

Scientific paper

Application of Carrier Element Free Coprecipitation (CEFC) Method for Determination of Co(II), Cu(II) and Ni(II) Ions in Food and Water Samples

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Abstract

A simple and highly sensitive separation and preconcentration procedure, which has minimal impact on the environment, has been developed. The procedure is based on the carrier element free coprecipitation (CEFC) of Co(II), Cu(II), and Ni(II) ions by using 2-[4-[2-(1H-indol-3-yl)ethyl]-3-(4-methylbenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl]-N'-(pyridin-2-yl methylidene)acetohydrazide (IMOTPA), as an organic coprecipitant. The levels of analyte ions were determined by flame atomic absorption spectrometry (FAAS). The detection limits for Co(II), Cu(II) and Ni(II) ions were found to be 0.40, 0.16 and 0.17 $\mu\text{g L}^{-1}$, respectively, and the relative standard deviations for the analyte ions were lower than 3.0%. Spike tests and certified reference material analyses were performed to validate the method. The method was successfully applied for the determination of Co(II), Cu(II) and Ni(II) ions levels in sea and stream water as liquid samples and red pepper, black pepper, and peppermint as solid samples.

Keywords: Heavy metals, separation, preconcentration, carrier element free coprecipitation, flame atomic absorption spectrometry

1. Introduction

Heavy metals, such as cobalt, copper, and nickel, are non-biodegradable in the environment and can accumulate in living organisms, especially in human bodies. They cause significant diseases in central nervous system, damage the mental health, change the blood composition, and deteriorate the normal functions of vital organs.^{1–5} One of the important tasks of the analytical chemist is to analyze and detect the trace and toxic elements since these elements have significant hazardous impacts on humans, environment, and other living organisms.⁶ Flame atomic absorption spectrometry (FAAS) is the most widely used technique to determine the trace and toxic elements in various environmental materials and water samples including waste, sea, stream, river, and tap waters, since this technique is highly selective, versatile, economical and faster

than the alternative determination methods.^{7–11} A preconcentration step combined with matrix separation is often required prior to the determination of the analyte ions in environmental samples, which generally contain high amounts of interfering matrix components and low concentration of trace elements being analyzed. Remarkable efforts in various directions have been spent in the last few decades to develop separation and pre-concentration procedures for the preparation of the samples for the trace element analysis.¹² The methods developed for this purpose is based on ion exchange,¹³ membrane filtration,¹⁴ solid phase extraction,^{15–16} coprecipitation,^{17–18} fire-assay,¹⁹ cloud point extraction,²⁰ liquid-liquid extraction,²¹ and electroanalytical techniques.²²

Coprecipitation method is one of the commonly utilized techniques for separation and preconcentration of

trace metal ions because it is simple, fast, and it provides opportunity to reach high preconcentration factors and to consume less organic solvents. In addition to these advantages, the coprecipitation method allows the application of separation and preconcentration of analyte ions in a single step.^{23–25} In this method, various organic or inorganic coprecipitants can be used as efficient metal ion collectors to preconcentrate and separate several analyte ions from the matrix simultaneously.²⁶ In order to preconcentrate the trace metal ions in aqueous media various metal hydroxides including magnesium,²⁷ indium,²⁸ ytterbium,²⁹ gallium³⁰ etc. have been used as inorganic coprecipitants, and dithiocarbamates, N-cetyl N,N,N trimethyl ammonium bromide,³¹ pyrrolidine-dithiocarbamate,³² 3-ethyl-4-(*p*-chlorobenzylideneamino-4,5-dihydro-1H-1,2,4-triazol-5-one²⁶ etc. have been used as organic coprecipitants. For efficient precipitation with organic coprecipitants, large amounts of a carrier element (Cu, Bi, Ni, Co etc.), which may interfere with the preconcentration processes, are needed in the medium. In recent years, a new coprecipitation method called as “carrier element free coprecipitation (CEFC)”, in which no carrier element is needed and only an organic ligand is used for the formation of the precipitate, has been developed. Since there is no contamination and background adsorption risks in CEFC method, as described above, the technique is advantageous compared to the similar methods for separation and preconcentration of heavy metals.^{23,33}

In this paper the CEFC method was applied for separation and preconcentration of Co(II), Cu(II), and Ni(II) ions in environmental real samples by using IMOTPA as the organic coprecipitant without using a carrier element. The analytical applications of IMOTPA were investigated, and it was utilized for the first time in separation and preconcentration of metal ions by CEFC method. The influences of various analytical parameters such as pH of the aqueous solution, quantity of IMOTPA, sample volume, standing time, and centrifugation rate and time were investigated on the recovery of the metal ions examined. The method was validated by analyzing certified reference materials and spike tests. The procedure was successfully applied to sea water and stream water as liquid samples and red pepper, black pepper, and peppermint as solid samples.

2. Experimental

2.1. Apparatus

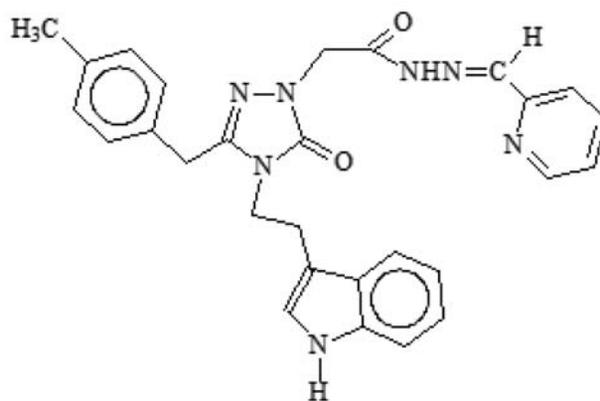
Metal ion concentrations were determined by using a Perkin Elmer AAnalyst400 atomic absorption spectrometer equipped with a 10 cm air/acetylene-burner head, having a deuterium background correction. The settings for all instruments were chosen as recommended in the manufacturer's manuals. Hanna pH-211 digital (HANNA instruments/Romania) pH meter with glass electrode was

used to measure the pH of the solutions. The centrifugation of the solutions was performed using Sigma 3-16P (Sigma Laborzentrifugen GmbH, Germany) centrifuge. The solid samples were digested in Milestones Ethos D (Milestone Inc./Italy) model closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C).

2.2. Reagents and Solutions

All of the chemical reagents were purchased from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland), and all of the solutions were prepared in distilled/deionized water. The standard and working solutions of Co(II), Cu(II) and Ni(II) ions were prepared daily by the dilution of 1000 mg L⁻¹ stock solutions of the given elements purchased from Sigma and Aldrich.

In this study, IMOTPA (Scheme 1), used as a coprecipitating agent, was synthesized in the organic chemistry research laboratory (Karadeniz Technical University, Faculty of Science, Chemistry Department). The detailed information of its synthesis was given in the literature.³⁴ 0.1% (w/v) IMOTPA solution was prepared by dissolving it in dimethyl sulfoxide and ethanol (1:4) mixture. The certified reference material, sandy soil standard (CRM-SA-C Sandy Soil C), was procured from High-Purity Standard Inc.



Scheme 1: Chemical structure of IMOTPA

2.3. Model Studies for Coprecipitation

In the present study three metal ions were investigated simultaneously. For that purpose, firstly a mixture of the metal ion solution consisting of 15 mg L⁻¹ of Co(II), 30 mg L⁻¹ of Cu(II) and 50 mg L⁻¹ of Ni(II) ions was prepared. Then 0.5 mL of this solution was added to 50.0 mL of an aqueous solution. In the present case, the working solution consists of 7.5 µg of Co(II), 15.0 µg of Cu(II) and 25.0 µg of Ni(II) ions. The solution was placed in a centrifuge tube, and the pH of the solutions was adjusted to

6.5 by using diluted HCl and NaOH solutions. Then 1.0 mL of coprecipitating agent (0.1%, w/v) was added. After standing for 10 min, the solution was centrifuged at 3000 rpm for 5 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 1.0 mL of conc. HNO₃. Final volume was completed to 5.0 mL with distilled/deionized water, and then the levels of analyte ions in the final solution were determined by FAAS.

2. 4. Analysis of Real Samples

The solid samples (black pepper, red pepper and peppermint) were microwave digested prior to the application of the present separation and preconcentration procedure. For that purpose, 0.750 g of red pepper, black pepper and peppermint and 0.200 g of CRM-SA-C Sandy Soil C were weighed into Teflon vessels, separately. 6 mL of HNO₃ and 2 mL of H₂O₂ for black pepper, red pepper and peppermint, 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. 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 irradiations the pressure was kept at 45 bars, and the ventilation was 3 min. At the end of the microwave digestion, the sample volume was completed to 50 mL with distilled/deionized water, and then the method was applied.

The present separation and preconcentration procedure was applied to determine the levels of Co(II), Cu(II) and Ni(II) ions in sea water (Black sea, Trabzon/Turkey) and stream water (Şana Stream, Trabzon/Turkey). For that purpose the water samples were filtered through a cellulose membrane filter of 0.45 µm pore size, and after acidification with 1% nitric acid solution, they were stored at 4 °C in a refrigerator in polyethylene bottles. Before the experiments, the pH of the samples was adjusted to 6.5. After addition of the required amount of IMOTPA, the preconcentration procedure given in "Model studies for coprecipitation" section was applied.

3. Results and Discussion

3. 1. Optimization Parameters

Solution pH is one of the most important parameters affecting the quantitative recoveries of the analyte ions. The effects of pH on the recoveries of Co(II), Cu(II) and Ni(II) ions were investigated by varying the pH values in the range of 2.0–10.0 under the optimum conditions. The quantitative recovery values were obtained for the analyte ions in the pH range of 6.0–10.0 (Fig. 1), so further experiments were performed at pH 6.5. Because pH 6.5 is very close to the neutral pH value,

low quantity of reagent is required to maintain the pH which also reduced the contamination risk. The lower amount of reagent use and thus reduced risk of contamination may be considered as one of the advantage of the method.

In order to study the effect of the amount of IMOTPA on the coprecipitation of the analyte ions, the experiments were conducted at six different IMOTPA quantities in the range of 0–3.0 mg under the optimum conditions. A graph of the recovery values of Co(II), Cu(II) and Ni(II) ions versus the amount of IMOTPA was plotted from the obtained data (Fig. 2). The recovery values were below 20% for Co(II) and Ni(II) ions and below 70% for Cu(II) ions when IMOTPA was not added to the solution. The quantitative recovery values were obtained after 1.0 mg (1 mL of 0.1%, w/v) of IMOTPA amount. From the obtained results, it is seen that IMOTPA is necessary for the quanti-

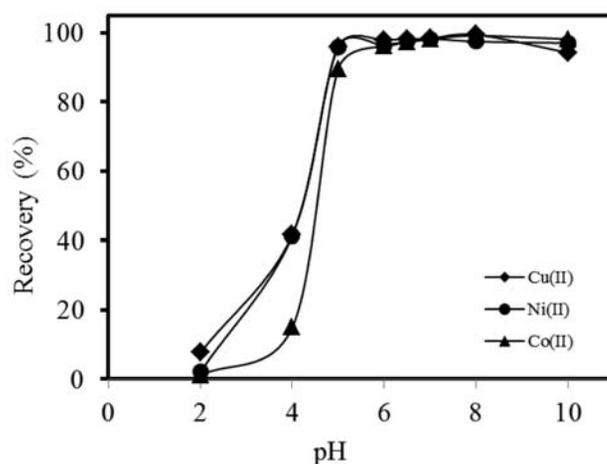


Fig. 1: Effect of pH on the recoveries of analyte ions ($N=3$, sample volume: 50 mL, quantity of IMOTPA: 1.0 mg, standing time: 10 min, centrifugation rate: 3000 rpm, centrifugation time: 5 min)

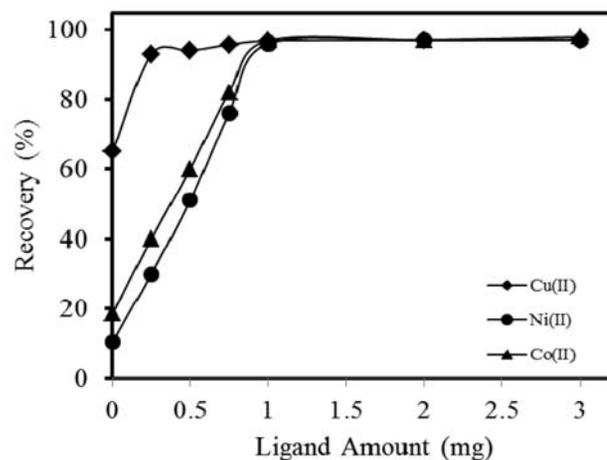


Fig. 2: Effect of IMOTPA amount on the recoveries of analyte ions ($N=3$, sample pH: 6.5, sample volume: 50 mL)

tative and simultaneous recoveries of Co(II), Cu(II) and Ni(II) ions, hence 1.0 mg of IMOTPA was added to the solutions for all subsequent tests.

The effects of standing time and centrifugation time and rate on the recovery of the analyte ions were also investigated because these parameters are the important factors affecting the formation and quality of the precipitate. For that purpose, the presented coprecipitation procedure was also conducted in the standing time range of 1–60 min, centrifugation time range of 5–20 min, and centrifugation rate range of 1000–3500 rpm. For the quantitative and simultaneous recoveries of Co(II), Cu(II) and Ni(II) ions, the optimum standing time and centrifugation time and rate were determined as 10 min, 5 min and 3000 rpm, respectively.

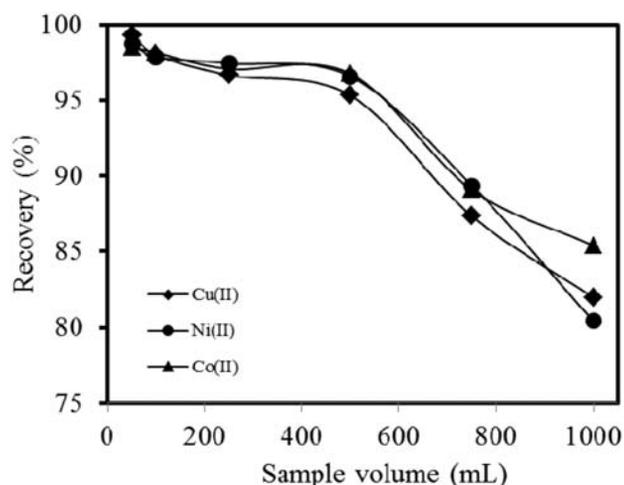


Fig. 3: Effect of sample volumes on the recoveries of analyte ions ($N=3$, sample pH: 6.5)

In order to test the efficiency of the coprecipitation process for the determination of the analyte ions in water samples, the effects of the sample volume were also examined in the sample volume range of 50–1000 mL by using model solutions. The analyte ions were quantitatively recovered in the sample volume ranges of 50–500 mL (Fig. 3). After 500 mL of sample volume, the recoveries decreased considerably so the sample volume was optimized as 500 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 (500 mL) and the lowest final volume (5 mL), and it was found as 100.

3. 2. Influences of Matrix Ions

As mentioned in the introduction section, heavy metal ions may be present together with the interfering matrix ions in environmental real samples. In order to study the effects of various foreign ions on the presented separation and preconcentration procedure, different amounts of each foreign ions, which are the major components of sea and stream water, were added to the model solutions containing 7.5 μg of Co(II), 15.0 μg of Cu(II) and 25.0 μg of Ni(II) ions. As can be seen from Table 1, significant interference effects were not noticed on the coprecipitation of the studied analyte ions in the presence of interfering anions and cations and also transition metal ions at mg L^{-1} levels under the optimum conditions. Consequently, the proposed CEFC method could be applied to the samples containing high amount of salts and some transition metal ions at given concentration levels as in Table 1.

Table 1: Influences of some foreign ions on the recoveries of analyte ions ($N=3$, sample pH: 6.5, sample volume: 50 mL, quantity of IMOTPA: 1.0 mg (1.0 mL 0.1% (w/v)), standing time: 10 min, centrifugation rate: 3000 rpm, centrifugation time: 5 min)

Ions	Added as	Conc. (mg L^{-1})	Recovery (%)		
			Cu(II)	Ni(II)	Co(II)
Na^+	NaCl	5000	97.6 ± 2.4	98.0 ± 3.5	98.0 ± 1.6
K^+	KCl	1000	98.3 ± 0.5	98.9 ± 0.3	99.5 ± 0.1
Ca^{2+}	CaCl_2	1000	101.7 ± 0.5	98.2 ± 1.3	97.5 ± 1.2
Mg^{2+}	$\text{Mg}(\text{NO}_3)_2$	1000	98.3 ± 2.4	96.2 ± 2.2	97.3 ± 0.9
PO_4^{3-}	Na_3PO_4	1000	92.4 ± 3.9	92.9 ± 3.8	94.9 ± 2.7
SO_4^{2-}	Na_2SO_4	1000	93.8 ± 2.0	96.4 ± 0.6	97.0 ± 1.0
CO_3^{2-}	Na_2CO_3	1000	95.2 ± 1.0	93.6 ± 1.6	91.5 ± 0.3
NO_3^-	NaNO_3	5000	96.6 ± 2.0	94.9 ± 1.6	95.5 ± 2.3
I^-	KI	250	97.9 ± 1.0	98.9 ± 2.2	99.6 ± 0.1
NH_4^+	NH_4NO_3	250	95.2 ± 5.9	92.7 ± 4.7	94.2 ± 3.5
F^-	NaF	50	91.7 ± 2.0	91.1 ± 0.6	92.4 ± 0.5
Pb(II), Al(III), Cr(III), V(V), Cd(II), Mn(II)	*	25	96.6 ± 1.0	97.3 ± 3.1	96.4 ± 3.5
Mixed ^a			99.0 ± 4.4	98.4 ± 2.2	95.3 ± 2.4

* V(V) added as V_2O_5 , other ions added as their nitrate salts.

^a 5708 mg L^{-1} Na^+ , 8388 mg L^{-1} Cl^- , 2030 mg L^{-1} NO_3^- , 250 mg L^{-1} K^+ , Ca^{2+} , Mg^{2+} , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , 100 mg L^{-1} I^- , F^- , NH_4^+ , 10 mg L^{-1} Pb(II), Al(III), Cr(III), V(V), Cd(II), Mn(II)

3. 3. Analytical Performance of the Method

The analytical performance of the proposed separation and preconcentration method based on CEFC was evaluated from the results obtained by FAAS measurements. The precision of the method, expressed as relative standard deviation (RSD), was determined after analyzing a series of ten replicate solutions under the optimum conditions mentioned in “*Model studies for coprecipitation*” section, and it was found to be 2.7%, 1.9%, and 2.4% for Co(II), Cu(II) and Ni(II) ions, respectively.

The limit of detection (LOD) for Co(II), Cu(II) and Ni(II) ions calculated as three times the standard deviation of 10 replicate measurements of the blank samples were found to be 0.40, 0.16 and 0.17 $\mu\text{g L}^{-1}$ for Co(II), Cu(II) and Ni(II) ions, respectively.

and peppermint samples. As can be seen from the Tables 2 and 3, a good concordance was obtained between the added and measured analyte amounts, so it can be concluded that the proposed coprecipitation method could be successfully applied for separation and preconcentration of Co(II), Cu(II) and Ni(II) ions from environmental solid and liquid samples.

The CRM-SA-C Sandy Soil C, as a certified reference material, was also used for the method validation. There is a good concordance between the obtained and certified values (Table 4).

The present CEFC method was finally applied to the real solid (red pepper, black pepper and peppermint) and liquid samples (sea and stream water). The results obtained from the real samples are summarized in Table 5.

Table 2: Spiked recoveries of analyte ions from water samples ($N: 3$, sample pH: 6.5, sample volume: 50 mL, quantity of IMOTPA: 1.0 mg, final volume: 5.0 mL)

Element	Added (μg)	Sea water		Stream water	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Cu(II)	0	BDL*		BDL	
	6.0	6.07 ± 0.09	101.2	5.82 ± 0.07	97.0
	12.0	11.95 ± 0.78	99.6	11.80 ± 0.42	98.3
Ni(II)	0	BDL		BDL	
	10.0	9.94 ± 0.09	99.4	9.91 ± 0.06	99.1
	20.0	18.50 ± 0.99	92.5	18.20 ± 0.57	91.0
Co(II)	0	BDL		BDL	
	3.0	2.95 ± 0.05	98.3	2.87 ± 0.06	95.7
	6.0	5.68 ± 0.33	94.7	5.76 ± 0.13	96.0

*Below detection limit

Table 3: Spiked recoveries of analyte ions from solid samples ($N: 3$, sample pH: 6.5, quantity of IMOTPA: 1.0 mg, sample quantities: 0.75 g of red pepper, black pepper and peppermint, final volume: 5.0 mL)

Element	Added (μg)	Red pepper		Black pepper		Peppermint	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Cu(II)	0	9.44 ± 0.06	–	13.00 ± 0.28	–	10.55 ± 0.35	–
	6.0	15.15 ± 1.06	95.2	18.82 ± 0.99	97.0	16.45 ± 0.49	98.3
	12.0	20.65 ± 0.92	93.4	24.43 ± 1.56	95.2	21.7 ± 0.99	93.0
Ni(II)	0	6.12 ± 0.04	–	6.31 ± 0.03	–	3.23 ± 0.01	–
	10.0	15.45 ± 1.91	93.3	16.10 ± 0.42	97.9	12.35 ± 0.21	91.2
	20.0	24.95 ± 2.05	94.1	26.70 ± 0.57	102.0	22.05 ± 0.35	94.1
Co(II)	0	1.24 ± 0.02	–	1.21 ± 0.04	–	1.14 ± 0.02	–
	3.0	4.20 ± 0.03	98.7	4.16 ± 0.10	98.3	3.94 ± 0.09	93.3
	6.0	6.82 ± 0.04	93.0	7.10 ± 0.02	98.2	6.77 ± 0.17	93.8

3. 4. Method Validation and Applications to Real Samples

The spike/recovery tests was used in order to evaluate the accuracy of the presented coprecipitation method for the separation and preconcentration of Co(II), Cu(II) and Ni(II) ions. For this purpose different amounts of Cd(II), Co(II) and Ni(II) ions were spiked in 50 mL of sea and stream water and 0.750 g of red pepper, black pepper

Table 4: Application of the present method to the certified reference material ($N:3$, quantity of Sandy Soil C: 0.200 g, final volume: 5.0 mL)

Element	CRM-SA-C Sandy Soil C	
	Certificated value ($\mu\text{g g}^{-1}$)	Found value ($\mu\text{g g}^{-1}$)
Cu(II)	63.6 ± 4	64.1 ± 1.2
Ni(II)	48.4 ± 3.0	48.0 ± 1.7
Co(II)	12.4 ± 0.6	12.7 ± 0.3

Table 5: Analyte levels in real solid/liquid samples after being applied the presented coprecipitation procedure (N : 3, sample volumes: 500 mL, sample quantities: 0.750 g of red pepper, black pepper and peppermint, final volumes: 5.0 mL)

Element	Liquid samples		Solid samples		
	Sea water ($\mu\text{g L}^{-1}$)	Stream water ($\mu\text{g L}^{-1}$)	Red pepper ($\mu\text{g g}^{-1}$)	Black pepper ($\mu\text{g g}^{-1}$)	Peppermint ($\mu\text{g g}^{-1}$)
Cu(II)	4.80 ± 0.28	29.10 ± 0.71	12.58 ± 0.08	17.33 ± 0.38	14.07 ± 0.47
Ni(II)	6.52 ± 0.08	13.88 ± 0.19	8.16 ± 0.06	8.41 ± 0.04	4.31 ± 0.02
Co(II)	1.75 ± 0.16	6.65 ± 0.07	1.65 ± 0.03	1.61 ± 0.05	1.53 ± 0.03

4. Conclusion

For the accurate and precise determination of Co(II), Cu(II) and Ni(II) ions in environmental solid and liquid samples, a simple, fast, economical and sensitive separation and preconcentration method based on CEFC strategy was proposed. IMOTPA, as an organic coprecipitating agent, provides effective and quantitative separation and preconcentration of Co(II), Cu(II) and Ni(II) ions by collecting the analyte ions simultaneously on itself without needing a carrier element. Therefore, the contamination risk for the analyte ions from a carrier element was eliminated. The proposed CEFC method is also environmentally friendly since this method enables the use of lower amounts of chemicals. 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.^{17,25,31,35–39} The proposed method has high preconcentration factor, low RSD, relatively low LOD values and advantageous neutral working pH value when compared with the other methods reported in Table 6. The method was successfully applied for the determination of Co(II), Cu(II) and Ni(II) ions in environmental solid and liquid samples with a low detection limit and high accuracy and precision.

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Table 6: Comparison of the presented method with some recent studies based on coprecipitation reported in literature

Analytes	Co-precipitating agent	PF	LOD($\mu\text{g L}^{-1}$)	RSD (%)	pH	Ref.
Cu(II), Cd(II)	MEFMAT	50	0.45–1.49	<3.5	6.8	17
Cu(II)	Acetohydrazide derivative	50	0.31	1.6	5	25
Cu(II), Co(II), Pb(II), Cd(II), Fe(III), Cr(III), Mn(II)	CTAB	10	0.22–4.30	<5	10	31
Cu(II), Co(II), Ni(II), Pb(II), Cd(II), Fe(III), Mn(II)	Thulium(III) hydroxide	120	0.10–1.60	–	11	35
Cu(II), Co(II), Ni(II), Pb(II), Cd(II), Fe(III)	Zirconium(IV) hydroxide	25	0.27–2.50	<8	8	36
Cu(II), Co(II), Ni(II), Pb(II), Cd(II), Fe(III), Mn(II)	Samarium hydroxide	50	0.4–24.0	<10	12.2	37
Cu(II), Ni(II), Pb(II), Cd(II), Fe(III), Mn(II), Zn(II)	Co-diethyldithiocarbamate	225	4–64	<7	6	38
Ni(II), Cd(II), Pb(II)	Copper hydroxide	100	2.0–7.0	–	9	39
Cu(II), Co(II), Ni(II)	IMOTPA	100	0.16–0.40	<3	6.5	Current work

PF: Preconcentration Factor; LOD: Limit of detection; RSD: Relative Standard Deviation; CTAB: N-cetyl N,N,N trimethyl ammonium bromide; MEFMAT: 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

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Povzetek

Razvili smo preprost in zelo občutljiv postopek ločbe in predkoncentracije z minimalnim vplivom na okolje. Postopek je osnovan na soobarjanju brezsilnega elementa (CEFC) ionov Co(II), Cu(II) in Ni(II) z uporabo 2–{4–[2–(1H–indol–3–il)etil]–3–(4–metilbenzil)–5–okso–4,5–dihidro–1H–1,2,4–triazol–1–il}–N’–(piridin–2–ilmetiliden) aceto–hidrazida (IMOTPA) kotorganskega obarjalnega reagenta. Koncentracijo ionov analita smo določili s plamensko atomsko absorpcijsko spektrometrijo (FAAS). Meje zaznave za Co(II), Cu(II) in Ni(II) so bile 0,40, 0,16 in 0,17 g L⁻¹, relativni standardni odkloni za te analite pa so bili ni ji od 3,0 %. Za validacijo metode smo izvedli teste z dodatki analita vzorcu ter analize certificiranih referencnih materialov. Metodo smo uspešno uporabili za določitev koncentracije Co(II), Cu(II) in Ni(II) ionov v tekočih vzorcih morske in potočne vode ter v trdnih vzorcih rdeče paprike, črnega popra in poprove mete.