

## Determination of Traces of Ni, Cu, and Zn in Wastewater and Alloy Samples by Flame-AAS after Ionic Liquid-Based Dispersive Liquid Phase Microextraction

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A procedure has been developed for simultaneous separation/preconcentration of copper, nickel, and zinc based on *in situ* ionic liquid-based dispersive liquid-liquid microextraction method as a prior step to their determination by flame atomic absorption spectrometry. The analytes reacted with sodium diethyl dithiocarbamate at pH 7 to form hydrophobic chelates, which were separated and preconcentrated in the ionic liquid phase. The method is fast, simple, accurate, and environmentally friendly. The parameters affecting the extraction efficiency of the proposed method such as the pH of sample solution, centrifugation time, type and volume of the dispersive solvent, and the salt effect were studied. Enrichment factors of 61.8, 61.2, and 40.0 and detection limits of 0.79, 0.93, and 0.71  $\mu\text{g L}^{-1}$  were obtained for copper, nickel, and zinc, respectively. The relative standard deviations based on six replicate measurements were between 1.0 and 2.7%. The method was successfully applied to the extraction and determination of these metals in wastewater and alloy samples.

**Keywords:** dispersive liquid-liquid microextraction, nickel, zinc, copper, ionic liquid, sodium diethyl dithiocarbamate

### Introduction

In the priority list of Agency for Toxic Substances and Disease Registry (ATSDR), Ni is at rank 57, Zn at 75, and Cu at 118.<sup>1</sup> Nickel is essential for many biological activities such as activation of some enzymes and enhancement of insulin activity.<sup>2</sup> Copper plays important roles in metabolism, including antioxidant effects, energy generation and incorporation of Fe into hemoglobin.<sup>3</sup> Zinc also has an important role in various biological systems, such as gene expression, protein-protein interaction, and neurotransmission.<sup>4</sup> Although nickel, copper, and zinc come into the category of essential trace elements, when they are taken at high levels, they can also produce toxic effects.<sup>5-8</sup> Thus, determination and monitoring of these toxic metals in industrial effluent, biological samples and food stuff are of prime concern.

The trace elements level in samples to be analyzed are sometimes lower than the detection limit of analytical instruments such as flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectrometry (ICP OES) and graphite furnace-atomic absorption spectrometry (GF-AAS).<sup>9,10</sup> Therefore, a suitable sample pretreatment step is a required step prior to the analysis. Several techniques including solid phase extraction,<sup>11,12</sup> liquid-liquid extraction,<sup>13-16</sup> cloud point extraction,<sup>17-19</sup> and co-precipitation<sup>20,21</sup> have been employed to solve this issue. Most of these techniques suffer from limitations that limit their application. Some examples of these limitations include significant chemical additives, solvent losses, large secondary wastes, unsatisfactory enrichment factors, complex equipment, and high time consumption.

Dispersive liquid-liquid microextraction (DLLME) overcomes some of the drawbacks of old sample preparation techniques.<sup>22-24</sup> It is simple, fast, and does not require large amounts of organic solvents.<sup>25,26</sup> Up to now, the original

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DLLME has undergone a number of modifications, including the use of ionic liquids (ILs) as suitable extraction solvents.<sup>27</sup> Within the use of ILs, a novel methodology called *in situ* IL formation dispersive liquid-liquid microextraction (*in situ* IL-DLLME) has recently been developed.<sup>28,29</sup> *In situ* IL-DLLME is based on the formation of a water-immiscible IL using a metathesis reaction between a water-miscible IL and anion exchange salt into sample solution. As a consequence, the hydrophilic IL is transformed to a hydrophobic IL which can act as an extraction phase. In the other words, hydrophobic IL is generated *in situ* in form of homogeneously dispersed fine drops, which generally leads to increase the extraction efficiency.

In this work, we employed *in situ* IL-DLLME as a sample preparation technique for simultaneous determination of copper, nickel, and zinc in alloy and water samples. Analysis was executed by FAAS. Effects of various experimental factors on the extraction recoveries were studied.

## Experimental

### Instrumentation

A Varian model SpectrAA-220 flame-atomic absorption spectrometer (Varian, Palo Alto, CA, USA), equipped with a deuterium background correction and air-acetylene flame was used for the analysis. The instrumental parameter was adjusted as recommended by the manufacturer. A copper, nickel, and zinc hollow cathode lamps operating at 10 mA were utilized as the radiation source.

The pH values were controlled with a Metrohm 691 pH-meter (Metrohm, Herisau, Switzerland) supplied with a glass-combined electrode. The phase separation was conducted with a centrifuge instrument (Heraeus centrifuge, Sepatech, Osterode, Germany).

### Reagents and solutions

All reagents used were of analytical reagent grade. Double-distilled water was used through the study. Zinc(II), copper(II), and nickel(II) stock standard solutions of 1000.0 mg L<sup>-1</sup> were purchased from Merck (Darmstadt, Germany). All working standard solutions were prepared daily by appropriate diluting the stock solution. Methanol, ethanol, acetone, NaCl, HNO<sub>3</sub>, HCl, HF, and H<sub>2</sub>O<sub>2</sub> 30% were also obtained from Merck. The solutions of the chelating agent were prepared daily by dissolving appropriate amounts of Na-DDTC (Hopkin & Williams Ltd., Chadwell Heath, Essex, UK) in doubly-distilled water. 1-Butyl-3-methyl imidazolium chloride ([BMIM][Cl])

was synthesized in our laboratory by a literature procedure<sup>30</sup> and the purity of RTILs was checked by <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra. Sodium hexafluorophosphate (NaPF<sub>6</sub>) was purchased from ACROS (Geel, Belgium). For the pH adjustment, buffer solution (Titrisol, Merck, Darmstadt, Germany) have been used. Pipettes and vessels used for trace analysis were stored in 10% nitric acid of Merck for at least 24 h and washed four times with double-distilled water before use.

### Dispersive liquid-liquid microextraction procedure

Aliquots of 10.0 mL of the solutions containing Ni<sup>II</sup>, Cu<sup>II</sup>, and Zn<sup>II</sup> were adjusted to pH 7.0 by adding 2 mL buffer solution and then transferred to screw cap glass test tubes (15.0 mL) with conic bottoms. To this solution 0.5 mL DDTC 1% and 0.3 g NaPF<sub>6</sub> were added and the mixture was gently shaken for about 2 min. Then, 0.5 mL methanol (dispersive solvent) containing 0.13 g [BMIM][Cl] (extraction solvent) was injected rapidly into the sample solution with the aid of a 2.0 mL glass syringe. At this stage, the metal-DDTC complex was extracted into fine droplets of [BMIM][PF<sub>6</sub>]. The obtained cloudy solution was centrifuged for 5 min at 5000 rpm. The upper aqueous phase was removed with a syringe and the formed IL-phase was mixed with 500 μL of methanol, and the concentration of the elements was then determined by FAAS.

The enrichment factor (EF) and extraction recovery (ER) of analytes were used to evaluate the extraction efficiency and calculated by the following equations:

$$EF = \frac{C_{IL}}{C_0} \quad (1)$$

$$ER = \frac{C_{IL}V_{IL}}{C_0V_{aq}} \times 100\% \quad (2)$$

where C<sub>IL</sub> and C<sub>0</sub> are concentration of analyte in the ionic liquid phase and in the aqueous samples before extraction, respectively. V<sub>IL</sub> and V<sub>aq</sub> are volume of ionic liquid phase and aqueous phase, respectively.

### Industrial wastewaters and alloy samples analysis

Two different samples were analyzed by the proposed procedure to evaluate its applicability. Wastewaters and alloys were collected from petrochemical company in Mahshahr, Iran. The water samples were firstly filtered through a 0.45 μm filter. 0.05 g of iron based alloy sample was heated over a hot plate in the glass beaker containing 10-15 mL *aqua regia* to dryness. After that, the residual

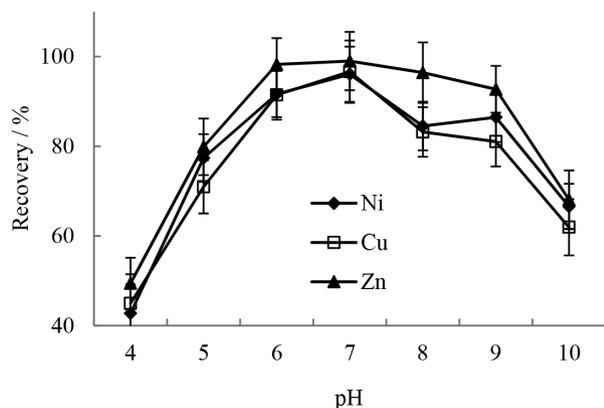
was dissolved and diluted with deionized water. 0.05 g of titanium based alloy sample was also heated on a hot plate in the glass beaker containing mixture of 5 mL *aqua regia* and 2 mL  $\text{H}_2\text{O}_2$ . Then, 5 mL of HF was added to it and diluted with deionized water.

## Results and Discussion

To obtain high extraction efficiency, it is necessary to investigate the effect of all parameters that may influence the performance of *in situ* IL-DLLME. The experimental parameters studied in this work include DDTC concentration, sample pH value, amounts of [BMIM][Cl] and  $\text{NaPF}_6$ , nature and volume of the dispersive solvent, centrifugation parameters, and ionic strength.

### Effect of pH

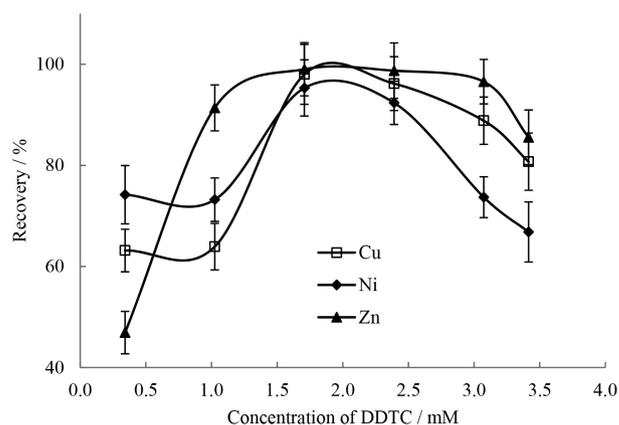
pH is one of the most important factors that affects almost all of the chemical processes. In this work, pH can affect the formation of the complexes and their subsequent extraction into organic phase.<sup>31</sup> The effect of pH of the solution on the extraction of metal-DDTC complex was studied by varying the pH within the range 4.0-10.0. Acidic media was not studied because DDTC is unstable in acidic media and rapidly decomposes to diethyl amine and carbon disulfide.<sup>32</sup> The results illustrated in Figure 1 reveal that at low and high pH levels, the studied metal ions are less likely to be extracted. The progressive decreases in extraction at  $\text{pH} < 7.0$  might be due to the competition of the proton with the analytes for the reaction with DDTC.<sup>22</sup> On the other hand, reduction in the response at higher pH values could be due to the hydroxide formation of metal ions under alkaline conditions. pH 7 seems to be a proper choice and thus, this pH was used for further studies. A 0.2 mol  $\text{L}^{-1}$  phosphate buffer solution was used for pH adjustment.



**Figure 1.** Effect of pH on the extraction efficiency of analytes by *in situ* IL-DLLME. Extraction conditions: analytes 100  $\mu\text{g L}^{-1}$ ; DDTC 0.5 mL; [BMIM][Cl] 0.13 g;  $\text{NaPF}_6$  0.3 g; methanol 1.0 mL

### Effect of DDTC concentration

The efficiency of analyte extraction is dependent on the quantitative formation of the complex between ligand and analytes. Thus, the influence of DDTC amount on extraction efficiencies was investigated in the range of 0.3-3 mM of ligand. The results, depicted in Figure 2, showed that recovery of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  were increased with the increase of DDTC amount from 0.3 to 1.7 mM. Based upon the results, the amount of 1.7 mM was chosen as optimum for further study.

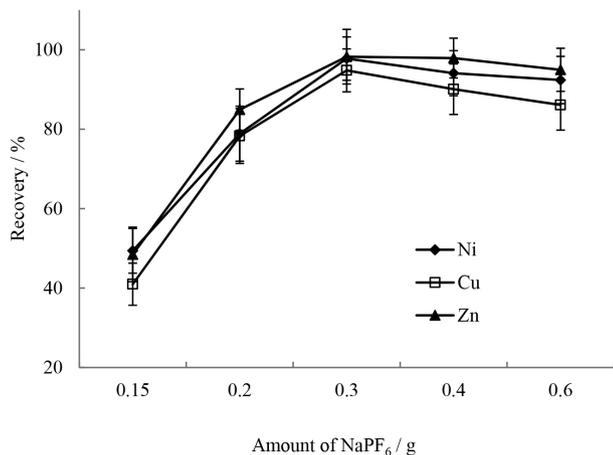


**Figure 2.** Effect of concentration of DDTC on the extraction of analytes by *in situ* IL-DLLME. Extraction conditions: analytes 100  $\mu\text{g L}^{-1}$ ; pH 7.0; [BMIM][Cl] 0.13 g;  $\text{NaPF}_6$  0.3 g; methanol 1.0 mL.

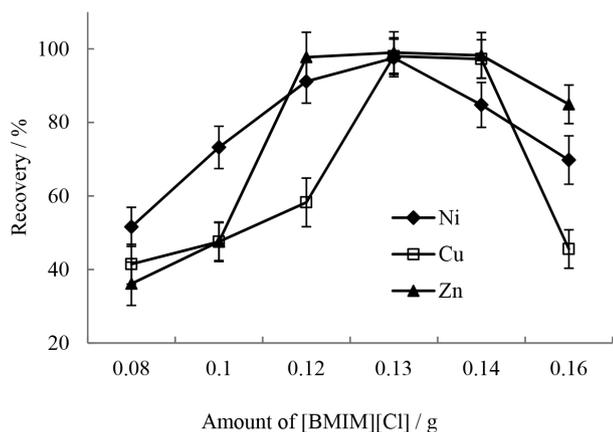
### Effect of amount of [BMIM][Cl] and $\text{NaPF}_6$

The influence of  $\text{NaPF}_6$  amount was investigated in the range of 0.15-0.6 g in the presence of 0.13 g [HMIM][Cl] and the results are presented in Figure 3. As can be seen, recovery of the metal ions increased with increasing the amount of  $\text{NaPF}_6$  up to 0.3 g and then remained nearly constant.

By adding  $\text{NaPF}_6$ , [BMIM][ $\text{PF}_6$ ] was formed. According to the common ion effect, the addition of  $\text{PF}_6^-$  would reduce the solubility of [BMIM][ $\text{PF}_6$ ] and consequently increase the extraction recovery.<sup>28</sup> The effect of [BMIM][Cl] amount was also studied in the range of 0.08-0.16 g in the presence of 0.3 g  $\text{NaPF}_6$  (Figure 4). The solutions containing different volumes of IL were subjected to the proposed procedure, while the other factors were constant. The recovery values increased by increasing the amount of [BMIM][Cl] due to the common ion effect and also increased in the sedimented phase volume. At lower amount of [BMIM][Cl], recovery of all analytes were greatly decreased. This can be explained by incomplete extraction into small [BMIM][Cl] drop. Thus, 0.13 g [BMIM][Cl] and 0.3 g  $\text{NaPF}_6$  was selected for this work.



**Figure 3.** Effect of NaPF<sub>6</sub> amount on the recovery of analytes. Extraction conditions: analytes 100 µg L<sup>-1</sup>; DDTC 0.5 mL; [BMIM][Cl] 0.13 g; pH 7.0; methanol 1.0 mL.

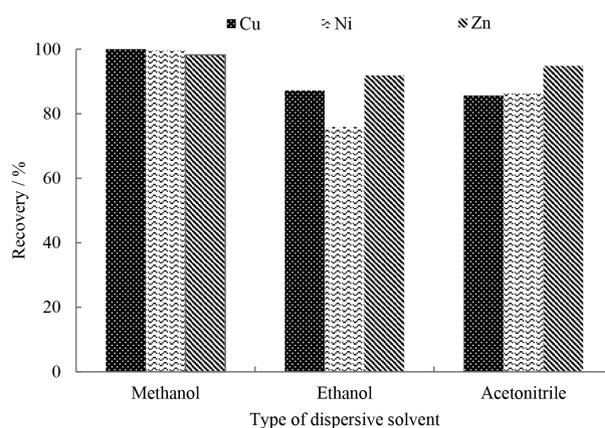


**Figure 4.** Effect of [BMIM][Cl] amount on the recovery of analytes. Extraction conditions: analytes 100 µg L<sup>-1</sup>; DDTC 0.5 mL; pH 7.0; NaPF<sub>6</sub> 0.3 g; methanol 1.0 mL.

#### Effect of type and volume of the dispersive solvent

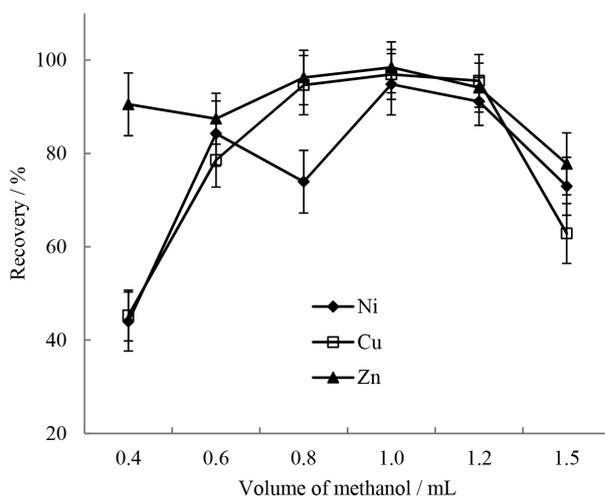
The main criterion for choosing a dispersive solvent is its miscibility in the organic phase and aqueous sample. For the sake of acquiring the most suitable dispersive solvent, three kinds of dispersive solvents including methanol, acetone, and ethanol were tested. A series of experiments was conducted in which 1.0 mL of different kinds of dispersive solvent was used and results were depicted in Figure 5.

It can be seen in Figure 5 that methanol was the most suitable dispersive solvent as it could give the highest recovery for the target analytes. So, methanol was selected as dispersive solvent for subsequent experiments. The effect of the volume of methanol as disperser solvent was examined on the recovery of Zn<sup>II</sup>, Cu<sup>II</sup>, and Ni<sup>II</sup>. The volume of methanol was changed over the range of 0.4-1.5 mL. As can be seen in Figure 6, the extraction efficiency first



**Figure 5.** Effect of type of dispersive solvent on the extraction efficiency of Cu<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>. Extraction conditions: analytes 100 µg L<sup>-1</sup>; DDTC 0.5 mL; [BMIM][Cl] 0.13 g; NaPF<sub>6</sub> 0.3 g; pH 7.0; dispersive solvent 1.0 mL.

increased and then decreased with increasing volume of methanol. It should be mentioned that at lower amounts of methanol, the cloudy solution was not completely formed, and hence the extraction recoveries of the analytes were relatively low. On the other hand, by increasing the volume of dispersive solvent the solubility of [HMIM][PF<sub>6</sub>] in the aqueous solution increased and the extraction recoveries decreased. Thereby, 1.0 mL methanol was chosen in the following works.

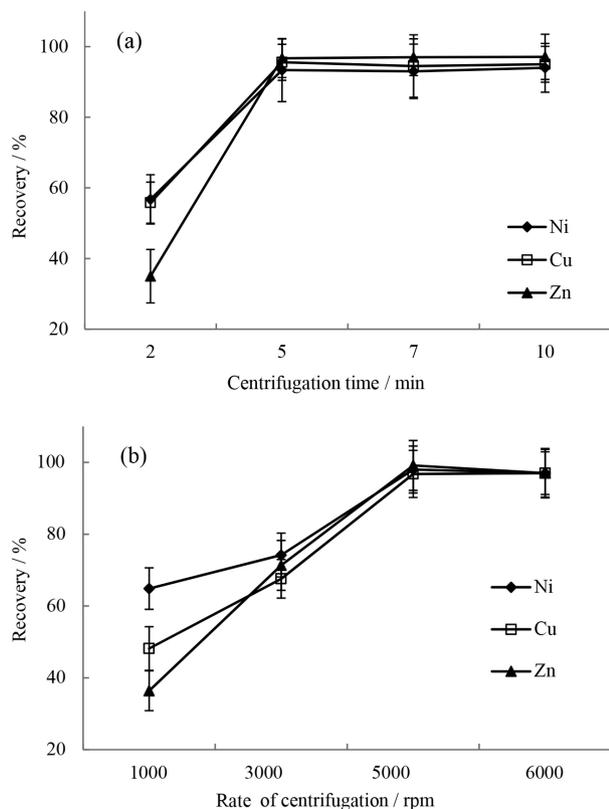


**Figure 6.** Effect of volume of dispersive solvent on the extraction efficiency of the metal ions. Extraction conditions: analytes 100 µg L<sup>-1</sup>; DDTC 0.5 mL; [BMIM][Cl] 0.13 g; NaPF<sub>6</sub> 0.3 g; pH 7.0.

#### Effect of centrifugal time

It is well known that in DLLME process, centrifugal time affects the volume of the settled phase and the concentration of analyte in the extraction phase.<sup>33</sup> In this regard, a set of similar experiments were conducted and the effect of centrifugal time was studied in the range of

2-10 min under the centrifugal speed of 5000 rpm. As shown in Figure 7a, the extraction recoveries of the three analytes increase when the centrifugal time increases to 5 min, and decrease slightly after that. Therefore, 5 min was selected as the optimal centrifugation time. The effect of centrifugation rate on the recovery of analytes was also studied in the range of 1000-5000 rpm. It was observed that centrifuging the cloudy mixture for 5 min at 5000 rpm results in an efficient and suitable phase separation (Figure 7b).



**Figure 7.** Effect of (a) time and (b) rate of centrifugation on the extraction efficiencies of analytes. Extraction conditions: analytes  $100 \mu\text{g L}^{-1}$ ; DDTC 0.5 mL; [BMIM][Cl] 0.13 g; NaPF<sub>6</sub> 0.3 g; methanol 1.0 mL; pH 7.0.

#### Effect of ionic strength

The influence of ionic strength on the extraction efficiency has been investigated universally in extraction and microextraction techniques. The increase of ionic strength often improves the extraction efficiency due to the salting out effect. However, the addition of salt had different effects when ionic liquids were used as the extraction solvent.<sup>33-35</sup> To study the salt addition, various experiments by adding different NaCl concentrations ( $0.0-1.0 \text{ mol L}^{-1}$ ) were performed. The volume of extraction phase was decreased by the addition of salt due to the increase in the solubility of the ionic liquid in water. The extraction recoveries of

analytes decrease with increase of NaCl. Therefore, further extractions were performed without any salt addition.

#### Effect of other ions

In the present study, DDTC was used in the sample solution as a complexing agent for Zn<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> ions. It can also react with other metal ions to form corresponding complexes and may interfere in extraction of the analytes. Thus, the influence of various co-existing ions in the water samples on the recoveries of the investigated metal ions was studied. The tolerance limit is defined as the largest amount of interfering ions causing a relative error  $\leq 5\%$  related to the preconcentration and determination of copper(II), nickel(II), and zinc(II). These tolerance limits for diverse ions are given in Table 1. From the results it was found that the method is fairly selective.

**Table 1.** Tolerance limits of interfering ions in the determination of  $100 \mu\text{g L}^{-1}$  of analytes

Ions	Mole ratio (ion / analytes)
Li <sup>I</sup> , K <sup>I</sup> , Na <sup>I</sup>	500
Ba <sup>II</sup> , Ca <sup>II</sup> , Mg <sup>II</sup>	250
Mo <sup>II</sup> , Mn <sup>II</sup>	100
Co <sup>II</sup> , Pb <sup>II</sup> , Cd <sup>II</sup>	10
Fe <sup>II</sup> , Cr <sup>III</sup>	5

#### Analytical figures of merit

To evaluate the proposed IL-DLLME method, the figures of merit of this method including linear range, reproducibility and limits of detection (LODs) were investigated under the optimized conditions. Linearity was observed in the range of  $4-180 \mu\text{g L}^{-1}$  for zinc, nickel, and copper with good correlation coefficient ( $r^2$ ) ranged from 0.994 to 0.995. The equations of calibration curves were  $y = 4.36 \times 10^{-4}x + 1.86 \times 10^{-2}$ ,  $y = 2.93 \times 10^{-4}x + 1.12 \times 10^{-2}$ , and  $y = 1.05 \times 10^{-3}x + 4.10 \times 10^{-2}$  for Cu<sup>II</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup>, respectively. Note that in these equations, y refers to absorbance unit and x is the concentration of analyte in  $\mu\text{g L}^{-1}$ . Limits of detection (LODs) based on 3 times of the standard deviation of the blank ( $3S_b$ ) under optimal experimental conditions were 0.79, 0.93,  $0.71 \mu\text{g L}^{-1}$  for Cu<sup>II</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup>, respectively. Limits of quantification (LOQs) based on 10 times of the standard deviation of the blank ( $10S_b$ ), were calculated as 2.63, 3.10, and  $2.37 \mu\text{g L}^{-1}$  for Cu<sup>II</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup>, respectively. The relative standard deviation (RSD) for 6 replicate measurements at  $40.0 \mu\text{g L}^{-1}$ , were 1.9, 2.7, 1.0% for Cu<sup>II</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup>, respectively. Enrichment factor for each analyte was calculated by equation 1. It

should be noted that the concentration of the analyte in the IL phase was calculated from the absorbance value recorded after extraction step and by using the calibration graph of the analyte in the aqueous phase (before extraction). The enrichment factors were found to be 61.2 for nickel, 61.8 for copper, and 40.0 for zinc.

#### Industrial wastewaters and alloy samples analysis

The practical applicability of the proposed method was evaluated by extracting the studied metal ions from wastewater and alloy samples.

Each sample was spiked with target species at different concentration levels and analyzed in triplicate using the proposed *in situ* IL-DLLME procedure. Analytical results and the recoveries were shown in Tables 2 and 3. Good agreements between the added and recovered analytes are observed in the results of Tables 2 and 3.

#### Comparison with other methods

Extraction and determination of the studied metal ions in wastewater and alloy samples by the proposed method was compared with other methods<sup>36-45</sup> and the results are shown in Table 4. It can be seen from Table 4 that extraction

time in the *in situ* IL-DLLME procedure is very short and only 7 min are needed before instrumental analysis. The present technique also provides good enrichment factor. From Table 4, it was found that *in situ* IL-DLLME procedure is a suitable procedure to simultaneous extraction and preconcentration of several analytes.

## Conclusions

It has been demonstrated that the *in situ* IL-DLLME method can be used for simultaneous separation and enrichment of copper, nickel, and zinc as DDTC complex. The obtained results showed that the method can be employed for preconcentration and determination of analytes by FAAS in wastewater and alloy samples. With using the *in situ* metathesis ionic liquid formation, the amount of the organic (ionic liquid) phase was minimized and the enrichment factor of the microextraction technique was improved. Low limit of detections and good precisions were also obtained for analytes.

## Acknowledgment

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**Table 2.** Determination of the analytes in petrochemical wastewater samples

Wastewater sample	Added / ( $\mu\text{g L}^{-1}$ )	$\text{Cu}^{\text{II}}$		$\text{Ni}^{\text{II}}$		$\text{Zn}^{\text{II}}$	
		Found <sup>a</sup> / ( $\mu\text{g L}^{-1}$ )	Recovery / %	Found <sup>a</sup> / ( $\mu\text{g L}^{-1}$ )	Recovery / %	Found <sup>a</sup> / ( $\mu\text{g L}^{-1}$ )	Recovery / %
1	0	< 0.79 <sup>b</sup>	–	6	–	58	–
	20	19.2 ± 0.3	96	24.7 ± 0.8	95	72.6 ± 2.1	93.1
	50	48.1 ± 0.9	96.2	57.3 ± 2.1	105.4	112.5 ± 1.3	105.5
2	0	10	–	35	–	64	–
	20	28.2 ± 0.9	93.9	59.3 ± 1.1	107.7	80.0 ± 2.2	95.2
	50	56.8 ± 1.2	94.7	89.7 ± 1.5	105.5	108.1 ± 2.1	94.8

<sup>a</sup>mean ± standard deviation (n = 3); <sup>b</sup>lower than limit of detection (LOD).

**Table 3.** Determination of the analytes in alloy samples

Alloy sample	Added / $\mu\text{g}$	$\text{Cu}^{\text{II}}$		$\text{Ni}^{\text{II}}$		$\text{Zn}^{\text{II}}$	
		Recovery / %	Found <sup>a</sup> / ( $\mu\text{g g}^{-1}$ )	Recovery / %	Found <sup>a</sup> / ( $\mu\text{g g}^{-1}$ )	Recovery / %	Found <sup>a</sup> / ( $\mu\text{g g}^{-1}$ )
1 Composition: 56%Fe, 26%Cr, 10%Ni, 2.5%Mo	0	46	–	–	–	< LOD (1.42) <sup>b</sup>	–
	2	84.6 ± 1.4	98.3	–	–	37.8 ± 1.4	94.5
	4	116.8 ± 1.0	92.7	–	–	73.6 ± 3.2	92.1
2 Composition: 0.28%Fe, 0.14%Cr, 98%Ti	0	12	–	36	–	56	–
	2	50.6 ± 0.6	97.1	81.6 ± 1.6	107.4	92.4 ± 1.4	96.3
	4	90.6 ± 1.2	98.4	119.4 ± 1.2	103.0	129.8 ± 0.8	95.4

<sup>a</sup>mean ± standard deviation (n = 3); <sup>b</sup>lower than limit of detection (LOD) (0.71  $\mu\text{g L}^{-1}$  or 1.42  $\mu\text{g g}^{-1}$ ).

**Table 4.** Comparison of the proposed method with other preconcentration methods for determination of the analytes

Method	Analytical technique	Analyte	EF	LOD / ( $\mu\text{g L}^{-1}$ )	Sample preparation time / min	Reference
DLLME	FAAS	Cu	42-48	3	5	36
FI-SPE	FAAS	Cu	21-43	0.93	2-4	37
CPE	GF-AAS	Cd, Pb, Cu, Ni, Mn	10	0.05	30	38
CPE	FAAS	Cd, Cu, Pb, Zn	55-64	0.27	45	39
TIL-UDLL $\mu$ E	GF-AAS	Ni, Cd	79	0.14	25	40
VALLME	FAAS	Cd	35	2.9	11	41
DLLME	ICP OES	Cr, Cu, Ni, Zn	–	0.23-0.55	ca. 10	42
CPE	ICP OES	Cu, Zn, Cd, Ni	9-10	1.0-6.3	65	43
CPE	UV-Vis spectrophotometer	Zn, Co, Ni	–	–	ca. 25	44
DLLME	MIS-FAAS	Ni	52.5	0.1	11	45
<i>in situ</i> IL-DLLME	FAAS	Ni, Zn, Cu	40-62	0.71-0.93	7	this work

EF: Enrichment factor; LOD: limit of detection; DLLME: dispersive liquid-liquid microextraction; FI-SPE: flow injection on-line SPE preconcentration; CPE: cloud point extraction; TIL-UDLL $\mu$ E: temperature-controlled ionic liquid-based ultrasound-assisted liquid-liquid microextraction; VALLME: vortex-assisted liquid-liquid microextraction; FAAS: flame atomic absorption spectroscopy; GF-AAS: graphite furnace-atomic absorption spectrometry; ICP OES: inductively coupled plasma optical emission spectroscopy; MIS-FAAS: microsample injection system coupled flame atomic spectrometry.

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