



Preconcentration of Cd(II) and Cu(II) ions by coprecipitation without any carrier element in some food and water samples

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ABSTRACT

A simple, rapid, sensitive and environmentally friendly separation and preconcentration procedure, based on the carrier element free coprecipitation (CEFC) of Cu(II) and Cd(II) ions by using an organic coprecipitant, 2-[[4-(4-fluorophenyl)-5-sulphonyl-4H-1,2,4-triazol-3-yl]methyl]-4-[[4-(4-fluorophenyl) methylene]amino]-5-(4-methylphenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (MEFMAT) was developed. The analyte ions were determined by flame atomic absorption spectrometric (FAAS) determinations. The optimum conditions for the coprecipitation process were investigated on several commonly tested experimental parameters such as pH of the solution, amount of MEFMAT, sample volume, standing time, centrifugation rate and time. The influences of some anions, cations and transition metals on the recoveries of analyte ions were also investigated, and no considerable interference was observed. The preconcentration factor was found to be 50. The detection limits for Cu(II) and Cd(II) ions based on the three times the standard deviation of the blanks ($N:10$) were found to be 1.49 and 0.45 $\mu\text{g L}^{-1}$, respectively. The relative standard deviations were found to be lower than 3.5% for both analyte ions. The method was validated by analyzing two certified reference materials (CRM-TMDW-500 Drinking Water and CRM-SA-C Sandy Soil C) and spike tests. The procedure was successfully applied to sea water and stream water as liquid samples and tobacco, hazelnut and black tea as solid samples.

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1. Introduction

Unlike organic pollutants, heavy metals such as cadmium, copper, lead, and chromium, are non-biodegradable in the environment and can be accumulated in living tissues particularly in human bodies causing significant diseases such as damage or reduced mental or central nervous function, damage to blood composition, lungs, kidneys, livers or other vital organs [1]. Hence the accurate and precise determinations of heavy metal ion concentrations in environmental samples are one of the main parts of analytical chemistry [2,3]. Flame atomic absorption spectrometry (FAAS) is a widely used technique for determination of heavy metal ions at trace levels in environmental solid and liquid samples due to its selectivity, low cost and easy instrument usage [4]. Nevertheless, the lower levels of analyte ions than the detection limits of FAAS and high interfering effects of the concomitants ions on the signal of the analytes, limit the direct determination of heavy metal ions by FAAS [5]. In order to overcome these limitations, separation and preconcentration methods like solid phase extraction [6–8], ion exchange [9], cloud point extraction [10–12], membrane filtration

[13], liquid–liquid extraction [14], coprecipitation [15], are used for trace metal ions prior to their detection by the instrumental techniques.

Coprecipitation is a commonly utilized technique for separation and preconcentration of trace metal ions because of some advantages including simplicity, rapidity, ability to attain a high preconcentration factor and low consumption of organic solvents. Other advantages of the method are those both separation and preconcentration steps that can be applied in the same step and several analyte ions can be preconcentrated and separated from the matrix simultaneously by using various organic or inorganic coprecipitants as efficient collectors of trace elements [16–18]. Several metal hydroxides, such as gadolinium [19], erbium [20], dysprosium [21], zirconium [22], and aluminum [23] have been used as inorganic coprecipitants for the preconcentration of trace metal ions from aqueous media. However, some of the metal ions themselves cause serious high-background absorption during the analysis because of their large quantities in the medium hence many drawbacks have arisen during the applications [4]. The organic coprecipitants, those which are able to form neutral chelates with metallic species such as 8-hydroxyquinoline [24], pyrrolidine dithiocarbamate [25], rubenic acid [26], and violuric acid [27], have been used in previous researches. However large amounts of a carrier element (Cu, Bi, Ni, Co etc.), which may cause interferences during the analysis, are necessary to be added to the medium in order to form a

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precipitate together with organic coprecipitants. So far most of the coprecipitation procedures including the use of organic or inorganic coprecipitants have been performed by using a carrier element. In recent years a new coprecipitation method without using a carrier element has been developed and thus this method has been called as “carrier element free coprecipitation (CEFC)” [28]. CEFC method has great advantages for separation and preconcentration of heavy metals because there are no contamination and background adsorption risks described above for metal ions from a carrier element [28–32].

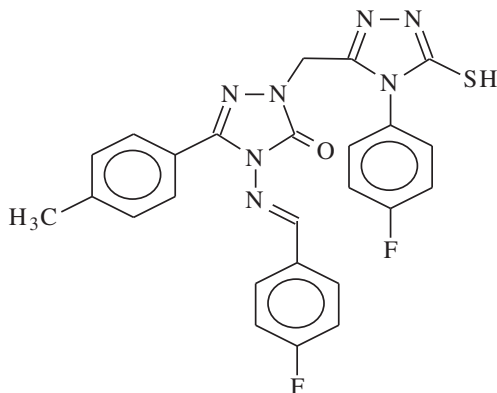
In the present study we applied the CEFC method for separation and preconcentration of Cu(II) and Cd(II) ions from aqueous solutions by using a triazole derivative, 2-[[4-(4-fluorophenyl)-5-sulphonyl-4H-1,2,4-triazol-3-yl]methyl]-4-[[4-(4-fluorophenyl) ethylene] amino]-5-(4-methylphenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (MEFMAT) as an organic coprecipitant without any carrier element. The influences of the various analytical parameters such as the effects of pH, quantity of MEFMAT, standing time, centrifugation rate and time, and sample volume, were investigated on the recoveries of the examined metal ions. The proposed method was applied to determine Cu(II) and Cd(II) ions in several solid and liquid environmental samples.

2. Experimental

2.1. Apparatus and reagents

A Unicam AA-929 model Flame Atomic Absorption Spectrometer was used for determination of analytes in solutions. All measurements were carried out in an air/acetylene flame with a 10-cm-long burner head. The instrumental parameters were those recommended by the manufacturer. The pH measurements were made on Hanna pH-211 (HANNA instruments, Romania) digital pH meter with glass electrode. pH meter was calibrated with standard buffer solutions. Sigma 3-16P (Sigma Laborzentrifugen GmbH, Germany) model centrifuge was used to centrifuge solutions. Milestone Ethos D (Milestone Inc., Italy) closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was operated for digestion of the solid samples.

All of the chemicals used in this work were analytical grade from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Distilled/deionized water (Millipore Milli-Q system) was used for all dilutions. Working solutions of Cu(II) and Cd(II) ions were prepared by diluting a stock solution of 1000 mg L⁻¹ of the given elements supplied by Sigma and Aldrich. Dilute HCl (Merck) and NaOH (Merck) solutions were used for pH adjustments. MEFMAT (Scheme 1) used as a coprecipitating agent was synthesized [33] in the organic chemistry research laboratory (Karadeniz Technical University, Faculty of Arts and Science, Chemistry Department). For separation and preconcentration experiments, 0.2% (w/v) MEFMAT solution was prepared in the mixture of dimethyl



Scheme 1. Chemical structure of MEFMAT.

sulfoxide and ethanol (1:4). The certified reference materials, drinking water standard (CRM-TMDW-500) and sandy soil standard (CRM-SA-C), used in the experimental studies, were obtained from High-Purity Standard Inc.

All glassware and plastic materials used were soaked in 10% (v/v) nitric acid solution for 1 day before use then cleaned repeatedly with distilled/deionized water. For storage of water samples prior to analysis, polypropylene bottles were used.

2.2. Model working

The performance of the present CEFC method was tested firstly by using model solutions prior to preconcentration of the analyte ions from real samples. For that purpose, 3.0 mL of coprecipitating agent solution (0.2% (w/v)) was added into a 50 mL of aqueous solution containing 12.5 µg of Cu(II) and 2.5 µg of Cd(II) ions. The pH of the solution was adjusted to 6.8. After standing for 20 min, the solution was centrifuged at 3000 rpm for 10 min. The supernatant was removed and the precipitate remained adhering to the tube was dissolved with 1.0 mL of conc. HNO₃. The final volume was completed to 5.0 mL with distilled/deionized water, and then the content was analyzed by FAAS for determination of analyte ions.

2.3. Analysis of real samples

The present coprecipitation procedure based on CEFC method was applied to various environmental liquid (seawater and stream water) and solid (tobacco, black tea and hazelnut) real samples. As certified reference materials; CRM-TMDW-500 Drinking Water and CRM-SA-C Sandy Soil C were used. Various amounts of analyte ions were also spiked to solid and liquid real samples.

The solid samples were digested with a closed microwave digestion system prior to the application of the present method. For that purpose, 0.75 g of tobacco, 0.5 g of black tea and hazelnut samples and 0.1 g of CRM-SA-C Sandy Soil C were weighed with a sensitivity of 0.1 mg into Teflon vessels, separately. 6 mL of HNO₃, and 2 mL of H₂O₂ for tobacco, black tea and hazelnut samples, 4.5 mL of HCl, 1.5 mL of HNO₃, 1 mL of HF and 2 mL of H₂O₂ for CRM-SA-C Sandy Soil C standard were added into the vessels. Digestion conditions for the microwave system for the samples were applied as (45 bar) 6 min for 250 W, 6 min for 400 W, 6 min for 650 W, 6 min for 250 W, vent: 3 min. After microwave digestion, the volume of the sample was made up to 50 mL with distilled water. Blanks were prepared in the same way as the sample but omitting the sample. The preconcentration procedure given in Section 2.2 was applied to the samples. The final volume was 5 mL.

In order to determine the concentration levels of Cu(II) and Cd(II) ions in real water samples; sea water (Black sea, Trabzon/Turkey) and stream water (Şana Stream, Trabzon/Turkey) were collected in prewashed (in turn with detergent, doubly distilled/deionized water, dilute HNO₃, and doubly distilled/deionized water) polyethylene bottles. The samples were filtered through a cellulose membrane filter of 0.45 µm pore size. Before the analysis, the pH values of the liquid samples (250 mL for seawater and stream water and 50 mL for CRM-TMDW-500 Drinking Water) were adjusted to 6.8. After addition of appropriate amount of 0.2% MEFMAT, the present CEFC procedure was applied to the samples. The final volumes of the solutions were diluted to 5 mL with distilled/deionized water. The levels of Cu(II) and Cd(II) ions in the samples were determined by FAAS.

3. Results and discussions

3.1. Effect of pH

The pH values of the working media directly affect the quantitative recoveries of the analyte ions. Hence the effect of pH on the coprecipitation system was evaluated in the range of 1–10. At too

acidic and basic pH values the recoveries of analyte ions were decreased as a result of increasing the solubilization of precipitate. The quantitative recovery values were obtained for both Cu(II) and Cd(II) ions in the pH range of 6.6–7.0 (Fig. 1) so pH 6.8 was selected as the working pH for all further experiments. This result may be an advantage for separation and preconcentration of trace metal ions from natural water samples. Because pH 6.8 is extremely close to the neutral pH low quantity of reagent is required to maintain the pH, which also reduced the contamination risk [22].

3.2. Effect of MEFMAT amount

The effects of MEFMAT amount on the recoveries of Cu(II) and Cd(II) ions were evaluated in the range of 0–7.0 mg (0–3.5 mL, 0.2% (w/v)) under optimal conditions. When the coprecipitation experiments were performed without adding any MEFMAT the recoveries of the analyte ions were not quantitative (below 20%). The recoveries of the analyte ions increased with increasing amount of MEFMAT. As can be seen in Fig. 2, Cu(II) ions could be recovered quantitatively in the range of 5.0–7.0 mg of MEFMAT while Cd(II) ions could be recovered 6.0–7.0 mg of MEFMAT. These results indicated that MEFMAT is necessary for quantitative and simultaneous recoveries of understudy analytes. All subsequent experiments were carried out with 6.0 mg (3.0 mL of 0.2% (w/v)) of MEFMAT.

3.3. Effect of standing time, centrifugation time and rate

Because of the standing time, centrifugation time and rate affect the quality of the precipitate that forms in aqueous medium, the effects of these experimental parameters on the recoveries of analyte ions were examined in detail. The coprecipitation experiments were performed in the standing time range of 1–30 min, centrifugation rate range of 1500–3500 rpm and centrifugation time range of 5–30 min. The quantitative recoveries of understudied analyte ions were obtained after the standing period of about 10 min for Cd(II) ions and 20 min for Cu(II) ions. The highest recovery values were obtained for both Cu(II) and Cd(II) ions after 3000 rpm of centrifugation rates and 10 min of centrifugation time. As a result, for quantitative recoveries of Cu(II) and Cd(II) ions, standing time, centrifugation time and rate were specified as 20 min, 3000 rpm and 10 min, respectively.

3.4. Effect of sample volume

The influences of sample volume on the recoveries of analyte ions were evaluated in the range of 50–1000 mL containing 12.5 µg of Cu(II)

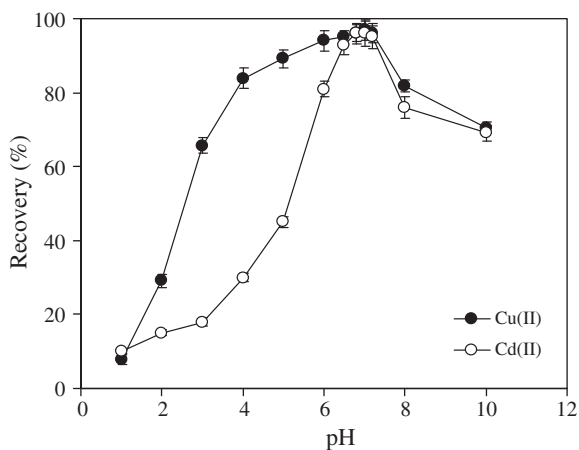


Fig. 1. Effect of pH on the recoveries of analyte ions ($N: 3$, sample volume: 50 mL, quantity of MEFMAT: 3.0 mL (0.2% (w/v)), standing time: 20 min, centrifugation rate: 3000 rpm, and centrifugation time: 10 min).

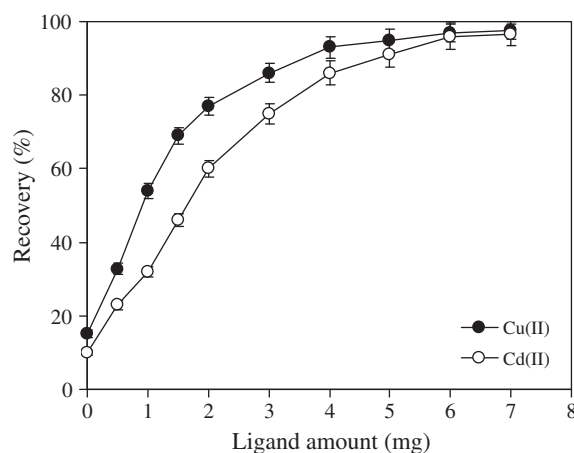


Fig. 2. Effect of MEFMAT amount on the recoveries of analyte ions ($N: 3$, sample pH: 6.8, and sample volume: 50 mL).

and 2.5 µg of Cd(II) by using model solutions. For the sample volumes above 50 mL, the precipitates formed in a polyethylene tube and solutions were separated from each other with centrifugation. For the sample volumes above 50 mL, the precipitates were filtered through a cellulose membrane filter of 0.45 µm pore size. As expected the recovery values decreased slowly with increasing the volume of the sample solution (Fig. 3). Above 250 mL of sample volume the recoveries of analyte ions were not quantitative. The preconcentration factor is calculated by the ratio of the highest sample volume and the lowest final volume, and it was found as 50 for both Cu(II) and Cd(II) ions when the final volume was 5.0 mL.

3.5. Effect of matrix ions

The interference from the matrix constitutes significant problems in the atomic absorption spectrometric determination of heavy metal ions in real samples [19]. In order to assess the possible analytical application of the recommended CEFC procedure, the effects of some foreign ions, which are the major components of sea water and stream water, were evaluated under the optimal conditions by contacting different amounts of anions and cations with fixed amounts of Cu(II) and Cd(II) ions (12.5 µg of Cu(II) and 2.5 µg of Cd(II) ions). Large numbers of ions at high concentration levels had no considerable effect on the determination of analyte ions. Also some of the transition metals at mg L^{-1} levels were not interfered on the recoveries of the

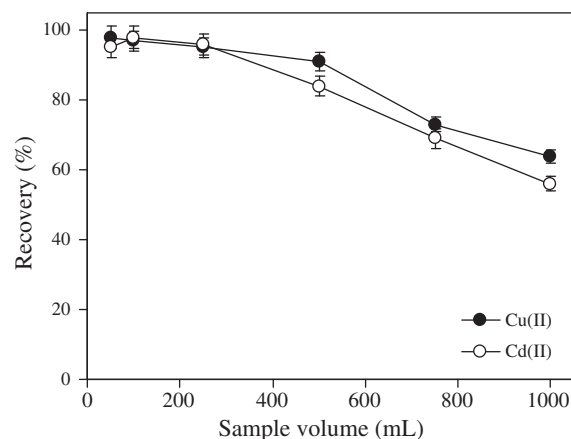


Fig. 3. Effect of sample volumes amount on the recoveries of analyte ions ($N: 3$ and sample pH: 6.8).

Table 1
Influences of some foreign ions on the recoveries of analyte ions (*N*: 3, sample pH: 6.8, sample volume: 50 mL, quantity of MEFMAT: 3.0 mL (0.2% (w/v)), standing time: 20 min, centrifugation rate: 3000 rpm, centrifugation time: 10 min).

Ions	Added as	Conc. (mg L ⁻¹)	Recovery (%)	
			Cu(II)	Cd(II)
Na ⁺	NaCl	5000	97.8 ± 0.8	98.3 ± 1.0
K ⁺	KCl	1000	101.0 ± 1.4	94.6 ± 0.6
Mg ²⁺	Mg(NO ₃) ₂	1000	96.4 ± 2.3	94.3 ± 1.8
Ca ²⁺	CaCl ₂	1000	96.8 ± 3.4	97.2 ± 1.4
CO ₃ ²⁻	Na ₂ CO ₃	1000	95.0 ± 0.9	96.1 ± 2.1
SO ₄ ²⁻	Na ₂ SO ₄	1000	99.2 ± 0.6	96.4 ± 2.5
NH ₄ ⁺	NH ₄ NO ₃	1000	97.2 ± 3.9	93.3 ± 1.6
Al ³⁺ , Fe ³⁺ , Pb ²⁺ , V ⁴⁺ , Cr ³⁺	*	25	97.4 ± 1.4	94.2 ± 1.1
Mixed ^a			96.8 ± 3.6	94.6 ± 3.4

*V⁴⁺ added as VOSO₄, other ions added as their nitrate salts.

^a 5310 mg L⁻¹ Na⁺, 8390 mg L⁻¹ Cl⁻, 2300 mg L⁻¹ NO₃⁻, 250 mg L⁻¹ K⁺, Ca²⁺, Mg²⁺, CO₃²⁻, SO₄²⁻, NH₄⁺, 10 mg L⁻¹ Al³⁺, Fe³⁺, Pb²⁺, V⁴⁺, Cr³⁺.

Table 2
Spiked recoveries of analyte ions from water samples (*N*: 3, sample pH: 6.8, sample volume: 50 mL, quantity of MEFMAT: 6.0 mg, final volume: 5.0 mL).

Element	Added (µg)	Sea water		Stream water	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Cu(II)	0	BDL*	–	BDL	–
	10.0	9.78 ± 0.39	97.8	9.95 ± 0.45	99.5
	20.0	20.13 ± 0.95	100.7	19.95 ± 1.10	99.7
Cd(II)	0	BDL	–	BDL	–
	2.5	2.35 ± 0.21	94.0	2.41 ± 0.15	96.4
	5.0	4.76 ± 0.32	95.2	4.74 ± 0.38	94.8

* Below detection limit.

analyte ions (Table 1). As a result the proposed separation and preconcentration method based on CEFC could be applied to the samples containing high amount of salts and some transition metal ions at given concentration levels in Table 1.

3.6. Analytical performance of the method

The analytical performance of the procedure can be calculated for the results from FAAS measurements. The precision of the method was evaluated as the relative standard deviations (RSD). In order to evaluate the precision of the determination of Cu(II) and Cd(II) ions (12.5 µg of Cu(II) and 2.5 µg of Cd(II) ions in 50 mL of aqueous solution) the procedure was repeated 10 times under optimum conditions mentioned above. The recoveries and RSD of Cu(II) and Cd(II) ions were found to be 98.5 ± 2.0 and 96.4 ± 3.2 at 95% confidence level, respectively.

The instrumental detection limits, defined as the concentration that gives a signal equivalent to three times the standard deviation of 10 replicate measurements of the blank samples ($\bar{X} \pm 3\sigma$, \bar{X} and σ are the mean value and the standard deviation of the blank measurements [34], respectively) for Cu(II) and Cd(II) ions were found to be 74.5 and 22.5 µg L⁻¹, respectively. The analytical or method detection limits that

were calculated by dividing the instrumental detection limit by the preconcentration factors (50) were found to be 1.49 µg L⁻¹ for Cu(II) and 0.45 µg L⁻¹ for Cd(II) ions.

3.7. Method validation and application to real samples

The accuracy of the present CEFC method was primarily tested by the technique of standard addition. For that purpose different amount of Cu(II) and Cd(II) ions were spiked in 50 mL of sea water, stream water and 0.75 g of tobacco and 0.5 g of black tea and hazelnut samples. The recommended CEFC procedure was applied to these samples. The results were given in Table 2 and 3. A good agreement was obtained between the added and measured analyte amounts. The results showed that the presented CEFC method can be applied for separation and preconcentration of Cu(II) and Cd(II) ions from environmental solid and liquid samples.

The certified reference materials (CRM-TMDW-500 Drinking Water and CRM-SA-C Sandy Soil C) were also used for the method validation. The statistical evaluation was applied to the results obtained from the accuracy study by using student's *t*-test, in order to decide the difference between \bar{X} (mean value) and X_R (value of

Table 3
Spiked recoveries of analyte ions from solid samples (*N*: 3, sample pH: 6.8, quantity of MEFMAT: 6.0 mg, sample quantities: 0.75 g of tobacco, 0.5 g of hazelnut and black tea, and final volume: 5.0 mL).

Element	Added (µg)	Tobacco		Hazelnut		Black tea	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Cu(II)	–	6.83 ± 0.17	–	6.11 ± 1.10	–	5.33 ± 0.67	–
	10.0	16.25 ± 0.36	94.2	15.89 ± 0.71	98.6	15.21 ± 0.46	99.2
	20.0	26.15 ± 0.51	96.6	24.37 ± 1.48	93.3	23.82 ± 0.81	94.0
Cd(II)	–	1.29 ± 0.28	–	BDL	–	BDL	–
	2.5	3.60 ± 0.13	92.4	2.45 ± 0.14	98.0	2.42 ± 0.53	96.8
	5.0	6.03 ± 0.30	94.8	5.02 ± 0.67	100.4	4.77 ± 0.67	95.4

Table 4Application of the present method to the certified reference materials ($N=3$ and quantity of MEFMAT: 6.0 mg).

Element	CRM TMDW-500 drinking water ^a		CRM-SA-C sandy soil ^b	
	Certified value ($\mu\text{g L}^{-1}$)	Found value ($\mu\text{g L}^{-1}$)	Certified value ($\mu\text{g L}^{-1}$)	Found value ($\mu\text{g L}^{-1}$)
Cu(II)	20.0 \pm 0.2	19.2 \pm 0.4	63.6 \pm 4.0	61.2 \pm 3.2
Cd(II)	10.0 \pm 0.1	9.9 \pm 0.2	109 \pm 8	103.0 \pm 7.1

^a Sample volume: 50 mL.^b Sample quantity: 0.1 g.**Table 5**Statistical evaluation of the results obtained in the accuracy study (Table 4) using student's t -test.

Certified Reference Materials	Elements											
	Cu(II)			Cd(II)								
	s	X _R	\bar{X}	X _R - \bar{X}	*ts/ \sqrt{N}	Compared	s	X _R	\bar{X}	X _R - \bar{X}	*ts/ \sqrt{N}	Compared
CRM TMDW-500 drinking water	0.4	20.0	19.2	0.8	1.0	0.4 < 1.0 (the same)	0.2	10.0	9.9	0.1	0.5	0.2 < 0.5 (the same)
CRM-SA-C sandy soil C	3.2	63.6	61.2	2.4	8.0	3.2 < 8.0 (the same)	7.1	109	103	6	17.6	7.1 < 17.6 (the same)

* t : 4.30 (95% confidence level), $N=3$, s : standard deviation, X_R : value of certified material, and \bar{X} : mean value.

certified material) is significant [35]. The results revealed good agreement between the observed values and certified values (Tables 4 and 5).

The CEFC method was applied to the determination of Cu(II) and Cd(II) ions in sea water (Blacksea, Trabzon/Turkey), stream water (Şana Stream, Trabzon/Turkey) and tobacco, black tea and hazelnut samples after having verified the accuracy of the method. After applying the preconcentration procedure to the samples, the obtained results were tabulated in Table 6.

3.8. Comparison of the method with the others

A comparison of the proposed method with other coprecipitation methods is summarized in Table 7 in terms of some analytical parameters including pH of the solutions, preconcentration factor, limit of detection, and relative standard deviation [17,18,26,28–32,36–38]. The present CEFC method is superior to those reported coprecipitation methods in literature in terms of no need to use a carrier element hence less consumption of chemicals and no contamination risk for

Table 6Analyte levels in real solid/liquid samples after being applied the presented coprecipitation procedure ($N=3$, sample volumes: 250 mL, sample quantities: 0.75 g of tobacco, 0.5 g of hazelnut and black tea, and final volume: 5.0 mL).

Element	Liquid samples		Solid samples		
	Sea water ($\mu\text{g L}^{-1}$)	Stream water ($\mu\text{g L}^{-1}$)	Tobacco ($\mu\text{g g}^{-1}$)	Hazelnut ($\mu\text{g g}^{-1}$)	Black tea ($\mu\text{g g}^{-1}$)
Cu(II)	2.42 \pm 0.21	5.04 \pm 0.33	9.11 \pm 0.24	12.22 \pm 2.92	10.66 \pm 0.85
Cd(II)	BDL [*]	BDL	1.72 \pm 0.38	BDL	BDL

* Below detection limit.

Table 7

Comparison of the CEFC method with some recent studies on coprecipitation reported in literature.

Analytes	Precipitant	Carrier Element	pH	PF	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Ref.
Pb(II), Cd(II), Cr(III), Ni(II), Mn(II)	dibenzylidithiocarbamate	Cu(II)	9.0	50	0.06–0.87	<10	36
Co(II), Pb(II), Cu(II), Fe(III), Zn(II)	2-Nitroso-1-naphthol-4-sulfonic acid	Ni(II)	8.0	25	0.50–2.67	3.8–7.5	17
Pb(II), Fe(III), Cd(II), Au(III), Pd(II), Ni(II)	rubeanic acid	Cu(II)	7.0	25–75	0.14–3.40	1–10	26
Au(III), Bi(III), Co(II), Cr(III), Fe(III), Mn(II), Ni(II), Pb(II), Th(IV), U(VI)	9-phenyl-3-fluorone	Cu(II)	7.0	30	0.05–12.9	0.8–2.7	37
Cd(II), Cu(II), Pb(II)	4-methylpiperidinedithiocarbamate	Bi(III)	5.0	200	0.18–0.50	<10	38
Cr speciation (Cr(III))	5-chloro-3-[4-(trifluoromethoxy) phenylimino]indolin-2-one (CFMEPI)	–	8.0	40	0.7	5	29
Cr(III), Fe(III), Pb(II), Zn(II)	3-phenyl-4-o-hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazole-5-one (POHBAT)	–	7.0	50–150	0.3–2.0	3–7	18
Fe(III), Cu(II), Cr(III), Zn(II), Pb(II)	3-benzyl-4-p-nitrobenzylidenamino-4,5-dihydro-1,2,4-triazole-5-on (BPNBAT)	–	7.0	50–150	0.3–2.0	1.6–6.0	28
Cr speciation (Cr(III))	3-phenyl-4-o-hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazole-5-one (POHBAT)	–	7.0	100	0.5	4	30
Cd(II), Cr(III), Co(II), Cu(II), N-cetyl N,N,N trimethylammonium bromide (CTAB)	Fe(III), Pb(II), Mn(II)	–	10.0	10	0.22–16.8	<5	32
Cr speciation (Cr(III))	3-ethyl-4-(p-chlorobenzylidenamino-4,5-dihydro-1H-1,2,4-triazol-5-one (EPHBAT)	–	8.0	50	1.0	<8	31
Cd(II), Cu(II)	2-[[4-(4-fluorophenyl)-5-sulphanyl-4H-1,2,4-triazol-3-yl]methyl]-4-[[4-(4-fluorophenyl)methylene]amino]-5-(4-methylphenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one	–	6.8	50	0.45–1.49	3.2–2.0	This work

PF: preconcentration factor, LOD: limit of detection, and RSD: relative standard deviation.

analyte ions from a carrier element. The proposed CEFC method has high preconcentration factor, low RSD, relatively low LOD and neutral working pH value when compared the other methods reported in Table 7.

4. Conclusions

The proposed CEFC method offers a simple, rapid, low cost and sensitive separation and preconcentration technique for accurate and precise determination of heavy metal ions in environmental solid and liquid samples. We have used an organic coprecipitant, MEFMAT, as the coprecipitating agent which provides effective and quantitative collection of Cu(II) and Cd(II) ions on itself without using a carrier element. Therefore there is no contamination risk for analyte ions from a carrier element. This also enables the usage of less chemicals than those of similar works in the literature hence it can be concluded that the CEFC method is environmentally friendly. The coprecipitated analyte ions can be sensitively determined by atomic absorption spectrometry without any influence of coprecipitant agent. Because MEFMAT is an organic compound, it is decomposed easily by flame and HNO₃. The procedure has been successfully applied to the real samples for the determination of Cu(II) and Cd(II) levels with acceptable accuracy and precision.

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