± 0.38	101.6
	7.50	7.58 ± 0.72	101.1	7.53 ± 0.49	100.4
Cd^{2+}	0	BDL	—	BDL	—
	0.50	0.53 ± 0.03	106.0	0.52 ± 0.01	104.0
	0.75	0.78 ± 0.02	104.0	0.76 ± 0.04	101.3

*Below the detection limit, N: number of repetitions.

Table 3. Spiked/recovery test results for the real solid samples (N: 3, pH: 6.0, quantity of coprecipitating agent: 1.5 mg, sample quantities: 0.75 g and final volume: 2.0 mL).

Element	Added (µg)	Tobacco		Black tea	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Pb^{2+}	0	0.62 ± 0.12	—	BDL	—
	5.00	5.73 ± 0.37	101.9	5.11 ± 0.36	102.2
	7.50	8.30 ± 0.84	102.2	7.56 ± 0.42	100.8
Cd^{2+}	0	0.14 ± 0.01	—	0.08 ± 0.02	—
	0.50	0.67 ± 0.02	104.6	0.59 ± 0.03	101.7
	0.75	0.92 ± 1.48	103.4	0.85 ± 0.04	102.4

Analytical Figure of Merit

After optimization, the method was validated by the parameters, relative standard deviation (RSD), limit of detection (LOD), limit of quantification (LOQ), spiked/recovery testing and analysis of certified reference materials (CRM).

The precision of a method is generally defined as RSD%. The developed method was repeated ten times through the model working solutions in the optimum conditions. From the obtained results (recovery values for each metal), the standard deviations and mean values were calculated, and the RSD values were determined for each metal by the following formula:

$$RSD\% = \frac{s}{\bar{x}} \times 100 \tag{1}$$

Table 4. Application of the present method to the certified reference material (N: 3, quantity of CRM-SA-C Sandy Soil C: 0.1 g and final volume: 5.0 mL).

| | CRM-SA-C sandy soil C | | |
| | Certified value ($\mu g\ g^{-1}$) | Found value ($\mu g\ g^{-1}$) | Recovery (%) |
Analyte			
Pb^{2+}	120.0 ± 8.0	116.4 ± 7.2	97.0 ± 4.1
Cd^{2+}	109.0 ± 8.0	105.5 ± 5.1	96.8 ± 3.4

Table 5. Analyte levels in real solid/liquid real samples after being applied the presented coprecipitation procedure (N: 3, sample volumes: 100 mL, sample quantities: 0.75 g and final volume: 2.0 mL).

| | Concentration ($\mu g\ L^{-1}$) | |
Sample	Pb^{2+}	Cd^{2+}
Sea Water, Trabzon	BDL	BDL
Stream water, Maçka/Trabzon	BDL	BDL
	Concentration ($\mu g\ g^{-1}$)	
	Pb^{2+}	Cd^{2+}
Tobacco	0.83 ± 0.05	0.19 ± 0.01
Black tea	BDL	0.11 ± 0.01

Where s represents standard deviation, and $\bar{x}$ is mean value. Through the results, percentage values of RSD were found as 5.7 and 4.8 for Pb^{2+} and Cd^{2+}, respectively.

LOD defined as the lowest analyte concentration was evaluated in this work as three-fold the standard deviation of 20 replicate measurements of the blank sample. On the other hand, LOQ; perhaps more useful than LOD, was considered 10-fold of the standard deviation for each analyte. For this, twenty blank solutions were prepared, and the method was applied to these blank solutions under the optimum conditions. After then, the standard deviations were calculated for each analyte. The following formulas were used for determining the LOD and LOQ values:

$$LOD = \frac{3s}{m} \tag{2}$$

$$LOQ = \frac{10s}{m} \tag{3}$$

where m represents slop of the calibration graph. LOD values of the method for Pb^{2+} and Cd^{2+} were found as 2.0 and 0.2 $\mu g\ L^{-1}$, respectively. In addition, LOQ values were also calculated as 6.0 and 0.6 $\mu g\ L^{-1}$.

By using solid–liquid real samples, the system was checked with another verification parameter which is spiked/recovery testing. There were the quantitative relations between added and found values (Tables 2 and 3).

Accuracy of the method was tested by using a certified reference material (CRM), CRM-SA-C Sandy Soil C. The CRM was solubilized by microwave irradiation. Then the general procedure was applied. The results obtained after measuring with FAAS are given in Table 4. It was concluded that the satisfactory results with the quantitative recovery values for each analyte were reached.

Application of the Method to the Real Samples

After the method was optimized with some analytical parameters and validated with the statistical parameters, it was applied to the solid–liquid real samples; tobacco, black

tea, stream water and sea water. The results from the real samples are given in Table 5.

CONCLUSION

The CEFC-based novel coprecipitation method which was developed in this study, showed a good performance for the quantitative determination of Pb^{2+} and Cd^{2+} ions at trace levels among the various solid-liquid environmental samples, and validated with the analytical parameters. Only about 30-min of period was sufficient for the implementation of the method. This method does not require the use of any carrier element. Thus, any interference may come from a carrier element is not a question during FAAS measurement, particularly. Only a suitable water-insoluble organic ligand as a coprecipitating agent is sufficient in order to form a precipitate which collects the metal ions on its own from aqueous solutions in the CEFC method.

The results demonstrated that the novel CEFC method which was developed and validated in this study is a strong alternative to other separation and preconcentration methods reported in the literature.

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