

## Original article

**Simultaneous separation and preconcentration of Ni(II) and Cu(II) ions by coprecipitation without any carrier element in some food and water samples**Celal Duran,<sup>1\*</sup> Sureyya O. Tumay,<sup>1</sup> Duygu Ozdes,<sup>2</sup> Huseyin Serencam<sup>3\*</sup> & Hakan Bektas<sup>4</sup>

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**Summary** 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 of Ni(II) and Cu(II) ions by using 2-{4-[2-(1H-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl]-N'-(pyrrol-2-ylmethylidene)acetohydrazide (ICOTPA), as an organic coprecipitant. The levels of analyte ions were determined by flame atomic absorption spectrometry. The detection limits for Ni(II) and Cu(II) ions were found to be 0.27 and 0.58  $\mu\text{g L}^{-1}$ , respectively, and the relative standard deviations for the analyte ions were lower than 4.0%. Spike tests and certified reference material analyses were performed to validate the method. The method was successfully applied for the determination of Ni (II) and Cu(II) ions levels in sea and stream water as liquid samples and red lentil and rice as solid samples.

**Keywords** Carrier element-free coprecipitation, flame atomic absorption spectrometry, heavy metals, preconcentration, separation.

**Introduction**

As heavy metal ions accumulate in organisms, they have been considered an eco-toxicological hazard of prime interest with increasing significance. They compete with the nutritional minerals in the body, thus rendering them unavailable to the necessary processes to maintain health. Unfortunately, there are no filtration systems for the food we eat, but we can decrease the amount of toxins we ingest (Divrikli *et al.*, 2006; Tuzen *et al.*, 2009). Both Ni(II) and Cu(II) can be met in various forms and concentrations in effluents of large variety of industries (Mendil *et al.*, 2013; Serencam *et al.*, 2013). While the nutritional values of copper are well known, nickel is known to lack health benefits. Many people can develop allergic reactions to materials containing nickel. In addition to the allergic property of nickel, its carcinogenic effect is also

commonly known (Ozdes *et al.*, 2012a). Main sources of copper pollution are copper mining and smelting, manufacture of copper alloys such as brass, electroplating with copper and its alloys and copper-based chemicals used in agriculture. As arsenic and mercury, copper is known to be the highest relative mammalian toxic species. The link between prolonged inhalations of sprays containing copper and lung cancer among exposed workers is well established (Imamoglu & Gunes, 2008; Senthil Kumar *et al.*, 2011).

Copper and nickel normally occur in the environment at extremely low levels: the need for sensitive and reliable methods to detect them in various environmental and food samples is clear. 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, because this technique is highly selective, versatile, economical and faster than the alternative determination methods (Pourreza & Ghanemi, 2006; Duran *et al.*, 2007; Tuzen & Soylak, 2009; Uluozlu *et al.*, 2010; Rajabi *et al.*, 2013). A preconcentration step

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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 analysed (Bulut *et al.*, 2008). Outstanding effort in various directions has been spent in the last few decades to develop separation and preconcentration procedures such as ion exchange (Kammerer *et al.*, 2011), membrane filtration (Iqbal *et al.*, 2012), solid-phase extraction (Wardencki *et al.*, 2004), coprecipitation (Soylak *et al.*, 2007; Tuzen *et al.*, 2008; Saracoglu *et al.*, 2012), fire assay (Jackson *et al.*, 1990), cloud point extraction (Duran *et al.*, 2012), liquid-liquid extraction (Talebi *et al.*, 2012) and electroanalytical techniques (Jorge *et al.*, 2007) to prepare the samples for the trace element determination process. Because the coprecipitation technique is simple and fast and yields high preconcentration factors, it is commonly used for separation and preconcentration of trace amounts of metals in aqueous solutions (Bulut *et al.*, 2009; Ozdes *et al.*, 2012b). 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 with a suitable organic ligand, such as *N*-cetyl-*N,N,N*-trimethylammonium bromide (Saracoglu & Soylik, 2010), pyrrolidine dithiocarbamate (Atsuya *et al.*, 1991), 3-phenyl-4-*o*-hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazole-5-one (Duran *et al.*, 2009), or inorganic ligand, such as hydroxides (Minami *et al.*, 2005). 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)' (Duran *et al.*, 2009, 2011; Saracoglu & Soylik, 2010; Serencam *et al.*, 2013).

This study is devoted to evaluate the separation and preconcentration conditions of Ni(II) and Cu(II) ions by using 2-[4-[2-(1*H*-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl]-*N'*-(pyrrol-2-ylmethylidene)acetohydrazide (ICOTPA) as an organic coprecipitating agent without using a carrier element prior to its flame atomic absorption spectrometric (FAAS) detections. The influences of various analytical parameters such as pH of the aqueous solution, quantity of ICOTPA, sample volume, standing time, and centrifugation rate and time were investigated on the recovery of the metal ions examined. The method was validated by analysing certified reference material and spike tests. The system was then applied to the preconcentration, matrix separation and determination of Ni(II) and Cu(II) ions in red lentil, rice and water samples.

## Experimental

### Apparatus

Metal ion concentrations were determined using a PerkinElmer<sup>®</sup> AAnalyst<sup>™</sup> 400 atomic absorption spectrometer equipped with a 10-cm air/acetylene-burner head, having a deuterium background correction (PerkinElmer, Inc., Shelton, CT, USA). The pH measurements were taken with a Hanna pH-211 digital pH meter (Sigma Laborzentrifugen GmbH, Milestone Inc., Bucuresti, Romania), equipped with a glass electrode. The solutions were centrifuged using a Sigma 3-16P centrifuge (Sigma-Aldrich Laborzentrifugen GmbH, Osterode am Harz, Germany). The solid samples were digested in a Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C; Milestone Inc., Italy).

### 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/deionised water. The standard and working solutions of the analyte ions were prepared by the dilution of 1000 mg L<sup>-1</sup> stock solutions produced by Sigma-Aldrich Laborzentrifugen GmbH.

ICOTPA (Fig. 1), which was used for the first time for an analytical application in this study, was synthesised according to the procedure provided in the literature (Bektas *et al.*, 2012). A 0.1% (w/v) ICOTPA solution was prepared by dissolving it in dimethyl sulphoxide and ethanol mixture as with the stoichiometric ratio of (1:4). The certified reference material, CRM-SA-C Sandy Soil C standard, was procured from High-Purity Standard Inc. (Charleston, SC, USA).

### Model studies for coprecipitation

In this study, two metal ions were investigated simultaneously. For that purpose, firstly a mixture of the

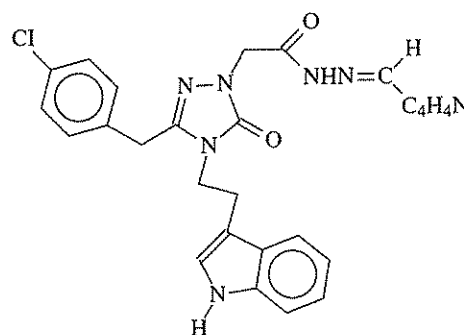


Figure 1 Chemical structure of ICOTPA.

metal ion solution consisting of  $5.0 \mu\text{g L}^{-1}$  of Ni(II) and  $10.0 \mu\text{g L}^{-1}$  of Cu(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  $2.5 \mu\text{g}$  of Ni(II) and  $5.0 \mu\text{g}$  of Cu(II) ions. The solution was placed in a centrifuge tube, and the pH of the solutions was adjusted to 7.5 using diluted HCl and NaOH solutions. Then, 2.0 mL of coprecipitating agent (0.1%, w/v) was added. After standing for 20 min, the solution was centrifuged at 1509g for 5 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 1.0 mL of conc.  $\text{HNO}_3$ . The final solution was brought to 2.0 mL volume with distilled/deionised water, and then the levels of analyte ions were determined by FAAS.

### Analysis of real samples

The present separation and preconcentration procedure was applied to determine the levels of Ni(II) and Cu(II) ions in seawater (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  $0.45 \mu\text{m}$  pore size. After acidification with 1% nitric acid solution, they were stored at  $4^\circ\text{C}$  in a refrigerator in polyethylene bottles. Before the experiments, the pH of the samples was adjusted to 7.5. After addition of the required amount of ICOTPA, the recommended procedure (as pointed out in the 'Model Studies for Coprecipitation' section) was applied.

The solid samples (red lentil and rice) were microwave-digested prior to the application of the present separation and preconcentration procedure. For that purpose, 0.750 g of red lentil and rice and 0.200 g of CRM-SA-C Sandy Soil C were weighed into separate Teflon<sup>®</sup> vessels. Six millilitre of  $\text{HNO}_3$  and 2 mL of  $\text{H}_2\text{O}_2$  for red lentil and rice; 4.5 mL of HCl, 1.5 mL of  $\text{HNO}_3$ , 1 mL of HF and 2 mL of  $\text{H}_2\text{O}_2$  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 these microwave irradiations, the pressure was kept at 45 bars and the ventilation was 3 min (Duran *et al.*, 2007). At the end of the microwave digestion, the sample volume was brought to 50 mL with distilled/deionised water and then the method was applied.

## Results and discussion

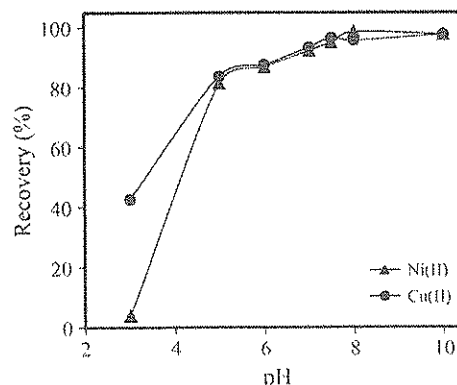
### Optimisation parameters

Studies on the effect of pH for the quantitative recoveries of Ni(II) and Cu(II) ions were carried out as

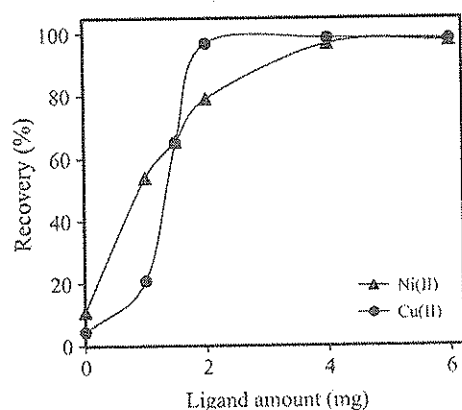
follows. Firstly, the effects of pH on the recoveries of Ni(II) and Cu(II) ions were examined in the solution pH range of 1.0–10.0 under optimum conditions. As it is seen from Fig. 2, the quantitative recovery values (>95%) were obtained for the analyte ions in the pH range of 7.5–10.0, so further experiments were performed at pH 7.5. For subsequent work during this investigation involving general applications, pH 7.5 was chosen as a working medium.

To obtain the impact of the quantity of ICOTPA on the coprecipitation of Ni(II) and Cu(II) ions, the experiments were carried out at different ICOTPA amounts ranging between 0.0 and 6.0 mg [0–3.0 mL, 0.1% (w/v)] under optimum conditions. It has been observed that the recovery yields of the Ni(II) and Cu(II) ions increased with the increase in the quantity of complexing agent, ICOTPA, up to a certain level. The yield of the recoveries for both Ni(II) and Cu(II) ions was not quantitative (below 11%), when ICOTPA was not added to the solution. As shown in Fig. 3, the recovery values increased rapidly with increasing the quantity of ICOTPA, but after reached to optimal quantity of complexing agent [2.0 mg, 2 mL, 0.1% (w/v) of ICOTPA], there was no change in the recovery yields. On this basis, 2.0 mg of ICOTPA was added to the solutions for all subsequent works.

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 5–30 min, centrifugation time range of 5–20 min and centrifugation rate range of 168–2054 g. As can be seen from the Table 1, for the quantitative and simultaneous recoveries of Ni(II) and Cu(II) ions, the optimum standing time and centrifugation time



**Figure 2** Effect of pH on the recovery of Ni(II) and Cu(II) ions ( $N = 3$ , sample pH 8.0, sample volume = 50 mL, final volume = 2.0 mL).



**Figure 3** Effect of ICOTPA amount on the recovery of Ni(II) and Cu(II) ions ( $N = 3$ , pH 8.0).

**Table 1** Effect of standing time, centrifugation rate and time on the recovery of analyte ions ( $N = 3$ , pH 7.5, sample volume = 50 mL, quantity of ICOTPA = 4.0 mg)

	Ni(II) (R, %)	Cu(II) (R, %)
Standing time (min)		
5	88.7 ± 2.0	90.9 ± 1.9
10	98.7 ± 2.3	92.3 ± 1.9
20	99.1 ± 2.3	95.2 ± 2.0
30	99.6 ± 2.3	99.5 ± 2.1
Centrifugation rate (g)		
168	80.0 ± 1.9	80.5 ± 1.7
671	97.0 ± 2.3	93.5 ± 2.0
1509	96.6 ± 2.3	98.1 ± 2.1
2054	99.6 ± 2.3	99.5 ± 2.1
Centrifugation time (min)		
5	95.0 ± 2.3	97.2 ± 2.1
10	97.1 ± 2.3	98.1 ± 2.1
15	99.2 ± 2.4	98.6 ± 2.1
20	99.6 ± 2.4	99.5 ± 2.2

and rate were determined as 20 min, 5 min and 1509 g respectively.

As the concentrations of aforementioned metal ions in real samples are very low, the optimisation 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 was investigated in the sample volume range of 50–1000 mL under optimum conditions. As can be seen from the 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 optimised as 250 mL in the application of the procedure for sea and stream waters. The preconcentration

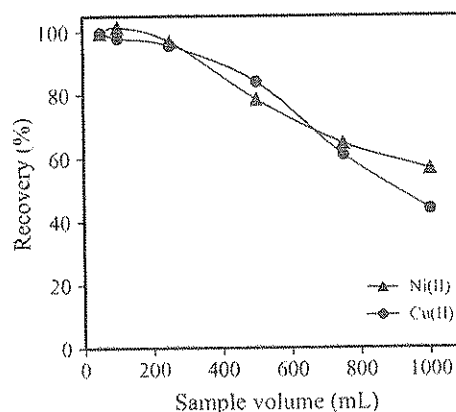
factor was calculated by the ratio of the highest sample volume (250 mL) and the lowest final volume (2 mL), and it was found as 125.

#### Effect of matrix ions

To evaluate the feasibility of the method for water analysis, the effects of some alkali, alkaline earth and transition metal cations and some anions found as major components in natural water samples 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 solutions containing 2.5 µg of Ni(II) and 5.0 µg of Cu(II) ions under the optimal conditions. As seen from Table 2, the existence of several anions and cations, and also transition metal ions at milligram per litre levels, has no notable effect on the separation and preconcentration of Ni(II) and Cu(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.

#### Analytical performance of the method

The precision of the presented CEFC method has been determined by applying the method to ten model solutions under optimum conditions mentioned above. Accordingly, the relative standard deviations (RSD) for 2.5 µg of Ni(II) and 5.0 µg of Cu(II) ions were found to be 2.23% and 3.56%, respectively. The analytical limit of detection (LOD) for analyte ions was calculated as three times the standard deviation of ten replicate measurements of blank samples. The limits of quantification were defined as ten times the standard deviation (s) of the blank ( $n = 10$ ). From the blank



**Figure 4** Effect of sample volumes on the recovery of Ni(II) and Cu(II) ions ( $N = 3$ , pH 8.0).

**Table 2** Influences of some foreign ions on the recoveries of analyte ions ( $N = 3$ , sample pH 7.5, sample volume = 50 mL, quantity of I-COTPA = 4.0 mg, standing time = 20 min, centrifugation rate = 1509 g, centrifugation time = 5 min)

Ions	Added as	Conc. (mg L <sup>-1</sup> )	Recovery (%)	
			Ni(II)	Cu(II)
Na <sup>+</sup>	NaCl	7600	92.0 ± 1.9	92.2 ± 3.5
K <sup>+</sup>	KCl	500	93.6 ± 2.8	103.1 ± 3.1
Ca <sup>2+</sup>	CaCl <sub>2</sub>	250	94.9 ± 0.3	99.3 ± 4.1
Mg <sup>2+</sup>	Mg (NO <sub>3</sub> ) <sub>2</sub>	500	92.5 ± 1.9	99.6 ± 1.9
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	5000	94.7 ± 3.1	102.2 ± 2.5
CO <sub>3</sub> <sup>2-</sup>	Na <sub>2</sub> CO <sub>3</sub>	500	96.2 ± 2.2	103.1 ± 2.5
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	250	93.8 ± 3.8	99.6 ± 3.8
PO <sub>4</sub> <sup>3-</sup>	Na <sub>3</sub> PO <sub>4</sub>	500	94.0 ± 3.4	91.8 ± 0.3
F <sup>-</sup>	NaF	50	92.0 ± 6.9	97.6 ± 2.8
NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> NO <sub>3</sub>	250	96.9 ± 4.4	98.7 ± 1.9
Pb(II), Al(III), Cr(VI), Fe(III), Mn(II)	*	25	91.1 ± 0.6	94.4 ± 1.6
Mixed <sup>†</sup>			96.0 ± 2.1	98.1 ± 3.0

\*Cr(VI) added as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, other ions added as their nitrate salts.

<sup>†</sup>8170 mg L<sup>-1</sup> Na<sup>+</sup>, 12 250 mg L<sup>-1</sup> Cl<sup>-</sup>, 2016 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>, 280 mg L<sup>-1</sup> K<sup>+</sup>, 250 mg L<sup>-1</sup> Ca<sup>2+</sup>, Mg<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, 100 mg L<sup>-1</sup> NH<sub>4</sub><sup>+</sup>, 50 mg L<sup>-1</sup> F<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, 10 mg L<sup>-1</sup> Pb(II), Al(III), Cr(VI), Fe(III) ve Mn(II).

measurements by FAAS, the analytical LOD was found to be 0.27 and 0.58 µg L<sup>-1</sup> and the limit of quantitation (LOQ) was found to be 0.82 and 1.73 µg L<sup>-1</sup> for Ni(II) and Cu(II) ions, respectively, when the sample volume was 250 mL and the final volume was 2.0 mL.

#### Application of the real samples

To demonstrate the accuracy of the proposed separation and preconcentration method, spiked/recovery tests were applied to solid and liquid samples: 0.750 g of red lentil and rice samples, sea water (Black Sea) and stream water (Şana Stream) under optimum conditions. Different amounts Ni(II) and Cu(II) ions were spiked to digested solid samples (Table 3) and liquid samples (Table 4), and then the recommended procedure, as pointed out in 'Model Studies for Coprecipitation' section, was applied to these solutions. The results revealed good congruence between the added and measured analyte amounts. 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 5).

The present CEFC method was finally applied to the real solid (red lentil and rice) and liquid samples (sea and stream water). The results obtained from the real samples are summarised in Table 6.

**Table 3** Spiked recoveries of Ni(II) and Cu(II) ions from solid samples ( $N = 3$ , pH 7.5, final volume = 2.0 mL)

Element	Added (µg)	Red lentil		Rice	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Ni(II)	0	BDL	—	BDL	—
	6.25	6.11 ± 0.10	97.7	5.90 ± 0.25	94.4
	12.5	12.08 ± 0.30	96.6	11.61 ± 0.62	92.8
Cu(II)	0	BDL	—	BDL	—
	6.25	6.39 ± 0.09	102.2	6.29 ± 0.02	100.6
	12.5	12.54 ± 0.03	100.3	11.86 ± 0.60	94.8

BDL, below detection limit.

**Table 4** Spiked recoveries of Ni(II) and Cu(II) ions from water samples ( $N = 3$ , sample pH 7.5, sample volume = 50 mL, final volume = 5.0 mL)

Element	Added (µg)	Sea water		Stream water	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Ni(II)	0	BDL	—	BDL	—
	6.25	6.19 ± 0.02	99.1	6.13 ± 0.04	98.1
	12.50	11.4 ± 0.82	91.1	11.8 ± 0.20	94.6
Cu(II)	0	BDL	—	BDL	—
	6.25	6.35 ± 0.20	101.6	5.66 ± 0.20	94.3
	12.50	11.6 ± 0.12	92.9	11.91 ± 0.45	99.16

BDL, below detection limit.

**Table 5** Application of the present method to the certified reference materials ( $N = 3$ , quantity of CRM-SA-C Sandy Soil C = 0.25 g, final volume = 5.0 mL)

Element	CRM-SA-C Sandy Soil C	
	Certificated value (µg g <sup>-1</sup> )	Found value (µg g <sup>-1</sup> )
Ni(II)	48.4 ± 3.0	46.3 ± 1.8
Cu(II)	63.6 ± 4.0	62.92 ± 4.2

**Table 6** Analyte levels in real solid/liquid samples after being applied the presented coprecipitation procedure ( $N = 3$ , sample volumes = 250 mL, sample quantities = 0.750 g of red lentil and rice, final volumes = 2.0 mL)

Element	Liquid samples (µg L <sup>-1</sup> )			
	Sea water	Stream water	Red lentil	Rice
Ni(II)	1.55 ± 0.06	2.12 ± 0.62	13.67 ± 1.53	7.48 ± 1.20
Cu(II)	13.30 ± 1.27	11.40 ± 0.84	7.55 ± 1.24	23.93 ± 1.28

## Conclusions

An accurate and precise preconcentration/matrix separation approach to assist in the measurement of low levels of Ni(II) and Cu(II) ions in red lentil and rice, and sea and stream water samples based on the CEFC method was investigated. The proposed method has the following advantages: simple, rapid and low analysis cost. The validity of the method is performed by the control analyses of standard reference material. The proposed CEFC method does not work well, if the reactants have very different solubility as well as different precipitate rate. ICOTPA, an organic coprecipitating agent (2-{4-[2-(1H-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl]-N'-(pyrrol-2-ylmethylidene)acetohydrazide), and allows effective and selective separation and preconcentration of Ni(II) and Cu(II) ions by collecting the analyte ion on itself without using a carrier element. Contamination risk for the analyte ions from a carrier element was therefore eliminated. The experiments have shown that the method is relatively free from interference of various foreign ions at allowable levels. The proposed method has high preconcentration factor, low RSD and relatively low LOD when compared to other methods reported in the literature (Saracoglu *et al.*, 2003; Soylak *et al.*, 2008; Citak *et al.*, 2009; Soylak & Aydin, 2011). In the light of the obtained results, it can be concluded that the recommended CEFC procedure could be successfully applied to routine determination of Ni(II) and Cu(II) ions level in food and water samples with acceptable accuracy, low detection limits and high precision.

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