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Simultaneous separation and preconcentration of Cd(II), Co(II), and Ni(II) ions in environmental samples by carrier element-free coprecipitation method prior to their flame atomic absorption spectrometric determination

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ABSTRACT

In the present study, Cd(II), Co(II), and Ni(II) ions were separated and preconcentrated via carrier element-free coprecipitation (CEFC) method by using an organic coprecipitating agent, 1,2-bis-(2-tosyl ethoxy) benzene (BTEB), prior to their flame atomic absorption spectrometric (FAAS) detections. The experimental conditions were optimized in terms of pH of the aqueous solution, BTEB amount, standing time, centrifugation rate and time, and sample volume. Under the optimum experimental conditions, the detection limits for Cd(II), Co(II), and Ni(II) ions were found to be 0.13, 0.67, and 0.46 $\mu g L^{-1}$, respectively, and the relative standard deviations for the analyte ions were found to be lower than 4.0%. The accuracy of the method was tested by analyzing certified reference material and spike tests. The method was applied to determine the levels of Cd(II), Co(II), and Ni(II) ions in sea and stream water, macaroni, red lentil, and cracked wheat samples.

Keywords: Heavy metals; Separation; Preconcentration; Carrier element free coprecipitation; Flame atomic absorption spectrometry

1. Introduction

Monitoring of heavy metal contamination is important in every product or service, but it is especially important in food industry because it may affect the health of large populations. Some of the heavy metals are essential for human body at trace levels, but above certain threshold concentrations they are considered as potentially toxic substances to human metabolism. Cd(II) and Ni(II) ions are two of the most toxic elements present in practically every ecosystem around the world [1]. Co(II) is an essential element for all living organisms and it is also central constituent of vitamin B_{12}, but the ingestion of relatively high levels of Co(II) may pose health risk problems to humans [2]. Environmental pollution caused by the

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aforementioned metals can originate from a variety of industrial applications such as electrolysis for various purposes, casting industry, surface finishing processes for metals, tannery, and battery manufacturing. The spread of these metals around the human habitat potentially causes health problems [3,4]. Hence, one of the notable roles of the analytical chemist is to analyze and detect these metals.

Flame atomic absorption spectrometry (FAAS) is one the most frequently used technique to determine the trace and toxic elements in various environmental solid samples and waters from various sources such as waste water, rain, sea, river, and tap water, since this technique is highly selective, economical, rapid than the similar methods, in addition to its versatility [5–7]. However, the direct determination of heavy metals by FAAS is generally difficult because of complex matrix and low concentration of metal ions in environmental samples. Therefore a separation and preconcentration process is usually necessary prior to FAAS measurements of the metal ions [8–11]. Outstanding effort in various directions has been spent in the last few decades to develop separation and preconcentration procedures such as ion exchange [12], membrane filtration [13], solid phase extraction [14–16], coprecipitation [17], fire-assay [18], cloud point extraction [19], liquid–liquid extraction [20], and electroanalytical techniques [21] to prepare the samples for the trace element determination process. Because the coprecipitation technique is simple, fast, and yields high preconcentration factors, it is commonly used for separation and preconcentration of trace amounts of metals in aqueous solutions [22–24]. In coprecipitation method, the precipitate, which collects the trace metal ions on its surface, may be occurred by the addition of a carrier element such as Ni, Cu, and Al, etc. with a suitable organic ligand like N-cetyl N,N,N trimethyl ammonium bromide [25], pyrolidine-dithiocarbamate [26], 3-phenly-4-o hydroxy benzylidenamino-4,5-dihydro-1,2,4-triazole-5-one [27], etc. or an inorganic ligand like hydroxides [28]. In the meantime, a new coprecipitation technique stems from the need for better separation and preconcentration of trace amounts of metals, in which no carrier element is needed and just an organic ligand is used for the formation of coprecipitating agent and called as "carrier element free coprecipitation (CEFC)" [22,25,27,29].

This study is devoted to evaluate the separation and preconcentration conditions of Cd(II), Co(II), and Ni(II) ions in environmental real samples by using 1,2-bis-(2-tosyl ethoxy) benzene (BTEB) as an organic coprecipitating agent without using a carrier element. BTEB was used for the first time as an organic coprecipitating agent for simultaneous separation and preconcentration of metal ions by a new CEFC method. The mechanisms of coprecipitation may vary in each case and the coprecipitation of Cd(II), Co(II), and Ni(II) ions by BTEB may include mainly electrostatic surface adsorption, besides inclusion and occlusion. In order to improve the efficiency of the proposed method, various experimental parameters influencing the coprecipitation process including pH of the aqueous solution, sample volume, quantity of coprecipitating agent, standing time, centrifugation rate, and time were investigated. Two certified reference materials, CRM TMDW-500 Drinking Water and CRM-SA-C Sandy Soil C, and spike tests were used to validate the method. The proposed method was successful in quantitatively coprecipitating Cd(II), Co (II), and Ni(II) ions in sea and stream water as liquid samples and macaroni, red lentil, and cracked wheat as solid samples.

2. Materials and methods

2.1. Apparatus

Cd(II), Co(II), and Ni(II) ions concentrations were analyzed by using a flame atomic absorption spectrometer, FAAS (Perkin–Elmer AAnalyst400). A digital pH meter (HANNA instruments/Romania) with a glass electrode was used for the adjustment of the pH value of the working solutions. The centrifugation of the solutions was performed using Sigma 3-16P (Sigma Laborzentrifugen GmbH, Germany) centrifuge. The solid samples were digested in a closed vessel microwave system (Milestones Ethos D (Milestone Inc./Italy)). The settings for all instruments were chosen as recommended in the manufacturer's manual book.

2.2. Reagents and solutions

All chemical reagents, except the coprecipitating agent, were produced by Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland) and all of the solutions were prepared in distilled/deionized water. The standard and working solutions of the analyte ions were prepared by the dilution of $1{,}000\,\mathrm{mg\,L^{-1}}$ stock solutions of them produced by Sigma–Aldrich.

The synthesizing process of the coprecipitating agent, BTEB, was performed in the inorganic chemistry research laboratory (Karadeniz Technical University, Faculty of Science, Chemistry Department). The details of this process have been given in the literature [30]. Fig. 1 shows the chemical structure of BTEB.

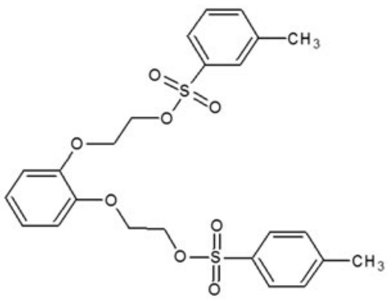

Fig. 1. Chemical structure of BTEB.

0.5% (w/v) BTEB solution was prepared by dissolving it in dimethyl sulfoxide and ethanol mixture as with the stoichiometric ratio of (1:4). The certified reference materials, CRM TMDW-500 Drinking Water and CRM-SA-C Sandy Soil C, were obtained from High-Purity Standard Inc.

2.3. Model studies for coprecipitation

50.0 mL of an aqueous solution containing 2.50 μg of Cd(II), 3.75 μg of Co(II), and 12.5 μg Ni(II) ions was placed in a centrifuge tube and the pH was then adjusted to the desired value by the addition of diluted HNO_3 and NaOH solutions. Then the coprecipitating agent was added to the solution with an amount of 15.0 mg (3.0 mL 0.5% (w/v)). The solution was left to stand for 30 min, then it was centrifuged for 10 min at 2,500 rpm, and then the supernatant was removed. The precipitate remained at the bottom of the tube was dissolved with 1.0 mL of conc. HNO_3. The final solution was completed to a volume of 5.0 mL by distilled/deionized water. The concentration of the analyte ions in the final solution were determined by FAAS.

2.4. Analysis of real samples

Another aim of this work was to apply the improved coprecipitation procedure to real samples. Sea water (Black sea, Trabzon/Turkey) and stream water (Şana Stream, Trabzon/Turkey) investigated in this study were sampled using polyethylene bottles. The water samples were filtered immediately after being collected by using a nitrocellulose membrane with a pore size of 0.45 μm (Millipore Corp.), and stored at 4℃ until they were used. The pH of the samples was adjusted to 7.0. After addition of the required amount of BTEB, the preconcentration procedure given above was applied.

The developed procedure was also applied to macaroni, red lentil, and cracked wheat as solid samples. They were microwave-digested prior to the application of the present separation and preconcentration procedure. For this purpose, 1.000 g of macaroni, 0.750 g red lentil, and 0.750 g of cracked wheat and 0.050 g of CRM-SA-C Sandy Soil C were weighed into Teflon vessels, separately. 6.0 mL of HNO_3 and 2.0 mL of H_2O_2 for macaroni, red lentil, and cracked wheat, and 4.5 mL of HCl, 1.5 mL of HNO_3, 1.0 mL of HF, and 2.0 mL of H_2O_2 for CRM-SA-C Sandy Soil C standard were added into the vessels. The digestion of the solid samples by microwave radiation was performed in four steps: 6 min for 250 W, 6 min for 400 W, 6 min for 650 W, and 6 min for 250 W. During all these microwave radiations, the pressure was kept at 45 bars, and the ventilation was 3 min. Digestion conditions for the samples were applied according to the literature [31]. At the end of the microwave digestion, the sample volume was made up to 50.0 mL with distilled/deionized water and then the method was applied.

3. Results and discussion

3.1. Effect of pH

Solution pH is one of the most important parameters affecting the quantitative recoveries of analyte ions. The effects of pH on the recoveries of Cd(II), Co(II), and Ni(II) ions were examined in the solution pH range of 1.0–10.0 under optimum conditions. The pH of the aqueous solution was adjusted to the desired value by careful addition of either dilute HNO_3 or NaOH solution. The results are depicted in Fig. 2. The distribution of cadmium hydroxide complexes indicates that Cd^{2+}, $Cd(OH)^+$, and $Cd(OH)_2$ are the most significant species below pH 12. At low total concentrations of cadmium, hydrolysis of Cd^{2+} becomes significant above about pH 9 [32]. Cobalt(II) ions tend to form $[Co(H_2O)_6]^{2+}$ complex in

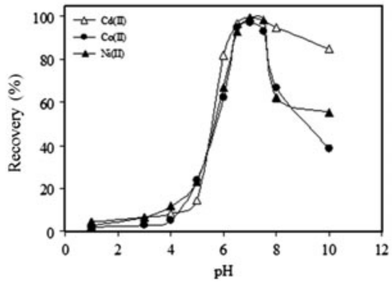

Fig. 2. Effect of pH on the recoveries of analyte ions (*N*: 3, sample volume: 50 mL, quantity of BTEB: 15.0 mg, standing time: 30 min, centrifugation rate: 2,500 rpm, centrifugation time: 10 min).

aqueous solution. The addition of nitric acid and sodium hydroxide gives $[CoCl_4]^{2-}$ and $Co(H_2O)_4(OH)_2$, respectively. Nickel(II) predominantly exists as cationic species (Ni^{2+}) or various hydolysis species (e.g. $NiOH^+$) at near-neutral pH [32,33]. The experimental results showed that maximum recovery values (> 95%) were obtained for the analyte ions in the pH range of 6.5–7.5, so all further experimental parameters were performed at pH 7.0. Because pH 7.0 is neutral pH value, low quantity of reagent is required to maintain the pH which also reduced the contamination risk. This result may be considered as one of the advantages of the method.

3.2. Effect of BTEB amount

To test the impact of the amount of BTEB on the coprecipitation of Cd(II), Co(II), and Ni(II) ions, the experiments were carried out at different BTEB amounts ranging between 0 and 20.0 mg under optimum conditions. A graph for the recovery values of Cd (II), Co(II), and Ni(II) ions vs. amount of BTEB was plotted from the obtained data (Fig. 3). The recoveries of the analyte ions were below 70% without adding BTEB. The recovery values of analyte ions increased with increasing the amount of BTEB. From the obtained results, it is seen that BTEB is necessary for quantitative and simultaneous recoveries of Cd(II), Co(II), and Ni (II) ions and the quantitative recoveries of analyte ions were obtained after addition of 15.0 mg (3.0 mL of 0.5% (w/v)) of BTEB, hence this amount of BTEB was added to the solutions for all subsequent works.

3.3. Effect of sample volume

As the concentrations of aforementioned metal ions in real samples are very low, the optimization of sample volume is required to obtain high preconcentration factors for the analysis of a real sample using presented coprecipitation method. Based on this, the effect of sample volume on the quantitative recoveries of the analyte ions were investigated in the sample volume range of 50–1,250 mL under optimum conditions. As can be seen from Fig. 4, the recovery values decreased with increasing the volume of the sample solution. After 250 mL of sample volume, the recoveries decreased considerably so the sample volume was optimized as 250 mL in the application of the procedure for sea and stream waters. The preconcentration factor was calculated by the ratio of the highest sample volume (250 mL) and the lowest final volume (5 mL), and it was found to be 50.

3.4. Effect of standing time, centrifugation rate and time

The influences of standing time, centrifugation time, and rate on the quantitative and simultaneous recoveries of Cd(II), Co(II), and Ni(II) ions were also examined because these are the important factors affecting the formation and quality of the precipitate. For that purpose, 15.0 mg of BTEB (3.0 mL 0.5% (w/v)) was added into a series of 50 mL of solutions, containing 2.50 μg of Cd(II), 3.75 μg of Co(II), and 12.5 μg Ni(II) ions at pH 7.0. Then the coprecipitation experiments were performed in the standing time range of 0–120 min, centrifugation rate range of 1,000–3,500 rpm, and centrifugation time range of 5–30 min. The optimum standing time, centrifugation time, and rate for the quantitative and simultaneous recoveries of analyte ions were determined as 30 min, 10 min, and 2,500 rpm, respectively.

3.5. Effect of matrix ions

In order to evaluate the applicability of the proposed method in the determination of the analyte ions in water samples, the effects of alkali, alkaline earth, some transition metal cations, and some anions were investigated. For this purpose, different amounts of each foreign ions, which are the major components of sea and stream water, were added to the model

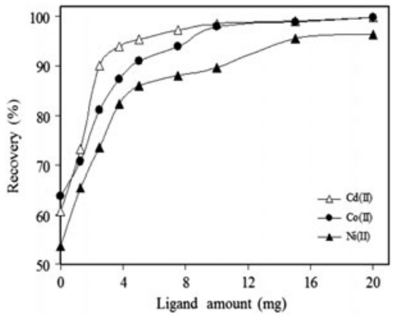

Fig. 3. Effect of BTEB amount on the recoveries of analyte ions (*N*: 3, sample pH: 7.0, sample volume: 50 mL).

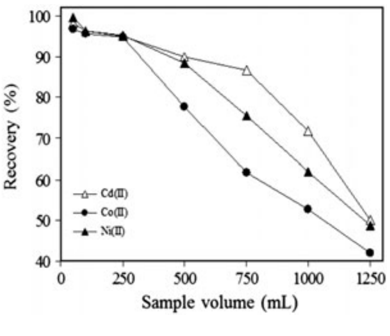

Fig. 4. Effect of sample volumes on the recoveries of analyte ions (*N*: 3, sample pH: 7.0).

Table 1
Influences of some foreign ions on the recoveries of analyte ions (*N*: 3, sample pH: 7.0, sample volume: 50 mL, quantity of BTEB: 15.0 mg, standing time: 30 min, centrifugation rate: 2,500 rpm, centrifugation time: 10 min)

Ions	Added as	Conc. ($mg\,L^{-1}$)	Recovery (%)		
			Cd(II)	Co(II)	Ni(II)
Na^+	NaCl	7,500	90.0 ± 4.0	96.8 ± 0.4	96.0 ± 1.1
K^+	KCl	500	100.1 ± 1.8	102.6 ± 1.5	94.6 ± 3.1
Ca^{2+}	$CaCl_2$	250	94.6 ± 2.4	98.9 ± 1.9	95.6 ± 2.3
Mg^{2+}	$Mg(NO_3)_2$	500	99.9 ± 0.2	100.5 ± 2.1	94.6 ± 2.5
NO_3^-	$NaNO_3$	5,000	93.9 ± 3.4	100.9 ± 2.7	91.4 ± 3.7
CO_3^{2-}	Na_2CO_3	500	97.6 ± 0.2	91.6 ± 2.9	98.8 ± 3.4
SO_4^{2-}	Na_2SO_4	250	97.4 ± 1.6	92.6 ± 1.7	96.4 ± 1.1
PO_4^{3-}	Na_3PO_4	500	99.9 ± 3.4	97.2 ± 0.5	92.6 ± 3.7
I^-	KI	250	92.3 ± 0.8	96.3 ± 0.4	97.4 ± 2.5
F^-	NaF	50	101.7 ± 0.8	99.6 ± 2.1	96.4 ± 2.3
CH_3COO^-	$NaCH_3COO$	50	97.6 ± 1.8	95.9 ± 3.9	99.0 ± 2.5
NH_4^+	NH_4NO_3	250	93.4 ± 0.9	97.5 ± 2.1	92.8 ± 4.0
Pb(II), Al(III), Cr(VI), Fe(III), Mn(II)	*	25	95.0 ± 0.6	96.4 ± 1.6	102.2 ± 2.5
Mixed[a]			91.7 ± 2.4	91.6 ± 3.7	95.6 ± 2.8

*Cr(VI) added as $K_2Cr_2O_7$, other ions added as their nitrate salts.

[a] 8,170 $mg\,L^{-1}$ Na^+, 12,250 $mg\,L^{-1}$, Cl^-, 2,016 $mg\,L^{-1}$ NO_3^-, 280 $mg\,L^{-1}$ K^+, 250 $mg\,L^{-1}$ Ca^{2+}, Mg^{2+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, 100 $mg\,L^{-1}$ I^-, NH_4^+, 50 $mg\,L^{-1}$ F^-, CH_3COO^-, 10 $mg\,L^{-1}$ Pb(II), Al(III), Cr(VI), Fe(III) and Mn(II).

Table 2
Application of the present method to the certified reference materials (*N*:3, CRM TMDW-500 Drinking Water: 50 mL, quantity of Sandy Soil C: 0.050 g, final volume: 5.0 mL)

Element	CRM TMDW-500 drinking water			CRM-SA-C sandy soil C		
	Certificated value ($\mu g\,L^{-1}$)	Found value ($\mu g\,L^{-1}$)	Recovery (%)	Certificated value ($\mu g\,g^{-1}$)	Found value ($\mu g\,g^{-1}$)	Recovery (%)
Cd(II)	10.0 ± 0.1	9.2 ± 0.5	92.0	109 ± 8	101 ± 6	92.7
Co(II)	25.0 ± 0.3	24.3 ± 1.6	97.2	12.4 ± 0.6	11.5 ± 0.5	92.7
Ni(II)	60.0 ± 0.3	58.6 ± 0.8	97.7	48.4 ± 3.0	44.6 ± 1.8	92.1

Table 3
Spiked recoveries of analyte ions from water samples (*N*: 3, sample pH: 7.0, sample volume: 50 mL, final volume: 5.0 mL)

Element	Added (μg)	Sea water		Stream water	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Cd(II)	0	BDL[a]	–	BDL	–
	1.0	0.94 ± 0.04	94.0	0.95 ± 0.03	95.0
	2.0	1.85 ± 0.06	92.5	1.91 ± 0.08	95.5
Co(II)	0	BDL	–	BDL	–
	2.0	1.87 ± 0.06	93.5	1.91 ± 0.08	95.5
	4.0	3.77 ± 0.11	94.2	3.79 ± 0.15	94.8
Ni(II)	0	BDL	–	BDL	–
	5.0	4.84 ± 0.15	96.8	4.76 ± 0.16	95.2
	10.0	9.54 ± 0.28	95.4	9.76 ± 0.33	97.6

[a] Below detection limit.

Table 4
Spiked recoveries of analyte ions from solid samples (*N*: 3, sample pH: 7.0, sample quantities: 1.000 g of macaroni, 0.750 g red lentil, and 0.750 g of cracked wheat, final volume: 5.0 mL)

Element	Added (μg)	Macaroni		Red lentil		Cracked wheat	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Cd(II)	0	0.16 ± 0.05	–	0.28 ± 0.06	–	0.13 ± 0.03	–
	1.0	1.10 ± 0.05	94.0	1.20 ± 0.08	92.0	1.08 ± 0.06	95.0
	2.0	1.99 ± 0.08	91.5	2.16 ± 0.14	94.0	2.00 ± 0.09	93.5
Co(II)	0	BDL	–	0.18 ± 0.03	–	0.40 ± 0.06	
	2.0	1.85 ± 0.09	92.5	2.06 ± 0.04	94.0	2.20 ± 0.08	90.0
	4.0	3.94 ± 0.12	98.5	3.85 ± 0.18	91.8	4.22 ± 0.13	95.5
Ni(II)	0	4.30 ± 0.64	–	3.63 ± 0.32	–	1.88 ± 0.25	–
	5.0	9.13 ± 0.36	96.6	8.24 ± 0.26	92.2	6.56 ± 0.23	93.6
	10.0	13.77 ± 0.51	94.7	13.11 ± 0.48	94.8	11.49 ± 0.41	96.1

Table 5
Analyte levels in real solid/liquid samples after being applied the presented coprecipitation procedure (*N*: 3, sample volumes: 250 mL, sample quantities: 1.000 g of macaroni, 0.750 g red lentil, and 0.750 g of cracked wheat, final volumes: 5.0 mL)

Element	Liquid samples (μg L^{-1})		Solid samples (μg g^{-1})		
	Sea water	Stream water	Macaroni	Red lentil	Cracked wheat
Cd(II)	5.84 ± 0.21	4.18 ± 0.18	0.16 ± 0.05	0.37 ± 0.08	0.17 ± 0.04
Co(II)	12.30 ± 0.69	11.40 ± 0.44	BDL	0.24 ± 0.04	0.53 ± 0.08
Ni(II)	8.60 ± 0.47	10.30 ± 0.59	4.30 ± 0.64	4.84 ± 0.42	2.51 ± 0.33

Table 6
Comparison of the present system with other coprecipitation system by FAAS

Analytes	Coprecipitating agent	PF	LOD (μg L^{-1})	RSD (%)	pH	Ref.
Cd(II), Co(II), Ni(II), Cu(II), Pb(II), Fe(III), Mn(II)	Thulium(III) hydroxide	120	0.10–1.60	–	11	[34]
Cd(II), Co(II), Ni(II), Cu(II), Pb(II), Fe(III)	Zirconium(IV) hydroxide	25	0.27–2.50	<8	8	[35]
Cd(II), Co(II), Ni(II), Cu(II), Pb(II), Mn(II)	Dysprosium(III) hydroxide	250	14.1–25.3	<7	11	[36]
Cd(II), Co(II), Ni(II), Cu(II), Pb(II), Fe(III), Mn(II)	Samarium hydroxide	50	0.4–24.0	<10	12.2	[37]
Cd(II), Co(II), Ni(II), Cu(II), Pb(II),	Cerium(IV) hydroxide	375	0.18–7.0	<9	10.5	[38]
Cd(II), Co(II), Ni(II)	BTEB	50	0.13–0.67	<4	7	This work

Note: PF: preconcentration factor; LOD: limit of detection; RSD: relative standard deviation; BTEB: 1,2-bis-(2-tosyl ethoxy) benzene.

solutions containing 2.50 μg of Cd(II), 3.75 μg of Co(II), and 12.5 μg of Ni(II) ions under the optimal conditions. As seen from Table 1, the existence of several anions and cations, and also transition metal ions at mg L^{-1} levels, has no notable effect on the separation and preconcentration of Cd(II), Co(II), and Ni(II) ions under the selected conditions. Consequently, it can be concluded that the recommended CEFC procedure can be performed to the samples that consist of various foreign ions at allowable levels.

3.6. Analytical performance of the method

The precision of the presented CEFC method has been determined by applying the method to 10 model solutions containing 2.50 μg of Cd(II), 3.75 μg of Co(II), and 12.5 μg Ni(II) ions under optimum conditions mentioned above. The relative standard deviations (RSD) of Cd(II), Co(II), and Ni(II) ions were found to be 3.5, 3.3, and 3.9%, respectively. The limit of detection (LOD) for the analyte ions, calculated as three times the standard deviation of 10 replicate measurements of the blank samples, were found to be 0.13, 0.67, and 0.46 $\mu g\,L^{-1}$ for Cd(II), Co(II), and Ni(II) ions, respectively, and the limit of quantitation (LOQ), calculated as nine times the standard deviation of 10 replicate measurements of the blank samples, were found to be 0.39, 2.01, and 1.38 $\mu g\,L^{-1}$ for Cd(II), Co(II), and Ni(II) ions, respectively, when the sample volume was 250 mL and the final volume was 5.0 mL.

3.7. Application of the real samples

The accuracy of the proposed separation and preconcentration method was primarily checked by analyzing two certified reference materials, CRM TMDW-500 Drinking Water, and CRM-SA-C Sandy Soil C, under optimum conditions. There is a good congruence between the obtained and certified values (Table 2). The validation of the proposed procedure was also performed to determine of Cd(II), Co(II), and Ni(II) ions content in different liquid and solid samples by applying standard addition technique. For this aim, different amounts Cd(II), Co(II), and Ni(II) ions were spiked in 50 mL of sea and stream water and 1.000 g of macaroni, 0.750 g red lentil, and 0.750 g of cracked wheat samples. As can be seen from the Tables 3 and 4, the results revealed good congruence between the added and measured analyte amounts. After making sure for the accuracy of the method, we applied it to determine the aforementioned metal ions level in some environmental real samples (Table 5).

4. Conclusions

The accurate and sensitive technique based on CEFC has been used for determination of Cd(II), Co(II), and Ni(II) ions in macaroni, red lentil, cracked wheat, and sea and stream water samples. The organic coprecipitating agent, BTEB, provides a quantitative and efficient collection of Cd(II), Co(II), and Ni(II) ions without using a carrier element. The experiments have shown that the method is relatively free from interference of various foreign ions at allowable levels. The method was compared with other reported coprecipitation methods in terms of pH of the solutions, preconcentration factor, limit of detection, and relative standard deviation [34–38]. The distinguished features of the present work are that the RSD and LOD values are relatively low, the working pH is near to neutral and the preconcentration factor of the method is relatively high when compared to other methods (Table 6). In the light of the obtained results, it can be concluded that the recommended CEFC procedure could be successfully applied to routine determination of Cd(II), Co(II), and Ni(II) ions level in environmental and food samples with acceptable accuracy, low detection limits, and high precision.

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