

## Simultaneous Homogeneous Liquid-Liquid Extraction of Ni(II) and Cu(II) Using New *vic*-Dioxime Derivative

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A new *vic*-dioxime derivative (2H-1,4-benzothioazine-2,3(4H)dionedioxime, Oxime I) has been synthesized and investigated as a selective complexing ligand for homogeneous liquid-liquid extraction and preconcentration of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions. Zonyl FSA has been applied as a phase separation agent. The influence of pH, type, and concentration of water-miscible organic solvent, Zonyl FSA, and Oxime I, as well as the effect of different diverse ions on extraction and determination of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions has been investigated. Under optimum conditions ([Oxime I]<sub>T</sub> = 1.2 × 10<sup>-3</sup> mol L<sup>-1</sup>, [THF]<sub>T</sub> = 16.7 % v/v, [FSA]<sub>T</sub> = 3.2 % m/v, pH = 4.5), 5 ng of each Ni<sup>2+</sup> and Cu<sup>2+</sup> in 5.5 mL aqueous phase was extracted quantitatively into 75 μL of the precipitated liquid phase. Limit of detection of the proposed method was 0.004 ng mL<sup>-1</sup> for Ni<sup>2+</sup> and 0.005 ng mL<sup>-1</sup> for Cu<sup>2+</sup>. The proposed method has been extended over extraction and determination of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions in different synthetic and natural water samples.

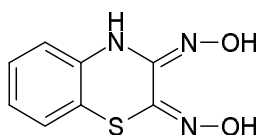
Zsyntetyzowano nową pochodną (2H-1,4-benzotiazyno-2,3(4H)dionodioksymu, oksym I) i badano ją pod kątem zastosowania jako kompleksującego ligandu do jednorodnej ekstrakcji ciecz-ciecz i wstępnego zateżenia jonów Ni<sup>2+</sup> i Cu<sup>2+</sup>. Jako czynnika rozdzielającego fazy użyto Zonylu FSA. Badano wpływ pH oraz wpływ rodzaju i stężenia mieszającego się z wodą rozpuszczalnika organicznego, Zonylu FSA i oksymu I, a także wpływ rozmaitych jonów na ekstrakcję i oznaczenie Ni<sup>2+</sup> i Cu<sup>2+</sup>. W optymalnych warunkach ([oksym I]<sub>T</sub> = 1,2 × 10<sup>-3</sup> mol L<sup>-1</sup>, [THF]<sub>T</sub> = 16,7 % v/v, [FSA]<sub>T</sub> = 3,2 % v/v, pH = 4.5), 5 ng Ni<sup>2+</sup> i Cu<sup>2+</sup> w 5,5 mL<sup>-1</sup> fazy wodnej wyekstrahowano do 75 μL strąconej fazy ciekłej. Granica wykrywalności proponowanej metody wynosi 0,004 ng mL<sup>-1</sup> w przypadku Ni<sup>2+</sup> i 0,005 ng mL<sup>-1</sup> w przypadku Cu<sup>2+</sup>. Metodę zastosowano do ekstrakcji i oznaczania Ni<sup>2+</sup> i Cu<sup>2+</sup> w syntetycznych i naturalnych próbkach wód.

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Homogeneous liquid-liquid extraction (HLLE) is an efficient preconcentration method that allows one to extract a solute from a homogeneous phase (three-component solvent system, or perfluorinated surfactant system) into a microscale-precipitated liquid phase, obtained by phase separation due to the change in pH, temperature, or ionic strength of the solution. Due to the homogeneity of the initial mixture of the solute and extractant, no interface exists between the aqueous and the organic phases, which means that the surface area of the interface is initially infinitely large and no vigorous mechanical shaking is necessary. In addition to the reduced extraction time, disposal costs, consumption of and exposure to organic solvents, HLLE procedure is simple and requires only addition of reagents [1]. Recently, HLLE has been successfully utilized for extraction of some organic and inorganic analytes in different matrices [2–8].

Vicinal dioximes (*vic*-dioximes) are important complexing ligands that have received considerable attention in biology and chemistry [9]. Transition metal complexes of these compounds have been of particular interest as biological model compounds and have been extensively investigated for their similarity to vitamin B<sub>12</sub> [10]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atom makes *vic*-dioximes amphoteric ligands which form corrin-type square-planar, square-pyramidal, and octahedral complexes with transition metal ions, such as Ni(II), Cu(II), Pd(II), Co(II), and U(VI) as central atoms [11]. Exceptional stability and unique electronic properties of these complexes can be attributed to their planar or octahedral structures, which are stabilized by hydrogen bonding [12]. High stability of the complexes with *vic*-dioxime ligands has been extensively utilized for various purposes, including trace metal analysis [13]. We have reported previously on the synthesis of a new *vic*-dioxime derivative (bis-(2-hydroxyphenylamino) glyoxime) and its application for selective solid phase extraction and concentration of ultra-trace amounts of copper(II) [14].

In this article, we report on the synthesis of a new *vic*-dioxime derivative (2H-1,4-benzothiazine-2,3(4H)dionedioxime, Oxime I) and its application as a complexing ligand in a new, simple, and efficient method for selective extraction and preconcentration of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions. FSA was used as a phase separation agent. Direct determination of Ni<sup>2+</sup> and Cu<sup>2+</sup> in a microdroplet formed in HLLE was performed by electrothermal atomic absorption spectrometry (ET-AAS).



2H-1,4-benzothiazine-2,3(4H)dionedioxime (Oxime I)

## EXPERIMENTAL

### Reagents

THF, DMSO, ethanol, methanol, and acetone (all from Merck) were of analytical reagent grade. Glyoxal, hydroxylamine hydrochloride, and 2-aminothiophenole, all used for synthesis, were purchased from Merck and used as received. Glyoxime was obtained in the reaction of glyoxal and hydroxylamine hydrochloride in an alkaline aqueous medium. Dichloroglyoxime was synthesized by chlorination of glyoxime in ethanolic solution at  $-20^{\circ}\text{C}$  [15]. Zonyl FSA (Aldrich) was used as received; it was a mixture of compounds with carbon numbers in their alkyl groups ranging from 6 to 10 ( $\text{CF}_3-(\text{CF}_2)_n-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{COOH}$ ,  $n = 1-5$ ). In this study, FSA diluted with water to 25% m/v was used. Buffer solution of pH 4.5 was prepared by mixing appropriate volumes of  $0.2 \text{ mol L}^{-1}$  acetic acid and  $0.2 \text{ mol L}^{-1}$  sodium acetate solutions.

Nickel(II) nitrate and other salts were of the highest available purity and were dried in vacuum over  $\text{P}_2\text{O}_5$ . Doubly distilled water was used throughout. Standard stock solution of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions ( $1000 \mu\text{g mL}^{-1}$ ) were prepared by dissolving appropriate amounts of their nitrate salts in 5 mL of concentrated nitric acid, and further dilution to 1000 mL with water. Working solutions were prepared by appropriate dilution of the stock solution.

### Synthesis of Oxime I

A solution of dichloroglyoxime (1.56 g, 10 mmol) in 17 mL of ethanol–water mixture (80 % v/v) and 1.5 g of sodium bicarbonate were added to the stirred solution of 2-aminothiophenole (2.5 g, 20 mmol) in 20 mL of absolute ethanol at the room temperature. The solution was stirred for 1 h and then 15 mL of distilled water were added. The mixture was stirred further for 5 h until the precipitate was formed. Crude product was collected by filtration and washed with a hot ethanol–water mixture (50 % v/v) to obtain 1.91 g of pure white precipitate (yield 91%, m.p.  $234.2-234.3^{\circ}\text{C}$ ). The structure of the synthesized compound was confirmed by CHN elemental analyzer, FTIR,  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR, MS, and XRD structure analyses [16].

### Apparatus

A Shimadzu AA6650 atomic absorption spectrometer with a GFA–EX7 graphite furnace, an ASC–6100 autosampler, and a  $\text{D}_2$  continuous source for background correction was utilized for determination of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions under the recommended conditions. An Eppendorf 5810 centrifuge was used. A Jenway 4030 digital pH-meter equipped with a combined glass-calomel electrode served for pH adjustments.

### General procedure

A sample solution (5.5 mL) containing 0.2 ng–20  $\mu\text{g}$  of each analyte ( $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ ), 1.5 mL of THF with 2 mg of Oxime I, and 1 mL of 25 % m/v FSA aqueous solution were placed in a 50 mL-in-volume cylindrical glass vial closed with a plastic cap. An acetic acid–sodium acetate buffer solution (1 mL) was then added in order to adjust pH of the mixture to 4.5. Final concentrations were:  $[\text{Oxime I}]_{\text{T}} = 1.2 \times 10^{-3} \text{ mol L}^{-1}$ ,  $[\text{THF}]_{\text{T}} = 16.7 \text{ \% v/v}$ ,  $[\text{FSA}]_{\text{T}} = 3.2 \text{ \% m/v}$ . The mixture was left for 5 min at the room temperature and then centrifuged at 2500 rpm for 15 min. The volume of the formed liquid phase was determined using a 100  $\mu\text{L}$ -in-volume microsyringe (500  $\mu\text{L}$ -in-volume microsyringe was used for the volumes larger than 100  $\mu\text{L}$ ) and transferred directly into the graphite tube of ET–AAS spectrometer. Concentrations of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions were determined against a reagent blank using suitable external linear calibration curves.

### Determination of nickel and copper in natural waters

Water samples were collected at clean surface zones, at a depth of 5–10 cm using acid wash bottles. After collecting, the samples were acidified and refrigerated in PVC containers until determination. First, a 50 mL-in-volume aliquot of each water sample was passed through a 45  $\mu\text{m}$  (Millipore) Nylon filter to remove any particles that might have been present. Subsequently,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions were extracted from a 5.5 mL-in-volume filtered samples using the proposed method, and then quantified as described in the previous section.

## RESULTS AND DISCUSSION

The presence of N and O donor atoms in Oxime I molecules was expected to increase their stability and selectivity towards transition metal ions over other metal ions, especially alkali and alkaline earth cations [17]. On the other hand, Ni(II) and Cu(II) ions are medium-strong Lewis acids that exhibit strong tendency to form complexes with N-ligands of medium-strong basic properties [18].

Preliminary experiments were carried out in order to investigate the performance of quantitative HLL of different transition metal ions using Oxime I. It has been found that  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Zn}^{2+}$  ions were successfully extracted from the solution of a medium pH into THF–FSA medium; extraction yield decreased in the following order:  $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Ag}^+ > \text{Fe}^{3+} > \text{Pb}^{2+} > \text{Cr}^{3+} > \text{Pd}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+}$ . Considering the obtained extraction order and lipophilicity of Oxime I, we have decided to examine its complexing properties in HLL in order to preconcentrate  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions and, subsequently, to directly determine by ET–AAS in a micro-droplet.

### Effect of pH

Fluorosurfactants, such as HPFOA ( $\text{pK}_a = 1.01$ ,  $20^\circ\text{C}$ ,  $I = 0.1$ ) and Zonyl FSA ( $\text{pK}_a = 6.5$ , 50 % v/v THF), dissolve in water at pH higher than acid dissociation constant of their carboxylic acid groups. If pH of the aqueous solution is lower than acid dissociation constant, carboxylic groups are protonated and fluorosurfactant precipitates as a needle-like crystalline solid. However, if a small amount of water-miscible organic solvent, such as THF, DMSO, DMF, dioxane, acetone, or acetonitrile is present in the solution, fluorosurfactant precipitates in the water-miscible liquid phase at a  $\mu\text{L}$ -scale, and the solute is then extracted into it [2].

In order to investigate the influence of pH on HLL extraction of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions, pH of aqueous samples was varied over the range of 3.0–6.5, and then the recommended procedure was followed. The highest extraction yield was obtained in the pH range 4.0–5.0. Due to dissolution limitation of FSA, no precipitated phase

was formed at pH higher than 6.5. Thus, pH of 4.5 was applied in further studies. It was adjusted with acetic acid-sodium acetate buffer solution.

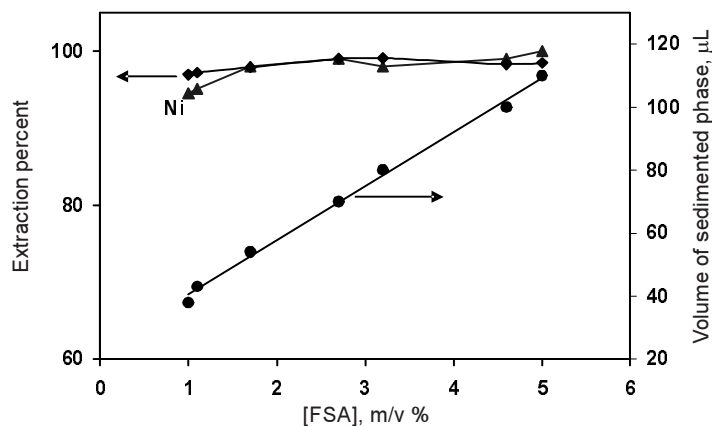
#### **Effect of water-miscible organic solvent**

DMSO, THF, and acetone were tested in HLL extraction of Ni<sup>2+</sup> and Cu<sup>2+</sup>. Oxime I has a limited solubility in acetone. DMSO leads to the formation of a solid sediment. Application of THF as a water-miscible organic solvent causes complete phase separation with the least amount of the solvent and produces viscous spherical drop suitable for handling with a micro-syringe. Thus, THF was selected for the subsequent experiments.

Concentration of THF in the initial homogeneous phase was optimized by varying THF volume over the range 8.0–50% v/v. It has been found that the extraction yield of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions was independent of THF content in the studied range. On the other hand, the volume of the precipitated liquid phase increased with the increasing volume of THF. Application of a high volume of THF resulted in a large volume of the precipitated liquid phase, which limited the concentration factor. For small volumes of THF, solid sediment instead of an oily droplet was formed. Hence, the optimum THF percentage volume of 16.7 was applied in HLLE of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions.

#### **Effect of FSA concentration**

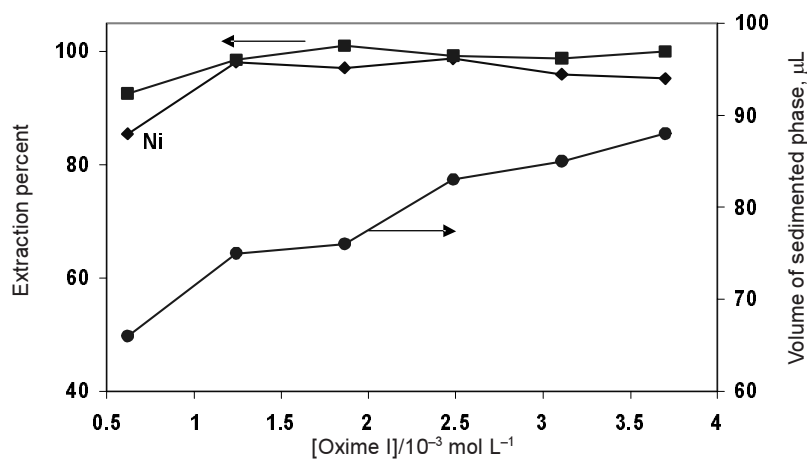
In order to estimate the optimum amount of FSA for quantitative HLL extraction of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions with Oxime I, extraction of 5 ng of each Ni<sup>2+</sup> and Cu<sup>2+</sup> from 5.5 mL of sample solutions was conducted by varying concentration of FSA in the range 1.0–4.5% m/v. In Figure 1 it can be seen that the percentage extraction yield of Ni<sup>2+</sup> and Cu<sup>2+</sup> is maximal in the FSA range 2.5–4.5% m/v. Hence, the subsequent HLLE experiments were carried out with 3.2% m/v content of FSA. Noteworthy, the volume of the precipitated liquid phase increased with the increasing concentration of FSA, due to more complete phase separation in the presence of a higher content of the surfactant (FSA). It appears from Figure 1 that there is a linear correlation between the concentration of FSA and the volume of the precipitated liquid phase.



**Figure 1.** Effect of FSA concentration on the percentage extraction yield and the volume of the precipitated liquid phase. Conditions: 5 ng of each  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions in 5.5 mL of sample solution;  $[\text{THF}]_{\text{T}} = 16.7\% \text{ v/v}$ ;  $\text{pH} = 4.5$

#### Effect of concentration of Oxime I

The effect of the concentration of Oxime I on the extraction yield of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions is shown in Figure 2. The extraction yield of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions is quantitative for the concentration of Oxime I higher than  $1.2 \times 10^{-3} \text{ mol L}^{-1}$ . At very high concentration of Oxime I, phase separation occurred before the extraction was completed, and some solid sediment remained close to the microdroplet. Thus, the concentration of  $1.2 \times 10^{-3} \text{ mol L}^{-1}$  of Oxime I was used in further studies.



**Figure 2.** Effect of the concentration of Oxime I on the percentage extraction yield and the volume of the precipitated liquid phase. Conditions: 5 ng of each  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions in 5.5 mL of sample solution;  $[\text{THF}]_{\text{T}} = 16.7\% \text{ v/v}$ ;  $[\text{FSA}]_{\text{T}} = 3.2\% \text{ m/v}$ ;  $\text{pH} = 4.5$

### Analytical performance

5.0, 10.0, 20.0, 30.0, 40.0, and 50.0 mL-in-volume sample solutions containing 5 ng of each Ni<sup>2+</sup> and Cu<sup>2+</sup> ions were examined under optimum experimental conditions ([Oxime I]<sub>T</sub> = 1.2 × 10<sup>-3</sup> mol L<sup>-1</sup>, [THF]<sub>T</sub> = 16.7 % v/v, [FSA]<sub>T</sub> = 3.2 % m/v, and pH = 4.5) applying the proposed method. In all cases, Ni<sup>2+</sup> and Cu<sup>2+</sup> ions were quantitatively extracted. This result has shown that the volume of the sample solution does not affect the extraction yield, since the concentrations of FSA, THF, and Oxime I were constant in all cases. Large sample solution volume leads to the formation of a large volume of the precipitated liquid phase. This has not been taken into account in similar previous studies [2–5].

Concentration factor is limited to the volume ratio of the sample solution and the precipitated liquid phase. Thus, the maximum concentration factor of the proposed method was 73 (*i.e.* 75 μL of the precipitated liquid phase was obtained from 5.5 mL of the sample solution).

Selective extraction and determination of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions from binary mixtures using Oxime I and in the presence of various metal ions has been investigated as well. 5.5 mL-in-volume aliquots of the solution containing 5 ng of each analyte (Ni<sup>2+</sup> and Cu<sup>2+</sup> ions) and different amounts of other cations were subjected to the recommended procedure. The results (Tab. 1) show that Ni<sup>2+</sup> and Cu<sup>2+</sup> ions in their binary mixtures were extracted almost completely, even in the presence of as much as 5.0 mg of some cations. Limit of detection (LOD) of the proposed method was studied under optimum experimental conditions. LOD values were calculated as 3σ of the blank divided by the concentration factor (73) and equalled to 0.004 and 0.005 ng mL<sup>-1</sup> for Ni<sup>2+</sup> and Cu<sup>2+</sup>, respectively. Reproducibility of HLL extraction and determination of 5 ng of each Ni<sup>2+</sup> and Cu<sup>2+</sup> ions from 5.5 mL of the sample solution was also studied. RSDs calculated for 10 replicate measurements were 3.8 % for Ni<sup>2+</sup> and 2.9 % for Cu<sup>2+</sup>.

**Table 1.** Recovery of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions from binary mixtures using Oxime I<sup>a</sup>

| Diverse ion      | Amount taken, μg | Recovery of Ni <sup>2+</sup> ions, % |                    | Recovery of Cu <sup>2+</sup> ions, % |                    |
|------------------|------------------|--------------------------------------|--------------------|--------------------------------------|--------------------|
| Na <sup>+</sup>  | 5000             | 96.7                                 | (1.9) <sup>b</sup> | 98.6                                 | (2.3) <sup>b</sup> |
| K <sup>+</sup>   | 5000             | 102.1                                | (2.4)              | 100.8                                | (3.1)              |
| Ca <sup>2+</sup> | 3000             | 99.1                                 | (2.3)              | 98.0                                 | (2.8)              |
| Mg <sup>2+</sup> | 3000             | 97.6                                 | (3.0)              | 96.4                                 | (3.6)              |
| Co <sup>2+</sup> | 1000             | 99.5                                 | (2.2)              | 101.2                                | (4.0)              |
| Zn <sup>2+</sup> | 1000             | 98.9                                 | (3.7)              | 97.2                                 | (2.6)              |

(Continuation on the next page)

**Table 1.** (Continuation)

|                  |      |       |       |       |       |
|------------------|------|-------|-------|-------|-------|
| Pd <sup>2+</sup> | 1000 | 96.9  | (2.5) | 97.7  | (3.1) |
| Pb <sup>2+</sup> | 1000 | 98.4  | (3.2) | 100.8 | (4.6) |
| Cd <sup>2+</sup> | 1000 | 103.4 | (3.5) | 99.3  | (1.2) |
| Ag <sup>+</sup>  | 500  | 99.9  | (2.0) | 97.9  | (3.2) |
| Cr <sup>3+</sup> | 500  | 99.2  | (1.8) | 102.7 | (3.0) |
| Fe <sup>3+</sup> | 300  | 97.0  | (3.1) | 97.7  | (3.8) |

<sup>a</sup> 5 ng of each Ni<sup>2+</sup> and Cu<sup>2+</sup> ions in 5.5 mL of sample solution; [FSA]<sub>T</sub> = 3.2 % m/v, [THF]<sub>T</sub> = 16.7 % v/v, [Oxime I]<sub>T</sub> = 1.2 × 10<sup>-3</sup> mol L<sup>-1</sup>, pH = 4.5.

<sup>b</sup> Numbers in the parentheses are %RSD calculated from three replicate analyses.

Applicability of the proposed method to the samples with different matrices has been also studied. For this purpose, separation and recovery of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions from three different synthetic samples (Tab. 2) have been investigated. In all cases Ni<sup>2+</sup> and Cu<sup>2+</sup> were recovered quantitatively.

**Table 2.** Recovery of 5 ng of each Ni<sup>2+</sup> and Cu<sup>2+</sup> ions from synthetic samples<sup>a</sup>

| Sample   | Recovery of Ni <sup>2+</sup> ions, % | Recovery of Cu <sup>2+</sup> ions, % |
|--|--------------------------------------|--------------------------------------|
| Synthetic sample 1 (Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> and Mg <sup>2+</sup> , 2 mg of each cation)  | 101.5 (2.9) <sup>b</sup>             | 99.8 (3.2) <sup>b</sup>              |
| Synthetic sample 2 (Zn <sup>2+</sup> , Co <sup>2+</sup> , Pb <sup>2+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup> and Ag <sup>+</sup> , 1 mg of each cation)  | 98.3 (2.6)                           | 100.8 (3.4)                          |
| Synthetic sample 3 (Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> and Mg <sup>2+</sup> , 1 mg of each cation and Zn <sup>2+</sup> , Co <sup>2+</sup> , Pb <sup>2+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup> and Ag <sup>+</sup> , 0.5 mg of each cation) | 99.0 (3.0)                           | 96.5 (2.8)                           |

<sup>a</sup> 5.5 mL of each sample solution was taken; [FSA]<sub>T</sub> = 3.2 % m/v, [THF]<sub>T</sub> = 16.7 % v/v, [Oxime I]<sub>T</sub> = 1.2 × 10<sup>-3</sup> mol L<sup>-1</sup>, pH = 4.5.

<sup>b</sup> Numbers in the parentheses are %RSD calculated from three replicate analyses.

The proposed procedure was also applied to the determination of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions in different natural water samples using standard addition method (Tab. 3).



**Table 3.** Results of determination of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions in different water samples applying the proposed method and standard addition procedure<sup>a</sup>

| Sample Site   | Ni <sup>2+</sup> ion, ng mL <sup>-1</sup> | Cu <sup>2+</sup> ion, ng mL <sup>-1</sup> |
|---|---|---|
| Rain water (Broojerd City)                                | 0.6 (2.9)                                 | 1.8 (3.6) <sup>b</sup>                    |
| Tap water (Lorestan University)                           | 12.3 (2.8) <sup>b</sup>                   | 22.5 (2.4)                                |
| Khorram-Abad River (near Robat-Namaki Village)            | 22.6 (4.1)                                | 66.7 (3.0)                                |
| Khorram-Abad River (near the city center, Shohada Bridge) | 23.9 (2.5)                                | 64.0 (2.8)                                |
| Khorram-Abad River (near Gilevaran Village)               | 22.0 (3.0)                                | 129.1 (2.3)                               |

<sup>a</sup> Four aliquots (5.5 mL) of each sample solution was taken and spiked with a standard solution containing Ni<sup>2+</sup> and Cu<sup>2+</sup> ions; [FSA]<sub>T</sub> = 3.2% m/v, [THF]<sub>T</sub> = 16.7% v/v, [Oxime I]<sub>T</sub> = 1.2 × 10<sup>-3</sup> mol L<sup>-1</sup>, pH = 4.5.

<sup>b</sup> Numbers in the parentheses are % RSD calculated from three replicate analyses.

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