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Research Article

Preconcentration by Coprecipitation of Copper and Nickel with Mo(VI)/Triazole Derivative System and Their Determinations by Flame Atomic Absorption Spectrometry in Food and Water Samples

A new separation and preconcentration technique based on coprecipitation of Cu(II) and Ni(II) ions by the aid of Mo(VI)/di-*tert*-butyl[methylenebis[5-(chlorobenzyl)-4*H*-1,2,4-triazol-3,4-diy]]biscarbamate (BUMECTAC) precipitate has been established. The Mo(VI)/BUMECTAC precipitate was dissolved by concentrated HNO₃ and the solution was completed to 5.0 mL with distilled/deionized water. The levels of the analyte ions were determined by flame atomic absorption spectrometer. The effects of experimental conditions like HNO₃ concentration, amount of BUMECTAC and Mo(VI), sample volume, etc. and also the influences of some foreign ions were investigated in detail on the quantitative recoveries of analyte ions. The preconcentration factors were found to be 40 for Cu(II) and 100 for Ni(II) ions. The detection limits for Cu(II) and Ni(II) ions based on 3σ (N:10) were 0.43 and 0.70 μg L⁻¹, respectively. The relative standard deviations were found to be lower than 4.0% for both analyte ions. The accuracy of the method was checked by spiked/recovery tests and the analysis of two certified reference materials (Environment Canada TM-25.3 and CRM-SA-C Sandy Soil C). The procedure was successfully applied to sea water and stream water as liquid samples and baby food as solid sample in order to determine the levels of Cu(II) and Ni(II) ions.

Keywords: Coprecipitation; Di-*tert*-butyl[methylenebis[5-(chlorobenzyl)-4*H*-1,2,4-triazol-3,4-diy]]biscarbamate; Flame atomic absorption spectrometry; Preconcentration

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1 Introduction

Heavy metals, one of the major sources of pollution, are generally present at trace levels in environmental samples. Although some of them (Fe, Cu, Mn, Zn, and Co, etc.) are essential micronutrients and have a variety of biochemical functions in all living organisms, when taken in excess they can be toxic. Besides a great number of metals like Ni, Pb, and Cd, etc., are non-essential as they are extremely toxic and harmful substances even at low concentrations [1, 2]. Therefore, the determination of heavy metal levels in environmental samples should be one of the most important tasks for analytical chemist in terms of protection of human health.

Due to lower analyte levels than the instrument's limit of detection and high interference effects from the matrix components of the analyzed samples, a separation and preconcentration method is generally required for heavy metal ions at trace levels prior to determination of them by instrumental techniques including

atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) [3, 4]. Several methods including solid phase extraction [5, 6], ion exchange [7], cloud point extraction [8, 9], electrochemical deposition [10], and coprecipitation [11], etc., have been extensively used for separation and preconcentration of heavy metal ions.

The coprecipitation method, which occurs with retention of metal ions at trace levels onto precipitate surface via various mechanisms including surface adsorption, ion exchange, surface precipitation, and occlusion, is one of the most efficient ways for separation and preconcentration of trace elements from the sample matrix [12]. The main advantages of the method are simplicity, short analysis time, high preconcentration factors, and low consumption of organic solvents. Furthermore, several analyte ions can be separated from the matrix simultaneously by using organic and inorganic coprecipitants as efficient collectors of trace metals [13]. Although a wide range of metal hydroxides such as aluminum [14], copper [15], ytterbium [16], indium [17], and terbium [18] can be used as inorganic coprecipitants for preconcentration of trace metal ions; organic coprecipitants like diethyldithiocarbamate [19], pyrrolidine dithiocarbamate [20], 4-methylpiperidinedithiocarbamate [21], chitosan [22], etc., are more recommended.

In the present study, a simple and rapid coprecipitation procedure is proposed for separation and preconcentration of Cu(II) and Ni(II)

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Abbreviations: BUMECTAC, di-*tert*-butyl[methylenebis[5-(chlorobenzyl)-4*H*-1,2,4-triazol-3,4-diy]]biscarbamate; CRM-SA-C, certified reference materials sandy soil C

ions by using an organic coprecipitant di-*tert*-butyl{(methylenebis[5-(chlorobenzyl)-4*H*-1,2,4-triazol-3,4-diyl]]biscarbamate (BUMECTAC), and Mo(VI) ions as carrier element, prior to their flame atomic absorption spectrometric determinations. Some advantages can be given of using BUMECTAC for separation and preconcentration of Cu(II) and Ni(II) ions. Although BUMECTAC, a triazole derivative, is harmful for human health when taken into body via ingestion, inhalation, or skin contact, there are no carcinogenic, mutagenic, and teratogenic effects of it available. According to our literature survey, 1,2,4-triazoles are associated with diverse pharmacological activities such as analgesic, antiasthmatic, diuretic, antibacterial, antifungal, and anti-inflammatory activities [23]. A non-toxic and environmentally friendly organic solvent, ethanol, was used for dissolution of BUMECTAC. As a result of decomposition of BUMECTAC easily by flame and HNO₃, no interferences have been observed from this compound during the flame atomic absorption spectrometry (FAAS) analysis.

The mechanisms of coprecipitation may vary in each case and the coprecipitation of Cu(II) and Ni(II) ions by BUMECTAC may include mainly electrostatic surface adsorption, besides surface precipitation and occlusion.

The experimental conditions including, HNO₃ concentration, quantity of BUMECTAC, standing time, centrifugation rate and time, and sample volume, etc. were evaluated on the quantitative recoveries of Cu(II) and Ni(II) ions. After validation of the method by certified reference materials and spike tests, it was applied to determine Cu(II) and Ni(II) ions in several solid and liquid environmental samples.

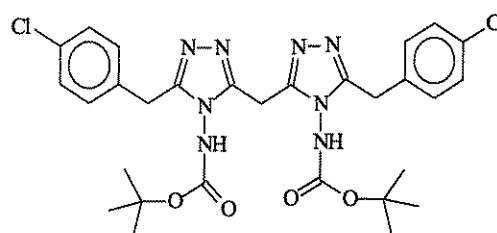
2 Experimental

2.1 Apparatus

The determinations of Cu(II) and Ni(II) ions were performed by using A Unicam model AA-929 Flame Atomic Absorption Spectrometer with an air/acetylene flame. The instrumental parameters were those recommended by the manufacturer. Sigma 3-16P (Sigma Laborzentrifugen GmbH, Germany) model centrifuge was used to centrifuge the solutions. Milestone Ethos D (Milestone Inc., Italy) closed vessel microwave system (maximum pressure 1450 psi and maximum temperature 300°C) was operated for digestion of the solid samples.

2.2 Reagents and solutions

All the chemicals used in this work were analytical grade of Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland), unless otherwise. Distilled/deionized water (Millipore Milli-Q system) was used throughout the experimental work. The single element stock solutions of the metal ions (1000 mg L⁻¹) in 0.5 M HNO₃ were diluted daily for obtaining reference and working solutions. The calibration curve was established using the standard solutions prepared by dilution of stock solutions. The calibration standards were not subjected to the preconcentration procedure. A stock solution of Mo(VI) (2.0 g L⁻¹) was prepared daily by dissolving appropriate amounts of (NH₄)₆Mo₇O₂₄ · 4 H₂O in small amounts of 0.5 M HNO₃ and diluting to 50 mL with distilled/deionized water. BUMECTAC (Scheme 1) used as a coprecipitating agent was recently synthesized as reported elsewhere [24]. For separation and preconcentration experiments, 0.2% w/v BUMECTAC solution was prepared in ethanol. The certified



Scheme 1. Chemical structure of BUMECTAC.

reference materials used in the experimental studies were Environment Canada TM-25.3 and Sandy Soil C (CRM-SA-C).

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.

2.3 Test procedure

The Mo(VI)/BUMECTAC coprecipitation system was tested with model solutions prior to its application to real samples. For that purpose, 25 mL of an aqueous solution containing 25 µg of Cu(II) and Ni(II) ions was placed in a centrifuge tube and 0.5 mL of 2 g L⁻¹ Mo(VI) solution as a carrier element was added to this solution. After addition of a certain amount of 5 M HNO₃ solution to adjust HNO₃ concentration to 0.05 M, 2.5 mL of coprecipitating agent solution (0.2% w/v) were added to the tube. After standing for 30 min, the solution was centrifuged at 3000 rpm for 25 min. The supernatant was removed and 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 content was analyzed by FAAS for determination of analyte ions.

2.4 Analysis of real samples

The developed coprecipitation procedure was applied to various environmental liquid and solid real samples in order to determine their Cu(II) and Ni(II) levels. As standard reference materials; Environment Canada TM-25.3 and CRM-SA-C Sandy Soil C were used. Various amounts of analyte ions were also spiked to solid and liquid real samples.

2.4.1 Analysis of water samples

Twenty-five milliliters of Environment Canada TM-25.3 were taken and the preconcentration procedure given in Section 2.3 was applied to these samples.

The sea water and stream water samples, provided from Blacksea, Trabzon/Turkey and 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 and acidified with HNO₃ and then stored at 4°C in a refrigerator. For determination of Cu(II) ions 200 mL and for Ni(II) ions 500 mL of sea water and stream water samples were taken. Before the analysis, the acidified water samples were neutralized and a certain amount of 5 M HNO₃ solution was added to adjust HNO₃ concentration to 0.05 M. After addition of appropriate amount of

2 g L^{-1} Mo(VI) and 0.2% BUMECTAC, the present coprecipitation 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 Ni(II) ions in the samples were determined by FAAS.

2.4.2 Analysis of solid samples

Baby food was selected as a solid sample in order to decide the applicability of the present coprecipitation method for preconcentration of Cu(II) and Ni(II) ions in real solid samples. And also to test the accuracy of the method for solid samples spike/recovery tests were performed for baby food and a solid standard reference material, CRM-SA-C Sandy Soil C, was used. The solid samples were digested with a closed microwave digestion system. For that purpose 0.5 g of baby food and 0.1 g of CRM-SA-C Sandy Soil C were weighed with a sensitivity of 0.1 mg into Teflon vessels separately. Six milliliters of HNO_3 and 2 mL of H_2O_2 for baby food sample, 4.5 mL of HCl, 1.5 mL of HNO_3 , 1 mL of HF, and 2 mL of H_2O_2 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 25 mL with distilled water. Blanks were prepared in the same way as the sample but omitting the sample. The preconcentration procedure given in Section 2.3 was applied to the samples. The final volume was 5 mL.

3 Results and discussion

3.1 Effect of HNO_3 concentration

Because of the Mo(VI)/BUMECTAC precipitate occurring in acidic medium, the effect of HNO_3 concentration on the recoveries of the analyte ions was evaluated in the HNO_3 concentration range of 0.001–1.0 M. The recoveries of analyte ions were decreased in too acidic medium as a result of increasing the solubilization of precipitate. The quantitative recovery values were obtained for both Cu(II) and Ni(II) ions at 0.05 M of HNO_3 concentration (Fig. 1) so in all the further experiments the HNO_3 concentration of the aqueous solutions was adjusted to 0.05 M.

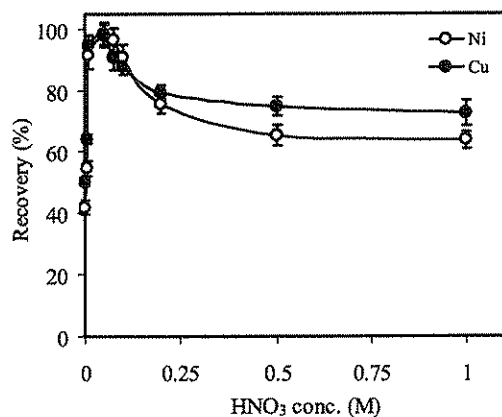


Figure 1. Effect of HNO_3 concentration on the recoveries of analyte ions ($N=3$, sample volume: 25 mL, quantity of BUMECTAC: 2.5 mL (0.2% w/v), quantity of Mo(VI): 0.5 mL (2 g L^{-1}), standing time: 30 min, centrifugation rate: 3000 rpm, centrifugation time: 25 min).

3.2 Effect of ligand amount

The effect of BUMECTAC amount on the recoveries of Cu(II) and Ni(II) ions was examined in the BUMECTAC amount range of 0–6.0 mg (0–3.0 mL, 0.2% w/v) under optimal conditions. The percentage recoveries of analyte ions were negligible (<2%) without adding BUMECTAC (Fig. 2). The results showed that the recoveries of analyte ions increased with increasing amounts of BUMECTAC and reached to quantitative values while using 4.0 mg of BUMECTAC for Cu(II) and 5.0 mg for Ni(II) ions. Hence it can be concluded that for quantitative and simultaneous recoveries of Cu(II) and Ni(II) ions BUMECTAC is necessary. For all subsequent works 5.0 mg (2.5 mL of 0.2% w/v) solution of BUMECTAC was used.

3.3 Effect of amounts of Mo(VI) as carrier element

The effects of amount of Mo(VI), as carrier element, on the recoveries of Cu(II) and Ni(II) ions were also investigated in the Mo(VI) amount range of 0–5.0 mg (0–2.5 mL, 2.0 g L^{-1}). The recoveries were below than 30% without Mo(VI). After addition of Mo(VI) ions, as a result of formation of Mo(VI)/BUMECTAC precipitate, the recovery values for both analyte ions increased until 1.0 mg of Mo(VI) amount and decreased by the addition of excess Mo(VI) (Fig. 3). This results showed that addition of a certain amount of Mo(VI) is necessary for quantitative recoveries of Cu(II) and Ni(II) ions. The decrease in the recoveries of analyte ions may be related with decomposition of the Mo(VI)/BUMECTAC complex with high amount of Mo(VI) ions. Similar results were obtained by Soyak and Erdogan [25] with Copper(II)–rubeanic acid coprecipitation system. In the light of these results, all further works were performed with 1.0 mg (0.5 mL of 2 g L^{-1}) of Mo(VI) ions as carrier element.

3.4 Effect of standing time, centrifugation time, and rate

The effects of standing time were evaluated in the range of 0–40 min by the addition of 1.0 mg of Mo(VI) (0.5 mL of 2 g L^{-1}) and 5 mg of BUMECTAC (2.5 mL of 0.2% w/v) into a series of 25 mL of aqueous solution containing 25 μg of Cu(II) and Ni(II) ions. After 30 min, quantitative recoveries were obtained and hence optimum standing

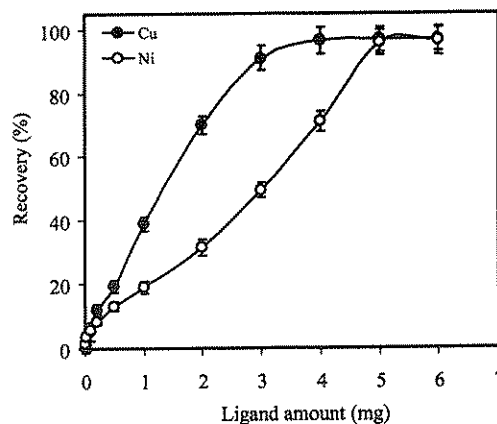


Figure 2. Effect of BUMECTAC amount on the recoveries of analyte ions ($N=3$, HNO_3 conc.: 0.05 M, quantity of Mo(VI): 0.5 mL (2 g L^{-1}), sample volume: 25 mL).

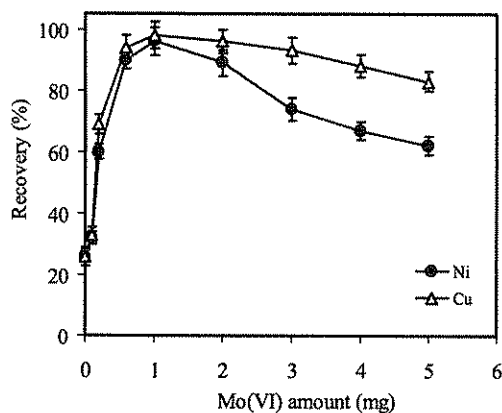


Figure 3. Effect of Mo(VI) amount on the recoveries of analyte ions ($N=3$, HNO_3 conc.: 0.05 M, quantity of BUMECTAC: 2.5 mL (0.2% w/v), sample volume: 25 mL).

time was specified as 30 min for all further experiments. This period was long enough for the formation of Mo(VI)/BUMECTAC precipitant and adsorption of Cu(II) and Ni(II) ions on the precipitant.

The effects of the centrifugation rate on the recoveries of analyte ions were evaluated in the range of 1000–3500 rpm under optimal conditions. The quantitative recoveries were obtained for both Cu(II) and Ni(II) ions at 3000 rpm (Fig. 4). And the effects of centrifugation time were tested in the range of 5–30 min at 3000 rpm. After 25 min, quantitative recoveries were obtained, so all the other works were performed at 3000 rpm for 25 min.

3.5 Effect of sample volume

In order to get a high preconcentration factor in the analysis of real samples, the influences of sample volume on the recoveries of studied metal ions were investigated in the sample volume range of 50–1000 mL containing 25 μg of Cu(II) and Ni(II) ions by using model solutions. While Cu(II) ions were quantitatively recovered in the sample volume range of 50–200 mL, Ni(II) ions were recovered in the range of 50–500 mL (Fig. 5). Hence in the analysis of sea water and

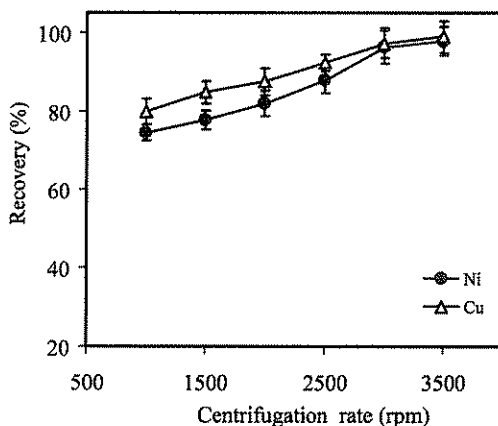


Figure 4. Effect of centrifugation rate on the recoveries of analyte ions ($N=3$, HNO_3 conc.: 0.05 M, quantity of BUMECTAC: 2.5 mL (0.2% w/v), standing time: 30 min, centrifugation time: 25 min).

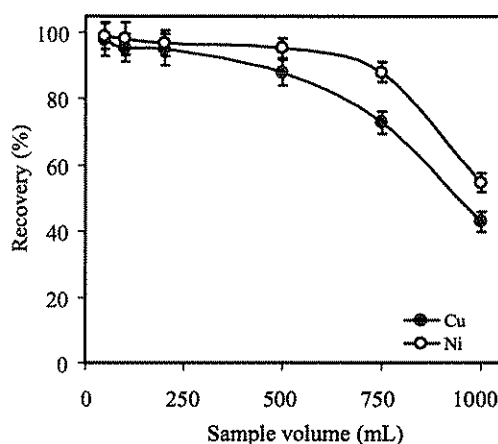


Figure 5. Effect of sample volumes amount on the recoveries of analyte ions ($N=3$, HNO_3 conc.: 0.05 M).

stream water samples, the sample volumes were selected as 200 mL for Cu(II) and 500 mL for Ni(II) ions. The preconcentration factor is calculated by the ratio of the highest sample volume and the lowest final volume, and it was found as 40 for Cu(II) and 100 for Ni(II) ions when the final volume was 5.0 mL.

3.6 Effect of foreign ions

In order to assess the possible analytical application of the recommended separation and preconcentration procedure based on coprecipitation, the effects of foreign ions, which may be present together with Cu(II) and Ni(II) ions in environmental real sample matrix, were evaluated under optimum experimental conditions. For these studies different amounts of each foreign ions were added to the model solutions containing 25 μg of Cu(II) and Ni(II) ions and the presented procedure was applied. In the presence of high concentration levels of interfering ions, the recoveries of analyte ions were quantitative with some exceptions. Also some of the transition metals at mg L^{-1} levels were not interfere on the recoveries of the analyte ions (Tab. 1). In the light of these results it can be concluded that the proposed method can be applied to the samples containing high amount of salts and some transition metal ions at concentration levels given in Tab. 1.

3.7 Analytical performance of the method

The reproducibility of the present method was evaluated by using 25 mL of model solutions containing 25 μg of Cu(II) and Ni(II) ions and the procedure was repeated for 10 times under optimal conditions. The relative standard deviation (RSD) of these determinations were found to be 3.6% for Cu(II) and 3.9% for Ni(II) ions.

In order to determine the instrumental detection limit, the procedure was applied to 25 mL of blank solutions. 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, were found to be $17.2 \mu\text{g L}^{-1}$ for Cu(II) and $70 \mu\text{g L}^{-1}$ for Ni(II) ions. The analytical or method detection limits (LOD) were calculated by dividing the instrumental detection limit by the preconcentration factors (40 for Cu(II) and 100

Table 1. Influences of some foreign ions on the recoveries of analyte ions ($N=3$, HNO_3 conc.: 0.05 M, sample volume: 25 mL, quantity of BUMECTAC: 2.5 mL (0.2% w/v), quantity of Mo(VI): 0.5 mL (2 g L^{-1}), standing time: 30 min, centrifugation rate: 3000 rpm, centrifugation time: 25 min)

Ions	Added as	Conc. (mg L^{-1})	Ni(II) Recovery (%)	Cu(II) Recovery (%)
Na^+	NaCl	5000	93.0 ± 1.7	92.0 ± 3.2
K^+	KCl	1000	90.5 ± 2.1	95.5 ± 2.8
Ca^{2+}	CaCl_2	1000	103.0 ± 1.4	94.2 ± 2.8
Mg^{2+}	$\text{Mg}(\text{NO}_3)_2$	1000	104.3 ± 1.9	96.0 ± 3.1
CO_3^{2-}	Na_2CO_3	1000	99.0 ± 3.3	97.0 ± 2.5
NO_3^-	NaNO_3	1000	102.5 ± 2.1	95.6 ± 0.7
PO_4^{3-}	Na_2PO_4	1000	96.0 ± 1.6	95.5 ± 2.6
SO_4^{2-}	Na_2SO_4	1000	96.0 ± 2.3	96.7 ± 2.4
NH_4^+	NH_4NO_3	1000	99.0 ± 1.2	95.0 ± 1.3
F^-	NaF	1000	103.5 ± 2.8	98.6 ± 2.1
CH_3COO^-	NaCH_3COO	1000	102.9 ± 2.6	99.3 ± 0.8
Al^{3+} , Cd^{2+} , Fe^{3+} , Zn^{2+} , Pb^{2+} , and V^{4+}	a)	25	99.5 ± 2.3	93.0 ± 1.9
Mixed ^{b)}			94.7 ± 0.9	91.4 ± 1.6

^{a)} V^{4+} added as VOSO_4 , other ions added as their nitrate salts.

^{b)} $5990 \text{ mg L}^{-1} \text{Na}^+$, $8390 \text{ mg L}^{-1} \text{Cl}^-$, $2530 \text{ mg L}^{-1} \text{NO}_3^-$, $250 \text{ mg L}^{-1} \text{K}^+$, Ca^{2+} , Mg^{2+} , CO_3^{2-} , PO_4^{3-} , SO_4^{2-} , NH_4^+ , F^- , and CH_3COO^- , $10 \text{ mg L}^{-1} \text{Al}^{3+}$, Cd^{2+} , Fe^{3+} , Zn^{2+} , Pb^{2+} , and V^{4+} .

for Ni(II) ions when final volume was 5.0 mL). The LOD values were found to be $0.43 \text{ } \mu\text{g L}^{-1}$ for Cu(II) and $0.70 \text{ } \mu\text{g L}^{-1}$ for Ni(II) ions.

3.8 Method validation and application to real samples

For the validation of the present coprecipitation method by the spike/recovery tests, different amounts of Cu(II) and Ni(II) ions were

Table 2. Spiked recoveries of analyte ions from water samples ($N=3$, HNO_3 conc.: 0.05 M, sample volume: 50 mL, quantity of BUMECTAC: 5.0 mg, quantity of Mo(VI): 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	–
	15.0	14.1 ± 0.6	94	14.8 ± 0.8	99
	25.0	23.8 ± 1.4	95	24.0 ± 1.0	96
Ni(II)	0	BDL	–	BDL	–
	15.0	13.8 ± 0.4	92	14.2 ± 0.6	95
	25.0	23.5 ± 1.1	94	23.4 ± 0.9	94

BDL, below detection limit.

Table 3. Spiked recoveries of analyte ions from solid sample ($N=3$, HNO_3 conc.: 0.05 M, sample volume: 25 mL, quantity of BUMECTAC: 5.0 mg, quantity of Mo(VI): 1.0 mg, baby food quantity: 0.5 g, final volume: 5.0 mL)

Element	Added (μg)	Baby Food	
		Found (μg)	Recovery (%)
Cu(II)	–	5.2 ± 0.4	–
	5.0	9.8 ± 0.3	92
	20.0	25.7 ± 0.9	102
Ni(II)	–	BDL	–
	5.0	4.8 ± 0.2	96
	20.0	18.8 ± 0.6	94

spiked in 50 mL of sea water, stream water, and 0.5 g of baby food samples and the recommended procedure was applied to these samples. The results were given in Tabs. 2 and 3. A good agreement was obtained between the added and measured analyte amounts. The results showed that the presented coprecipitation method can be applied for separation and preconcentration of Cu(II) and Ni(II) ions from environmental solid and liquid samples.

The standard reference materials (Environment Canada TM-25.3 and CRM-SA-C Sandy Soil C) were also used for the method validation. The obtained results were in good agreement with the certified values (Tab. 4).

The coprecipitation method was applied to the determination of Cu(II) and Ni(II) ions in sea water (Blacksea, Trabzon/Turkey), stream

Table 4. Application of the present method to the standard reference materials ($N=3$, quantity of BUMECTAC: 5.0 mg)

Element	Environment Canada TM-25.3 ^{a)}		CRM-SA-C Sandy Soil ^{b)}	
	Certified value ($\mu\text{g L}^{-1}$)	Found value ($\mu\text{g L}^{-1}$)	Certified value ($\mu\text{g g}^{-1}$)	Found value ($\mu\text{g g}^{-1}$)
Cu(II)	27.6	28.6 ± 1.3	63.6 ± 4.0	66.5 ± 3.2
Ni(II)	15.5	14.9 ± 0.9	48.4 ± 3.0	45.8 ± 2.7

^{a)} Sample volume: 25 mL.

^{b)} Sample quantity: 0.1 g.

Table 5. Analyte levels in real solid/liquid samples after being applied the presented coprecipitation procedure ($N=3$, sample volumes: 200 mL for Cu(II) and 500 mL for Ni(II) ions, baby food quantity: 0.5 g, final volumes: 5.0 mL)

Element	Liquid samples		Solid sample
	Sea water ($\mu\text{g L}^{-1}$)	Stream water ($\mu\text{g L}^{-1}$)	Baby food ($\mu\text{g g}^{-1}$)
Cu(II)	15.8 ± 0.3	11.5 ± 0.5	10.4 ± 0.4
Ni(II)	3.1 ± 0.2	BDL	BDL

Table 6. Comparison of the presented method with some recent studies on separation and preconcentration reported in literature

Technique	Analytes	System	Eluent	PF	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Ref.
Coprecipitation	Au(III), Bi(III), Co(II), Cr(III), Fe(III), Mn(II), Ni(II), Pb(II), Th(IV), and U(VI)	Cu(II)/9-phenyl-3-fluorone	HNO ₃	30	0.05–12.9	0.8–2.7	[3]
Coprecipitation	Cr speciation (Cr(III))	5-Chloro-3-[4-(trifluoromethoxy)phenylimino]indolin-2-one (CFMEPI)	HNO ₃	40	0.7	5	[11]
Coprecipitation	Au(III), Pd(II), and Pb(II)	Ni(II)/5-methyl-4-(2-thiazolyazo)resorcinol	HNO ₃	25	1.5–2.6	<10	[31]
Solid phase extraction	Cr speciation (Cr(VI))	Diethyldithiocarbamate/Amberlite XAD-2010	1 M HNO ₃ in acetone	25	1.28	3	[26]
Solid phase extraction	Mn(II), Co(II), Ni(II), Cu(II), Cd(II), and Pb(II)	Sodium diethyldithiocarbamate/Amberlite XAD-2010	1 M HNO ₃ in acetone	100	0.08–0.26	1.9–5.1	[27]
Solid phase extraction	Co(II), Ni(II), Cu(II), and Cd(II)	Ammonium pyrrolidinedithiocarbamate (APDC)/Amberlite XAD-2000	1 M HNO ₃ in acetone	200	0.07–0.23	<6	[32]
Cloud point extraction	Cr speciation (Cr(III))	Triton X-100/bis-[2-hydroxy-1-naphthaldehyde] thiourea	0.1 M HNO ₃ in methanol	58	0.18	2.3	[28]
Cloud point extraction	Cd(II), Pb(II), Pd(II), and Ag(I)	Triton X-114/bis[(1H-benzo [d]imidazol-2yl)ethyl] sulfane (BIES)	1 M HNO ₃ in methanol	30–48	1.4–2.8 ng mL ⁻¹	2.0–3.6	[29]
Cloud point extraction	Cu(II)	Triton X-114/thiamine	Ethanol/water (1:1)	10	0.29 ng mL ⁻¹	2.12	[30]
Coprecipitation	Ni(II) and Cu(II)	Mo(VI)/di- <i>tert</i> -butyl {methylenebis[5-(chlorobenzyl)-4H-1,2,4-triazol-3,4 diyl]} biscarbamate (BUMECTAC)	HNO ₃	40–100	0.43–0.70	3.6–3.9	This work

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

water (Şana Stream, Trabzon/Turkey), and baby food samples after being verified the accuracy of the method. After applying the preconcentration procedure to the samples, the obtained results were tabulated in Tab. 5.

4 Conclusions

The developed method, based on coprecipitation of Cu(II) and Ni(II) ions by the aid of Mo(VI)/BUMECTAC precipitate, offers a simple, rapid, and low cost separation and preconcentration technique for accurate and precise determination of Cu(II) and Ni(II) ions in environmental solid and liquid samples. The coprecipitated analyte ions can be sensitively determined by AAS without any influence of Mo(VI) and BUMECTAC. The data obtained from present coprecipitation method have been compared with those of recently reported heavy metal separation and preconcentration methods (Tab. 6) [3, 11, 26–32]. The proposed method is primarily superior to those reported methods in literature in terms of no need to consumption of organic solvent. And also the method has high preconcentration factor, low RSD, and relatively low LOD values when compared to the other methods reported in Tab. 6. The presented method was successfully employed for determination of Cu(II) and Ni(II) levels in sea water, stream water, and baby food samples.

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