Synthesis of a New α-Dioxime Derivative and Its Application for Selective Homogeneous Liquid-Liquid Extraction of Cu(II) into a Microdroplet Followed by Direct GFAAS Determination

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A fast and reliable method for the selective separation and preconcentration of Cu^{2+} ions using homogeneous liquid-liquid extraction was developed. A new α-dioxime derivative (2H-1,4-benzothioazine-2,3(4H)dione-dioxime, Dioxime I) was synthesized and investigated as a suitable selective complexing ligand for Cu^{2+} ions. Zonyl FSA (FSA) was applied as a phase-separator agent under the slightly acidic pH conditions. Under the optimal experimental conditions ([FSA] = 3.2% w/v, [THF] = 19.5% v/v, [Dioxime I] = 1.9×10^{-3} M, and pH = 4.7), 10 μg of Cu^{2+} in 5.2 mL aqueous phase could be extracted quantitatively into 80 μL of the sedimented phase. The maximum concentration factor was 65-fold. The limit of detection of the proposed method was 0.005 ng mL^{-1}. The reproducibility of the proposed method, on the 10 replicate measurements, was 1.3%. The influence of the pH, type and volume of the water-miscible organic solvent, concentration of FSA, concentration of the complexing ligand and the effect of different diverse ions on the extraction and determination of Cu^{2+} ions were investigated. The proposed method was applied to the extraction and determination of Cu^{2+} ion in different synthetic and natural water samples.

Key Words : Copper, Homogeneous liquid-liquid extraction, Dioxime
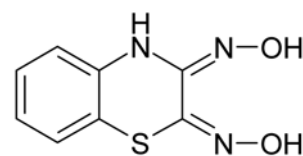
Introduction

Due to the demand for ultra-trace analysis, the need for powerful methods has increased, particularly for environmental analysis. Therefore, simple, rapid, cleaner and efficient techniques that can be performed easily are required.[1-3]

Homogeneous liquid-liquid extraction (HLLE) is a simple and powerful preconcentration method that reduces the extraction time, disposal costs, consumption of, and exposure to organic solvents. This method extracts the solute in a homogeneous solution into a very small sedimented phase formed from the solution by the phase-separation phenomenon. In HLLE, the initial condition is a homogeneous solution; namely, there is no interface between the water phase and the water-miscible organic solvent phase. In other words, the surface area of the interface is infinitely large initially. Accordingly, no vigorous mechanical shaking is necessary. The procedure is simple and requires only the addition of a reagent.[4] Recently, HLLE was successfully utilized for the extraction of some organic and inorganic analytes.[5-15] We have recently reported the successful use of HLLE as a suitable method for the separation and preconcentration of uranyl,[16] molybdenyl,[17] and silver(I).[18]

Vicinal dioximes (*vic*-dioximes) are important complexing ligands that have received considerable attention in biology and chemistry.[19] The transition metal complexes of these compounds have been of particular interest as biological model compounds and have been extensively investigated for their similarity with vitamin B_{12}.[20] The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make *vic*-dioximes amphoteric ligands which form corrin-type square-planner, square pyramidal and octahedral complexes with transition metal ion such as Cu(II), Ni(II), Pd(II), Co(II) and U(VI) as central atoms.[21] The exceptional stability and unique electronic properties of these complexes can be attributed to their planner or octahedral structures, which are stabilized by hydrogen binding.[22] The high stability of the complexes prepared with *vic*-dioxime ligands has been extensively used for various purposes including trace metal analysis.[23] We have previously reported on the synthesis of a new *vic*-dioxime derivative (bis-(2-hydroxy-phenylamino) glyoxime) and its use for selective extraction and concentration of ultra trace amounts of copper(II) by solid phase extraction.[24]

In this article, we report on the synthesis and application of a new α-dioxime derivative (2H-1,4-benzothioazine-2,3(4H)dionedioxime, Dioxime I), as a novel complexing ligand for the development of a simple and efficient method for the selective extraction and concentration of Cu^{2+} ions. Zonyl FSA was used as a phase-separator agent, and the direct determination of Cu^{2+} ion in the microdroplets formed from the HLLE was carried out using graphite furnace atomic absorption spectrometry (GFAAS).

Dioxime I

Experimental Section

Apparatus. A Shimadzu AA6650 atomic absorption spectrometer (AAS) equipped with a GFA-EX7 graphite furnace (with high-density graphite tube cuvettes), an ASC-6100 autosampler, and a D_2 continuous source for background correction was utilized for the determination of Cu^{2+} ions under the recommended condition. The optimum parameters of GFAAS instrument were as follow: wavelength: 324.8 nm; lamp mode: BGC-D2; lamp current: 6 mA; drying temperature: 250 ℃, 20 s; ashing temperature: 800 ℃, 23 s; atomization temperature: 2300 ℃, 40 s. An Eppendorf 5810 centrifuge was used for centrifugation. A Jenway 4030 digital pH meter equipped with a combined glass-calomel electrode was used for the pH adjustments.

Reagents. Ethanol, methanol, acetone, tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were of HPLC-grade from Merck. The materials for synthesis (2-aminothiophenole, glyoxal, and hydroxylamine hydrochloride) were bought from Merck and used as received. Glyoxime was prepared by reaction of glyoxal and hydroxylamine hydrochloride in an alkaline aqueous media. Dichloroglyoxime was synthesized by chlorination of glyoxime in an ethanol solution at –20 ℃.[25,26] Zonyl FSA was used as received from Aldrich, and was a mixture that contained components with carbon numbers in the alkyl group from 6 to 10. In this study, Zonyl FSA diluted to 25% w/v with water was used. The buffer solution was prepared at pH 4.7 by mixing appropriate volumes of 0.2 M acetic acid and 0.2 M sodium acetate solutions. The analytical-grade copper(II) nitrate and other salts were of the highest purity available and were dried in a vacuum over P_2O_5 before use. Doubly distilled deionized water was used throughout. The standard stock solution of Cu^{2+} ions (1000 μg mL^{-1}) was prepared by dissolving an appropriate amount of copper(II) nitrate in 5.0 mL of concentrated nitric acid, and diluted to 1000.0 mL with water. Working solutions were prepared by appropriate dilution of the stock solution.

$$CF_3\text{-}(CF_2)_n\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}COOH \quad n = 6\text{–}8$$

Zonyl FSA

Synthesis of 2H-1,4-benzothioazine-2,3(4H)dionedioxime. To a stirring solution of 2-aminothiophenole (2.5 g, 20 mmol) in 20.0 mL of absolute ethanol, a solution of dichloroglyoxime (1.56 g, 10 mmol) in 17.0 mL of ethanol-water mixture (80% v/v) and 1.5 g of sodium bicarbonate was added at room temperature. The solution was stirred for 1.0 h and then 15.0 mL of distilled water was added. The mixture was stirred for 5.0 h at room temperature, until precipitate was formed. The crude product was collected by filtration and was washed with hot ethanol-water mixture (50% v/v) to afford 1.91 g (*i.e.*, efficiency was 91%) of white pure precipitate with a crystal m.p. of 234.0-234.5 ℃. The identity and purity of Dioxime I were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, MS, CHN elemental analyzer, and XRD structure analyzer (Enraf-Nonius CAD4, Institute

of Organoelement Compounds (INEOS) of RAS, Vavilov Str., 28, Moscow 119991, Russia).

IR (KBr): v (cm^{-1}) = 3400 (NH), 2800-3400 (OH), 1600, 1640 (C=N), 1250 (C-N), 920, 980 (N-O); ^{1}H NMR (500 MHz, DMSO-d$_6$-25): δ (ppm) = 12.3 (2H, OH), 10.8 (2H, OH), 9.4 (bs, 2H, NH), 6.8-7.4 (8H, CH$_{Ar}$); ^{13}C NMR (500 MHz, DMSO-d$_6$-25): δ (ppm) = 137.5, 137.2, 133.7, 127.0, 125.9, 120.9, 116.6, 112.8; The mass spectrum, m/z (relative intensity): 209 (m$^+$, 100), 179 (100), 161 (100), 149 (46.4), 136 (100).

Homogeneous liquid-liquid extraction and quantification of Cu^{2+} ions. A sample solution (5.2 mL) containing 10 μg of Cu^{2+} ion, 1.5 mL of THF containing 3.0 mg of Dioxime I, and 1.0 mL of 25 w/v% FSA aqueous solution were placed in a 50.0 mL cylindrical glass vial fitted with a plastic cap. An acetic acid-sodium acetate buffer solution (1.0 mL) was then added in order to adjust the pH value of the mixture to 4.7. Thus, the final concentrations were [Dioxime I] = 1.9 × 10^{-3} M, [THF] = 19.5% v/v, [FSA] = 3.2% w/v, and pH = 4.7. The mixture was allowed to stand for 5 min at room temperature, and then centrifuged at 2500 rpm for 15 min. The volume of the sedimented phase was determined using a 100-μL micro-syringe and transferred directly into the graphite tube cuvette of a GFAAS. The Cu^{2+} ion concentration was then determined against a reagent blank using a suitable external linear calibration curve.

Determination of Cu^{2+} ion in the natural water samples. The samples were collected from the 5-10 cm depth of water, at the clean surface zones of the samples sites, using the acid wash bottles. After sampling, the samples were acidified and stored in the refrigerator using PVC containers to the time when the determination possibility was brought about. A 100.0 mL aliquot of the water sample was first passed through a 45 μm (Millipore) Nylon filter to remove any particles that may have been present in the natural water samples. The Cu^{2+} ion was extracted from a 5.2 mL portion of the thus-treated aliquot using the proposed method, and then quantified as described in the previous section.

Results and Discussion

The Cu(II) ion is an intermediate Lewis acid that exhibits a high tendency to form complexes with ligands containing N donor atoms with intermediate base properties.[27] On the other hand, the existence of N and O donating atoms in Dioxime I was expected to increase both the stability and selectivity of its complex over other metal ions, especially alkali and alkaline earth cations.[28]

Some preliminary experiments were carried out in order to investigate the quantitative HLLE of different transition metal ions using Dioxime I. It was found that Cu^{2+}, Ni^{2+}, Ag^+, Fe^{3+}, Pb^{2+}, Cr^{3+}, Pd^{2+}, Co^{2+}, and Zn^{2+} ions were sufficiently extracted from a solution with medium pH into a system containing THF and Zonyl FSA as a phase-separator agent, and extraction percent varied in the order of $Cu^{2+} > Ni^{2+} > Ag^+ > Fe^{3+} > Pb^{2+} > Cr^{3+} > Pd^{2+} > Co^{2+} > Zn^{2+}$. Thus, considering the observed extraction trend as well as the

liphophilicity of the dioxime derivative used, we decided to examine the capability of Dioxime I as a suitable complexing agent for the selective HLLE and preconcentration of Cu^{2+} ions followed by direct determination of the copper content in the formed sedimented microdroplet by GFAAS.

Effect of the pH. A fluorosurfactant, such as perfluorooctanoic acid (HPFOA, $pK_a = 1.01$, 20 °C, I = 0.1) or Zonyl FSA ($pK_a = 6.5$, 50%v/v THF), dissolves in water at a pH value higher than acid dissociation constant of its carboxylic acid group. If the pH of this aqueous solution is lower than its acid dissociation constant, the fluorosurfactant precipitates as a needle-like crystalline solid due to the charge neutralization of the carboxyl ion. However, if a small amount of water-miscible organic solvent, such as THF, DMSO, DMF, dioxane, acetone or acetonitrile, coexists in this system, the fluorosurfactant precipitates in the water-miscible liquid phase with a μL volume scale. The solute is then extracted into the sedimented phase.[5]

In order to investigate the influence of the pH on the HLLE of Cu^{2+} ions, the pH of aqueous samples was varied over the range of 3.5-6.5, by using 1.0 M solutions of either HNO₃ or NaOH, and the recommended procedure was followed. The results showed that the highest extraction percents were obtained in the pH range of 4.6-4.8. Due to the dissolution of Zonyl FSA, no precipitated phase was formed at pH values greater than 6.5. Thus, a pH value of 4.7 was used for further studies. An acetic acid-sodium acetate buffer solution was used in order to adjust the pH to 4.7.

Effect of nature and volume of the water-miscible organic solvent. Different organic solvents, such as acetone, THF and DMSO were tested for the HLLE of Cu^{2+} ions using Dioxime I. Dioxime I has limited solubility in acetone. On the other hand, using DMSO results in a solid sedimented phase. The application of THF as a water-miscible organic solvent causes complete phase-separation with the least amount of solvent, resulting in a viscose spherical drop suitable for handling with a micro-syringe. Thus, THF was selected for subsequent experiments. Furthermore, the volume of THF was optimized. For this, the volume percent of THF was varied over the range of 7.0-40% v/v (Fig. 1). It
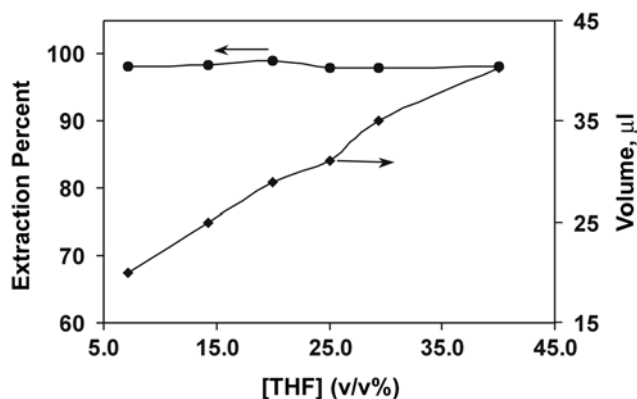
Figure 2. Effect of the FSA concentration on the percent extraction and the volume of the sedimented phase (10 μg of Cu^{2+} ions in 5.2 mL of sample solution, in the final solution: [THF] = 19.5% v/v and pH = 4.7).

is clear that the extraction percent of Cu^{2+} ions was independent of the volume percent of THF in the range studied. On the other hand, the volume of the sedimented phase increased with increasing the volume percent of THF. The high volume percents resulted in a high-volume sedimented phase and a low concentration factor, and low-volume percents caused a solid sedimented phase, instead of an oily drop. Hence, a 19.5 volume percent of THF was used as the optimal volume for the HLLE of Cu^{2+} ions using Dioxime I.

Effect of the Zonyl FSA concentration. In order to investigate the optimum amount of FSA on the quantitative HLLE of Cu^{2+} ions using Dioxime I, the extraction of 10 μg of Cu^{2+} ions from 5.2 mL of the sample solutions was conducted by varying the concentration of FSA in the range of 1.0-5.0% w/v (Fig. 2). As can be seen, the extraction percent of Cu^{2+} ions is maximal in the range of 2.7-4.6% w/v of FSA. Hence, subsequent HLLE experiments were carried out with 3.2% w/v of FSA. It should be noted that volume of the sedimented phase increases by increasing of the FSA

Figure 1. Effect of the volume percent of THF on the percent extraction and the volume of the sedimented phase (10 μg of Cu^{2+} ions in 5.2 mL of sample solution, pH = 4.7).
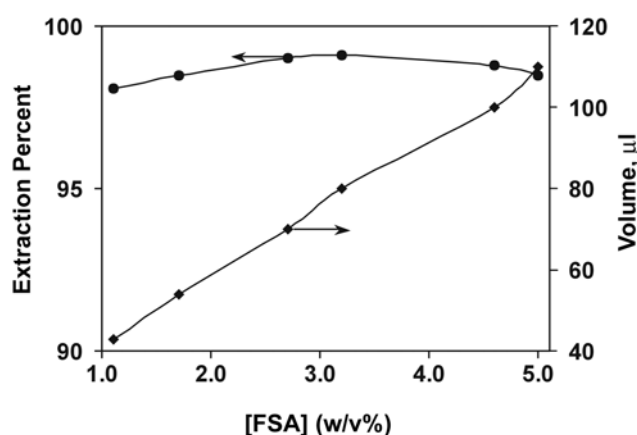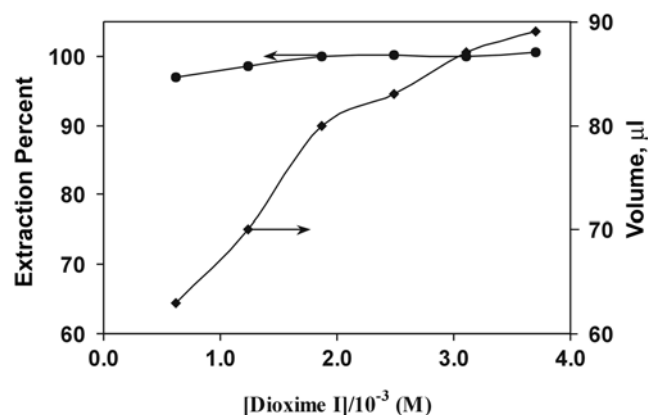
Figure 3. Effect of the Dioxime I concentration on the percent extraction of Cu^{2+} ions (10 μg of Cu^{2+} ions in 5.2 mL of sample solution, in the final solution: [THF] = 19.5% v/v, [FSA] = 3.2% w/v, and pH = 4.7).

concentration, due to more complete phase separation in the presence of a higher surfactant (FSA) concentration.

Effect of the Dioxime I concentration. The effect of the Dioxime I concentrations on the extraction percent of Cu^{2+} ions is shown in Figure 3. The results show that the extraction percent of Cu^{2+} ions was quantitative for Dioxime I concentrations higher than 1.9×10^{-3} M. In very high concentrations of Dioxime I, phase-separation occurred precociously before the extraction was completed, and some solid sediment around the drops remained. Thus, a concentration of 1.9×10^{-3} M of Dioxime I was used for further studies.

Analytical Performance

When 10 μg of Cu^{2+} ions in 5.0 to 30.0 mL of solutions were examined under the optimal experimental conditions ([FSA] = 3.2% w/v, [THF] = 19.5% v/v, [Dioxime I] = 1.9×10^{-3} M, and pH = 4.7) using the proposed method, the Cu^{2+} ion was quantitatively extracted in all cases. This shows that the volume of the sample solution does not affect the extraction percent because in all cases volume the concentrations of Dioxime I, THF and FSA are constant, and it is just enough to centrifuge the sample solution correctly using a suitable vessel. A high sample solution volume causes a high sedimented phase volume. This is a point that was not taken into account in similar previous studies.[4-10] The concentration factor is limited to the ratio of the sample solution and the sedimented phase volumes. Thus, the maximum concentration factor of the proposed method was 65-fold (*i.e.*, 80 μL of the sedimented phase was produced from 5.2 mL of the sample solution).

In order to investigate the selective extraction and determination of Cu^{2+} ions using Dioxime I from binary mixtures with various metal ions, and aliquot of a solution (5.2 mL) containing 10 μg of Cu^{2+} ions and different amounts of other cations were taken, and the recommended procedure was followed. The results (Table 1) show that the Cu^{2+} ions in the binary mixtures were extracted almost completely, even in the presence of up to 5.0 mg of some cations (Na^+ and K^+). The limit of detection (LOD) of the proposed method for the determination of Cu^{2+} ions was studied under the optimal experimental conditions. The LOD obtained from 3σ of the blank and dividing the resulting value to the concentration factor (*i.e.*, 65) was 0.005 ng mL^{-1}. The reproducibility of the proposed method

Table 1. Separation of Cu^{2+} ions from binary mixtures using Dioxime I[*]

Diverse ion	Amount taken (μg)	Recovery of Cu^{2+} ions (%)
Na^+	5000	97.3 (1.9)[#]
K^+	5000	97.8 (1.6)
Ca^{2+}	3000	98.1 (3.1)
Mg^{2+}	3000	96.9 (2.2)
Co^{2+}	1000	97.9 (3.8)
Zn^{2+}	1000	98.2 (2.9)
Pd^{2+}	1000	99.3 (2.1)
Pb^{2+}	1000	98.4 (2.9)
Cd^{2+}	1000	98.1 (3.9)
Ag^+	500	98.4 (2.3)
Cr^{3+}	500	98.7 (3.5)
Fe^{3+}	300	98.0 (3.1)

[*]10 μg of Cu^{2+} ions in 5.2 mL of sample solution was used. (In the final solution: [FSA] = 3.2% w/v, [THF] = 19.5% v/v, [Dioxime I] = 1.9×10^{-3} M, and pH = 4.7). [#]Values in the parentheses are %R.S.Ds. based on three replicate analyses.

for the HLLE and determination of 10 μg of Cu^{2+} ions from 5.2 mL of the sample solution was also studied. The results obtained in 10 replicate measurements revealed a relative standard deviation (R.S.D.) of 1.3%.

To evaluate the applicability of the proposed method to samples with different matrices, it was tested for the separation and recovery of Cu^{2+} ions from three different synthetic samples (Table 2). The selected cations are among the most popular cationic species that exist in many of the

Table 2. Recovery of 10 μg Cu^{2+} ions from the three synthetic samples[*]

Sample	Recovery (%)
Synthetic sample 1: (Na^+, K^+, Ca^{2+} and Mg^{2+}, 2 mg of each cation)	98.7 (2.4)[#]
Synthetic sample 2: (Zn^{2+}, Co^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+} and Ag^+, 1 mg of each cation)	98.1 (1.5)
Synthetic sample 3: (Na^+, K^+, Ca^{2+} and Mg^{2+}, 1 mg of each cation and Zn^{2+}, Co^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+} and Ag^+, 0.5 mg of each cation)	97.0 (3.6)

[*]5.2 mL of each sample solution was taken, (in the final solution: [FSA] = 3.2% w/v, [THF] = 19.5% v/v, [Dioxime I] = 1.9×10^{-3} M, and pH = 4.7). [#]Values in the parentheses are %R.S.Ds. based on three replicate analyses.

Table 3. Determination of Cu^{2+} ions in different natural water samples collected from different sites in Khorram-Abad city (Jun 2004)[*]

Sample Site	Cu^{2+} ion (ng mL^{-1})	
	Proposed Method	GFAAS
Tap water (Lorestan University)	20.7 (3.1)[#]	22.1 (1.8)
Khorram-Abad River (Near the Robat-Namaki Village)	70.1 (3.6)	73.4 (4.1)
Khorram-Abad River (Near the city center, Shohada Bridge)	61.4 (2.7)	65.1 (1.3)
Khorram-Abad River (Near the Gilevaran Village)	124.4 (4.2)	131.9 (2.1)

[*]5.2 mL of each sample solution was taken, (in the final solution: [FSA] = 3.2% w/v, [THF] = 19.5% v/v, [Dioxime I] = 1.9×10^{-3} M, and pH = 4.7).
[#]Values in the parentheses are %R.S.Ds. based on three replicate analyses.

natural or industrial water samples. The results show that, in all cases the Cu^{2+} ions recovery was quantitative. The proposed method was also applied to the determination of Cu^{2+} ions in four different natural water samples. A satisfactory agreement exists between the results obtained by the proposed method and those reported by direct determination of Cu^{2+} ions in the samples using GFAAS (Table 3).

Conclusions

Homogeneous liquid-liquid extraction utilizes a phase separation phenomenon from the homogenous solution and makes it possible to rapidly and powerfully concentrate analytes. A new α-dioxime derivative (2H-1,4-benzothio-azine-2,3(4H)dionedioxime, Dioxime I) was synthesized and investigated as a suitable selective complexing ligand for Cu^{2+} ions. A simple and efficient method for the selective separation and preconcentration of Cu^{2+} ions using HLLE was developed. The proposed HLLE method for the extraction and determination of Cu^{2+} ions is simple, selective and sensitive. The proposed procedure can be successfully applied to separation, preconcentration and determination of copper in real samples.

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