

Development of a Cloud-Point Extraction Method for Determination of Trace Amounts of Copper(II) in Water Samples¹

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Abstract—A simple and rapid cloud-point extraction method by using a Schiff base extractant, named bis(2-hydroxynaphthaldehyde)-1,2-propanediimine, is presented for preconcentration of trace amounts of copper ions in water samples, prior to the determination by flame atomic absorption spectrometry. The process is based upon the complexation of Cu(II) ions by the Schiff base. The formed complexes are soluble in a micellar phase composed by the non-ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114), and then are extracted into the surfactant-rich phase at above its cloud-point temperature. The effect of parameters influencing the extraction efficiency, such as aqueous solution pH, concentration of the Schiff base, amount of the surfactant, equilibration temperature and incubation time were investigated and discussed. Under the optimum experimental conditions, the calibration plot was linear in the range 1–400 µg/L with a limit of detection 0.3 µg/L. A preconcentration factor of 20 was achieved by the presented method. The proposed method was successfully applied for the determination of copper in various water samples.

Keywords: copper, preconcentration, cloud-point extraction, Schiff base, water samples

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Copper is known as one of the most important elements due to its vast applications in a variety of chemical industries [1]. In addition, it is an essential nutrient to all high plants and animals. Copper is found in the bloodstream of animals as a co-factor in various enzymes. This element promotes iron absorption from the gastrointestinal system and it is involved in the transport of iron from tissues into plasma. Nevertheless, copper can be also poisonous and even fatal to organisms. In fact, above a healthy limit, this element accumulates in the liver causing diarrhea, vomiting and transpiration [2]. The role of this element in industries and biological systems required the determination of its trace amounts in different samples. Various methods have been developed to achieve this goal. As instance, flame and graphite furnace atomic absorption spectrometry [3] and spectrophotometric [4] methods are as conventional techniques for copper determinations, but they suffer from their insufficient sensitivity in many environmental and biological samples. To overcome these problems, an enrichment and matrix elimination step is sometimes required before applying the mentioned techniques. To achieve these goals, many methods such as liquid-liquid extraction [5], solid phase extraction [6], membrane filtration [7], ion exchange [8], co-precipitation [9], hollow fiber solid phase microextraction [10] and single drop

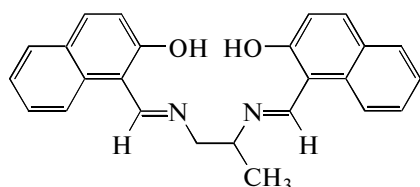
microextraction [11] were applied. Preconcentration based on cloud-point extraction (CPE), called also phase separation extraction and surfactant- or micelle-mediated phase separation, is becoming an important and practical application of surfactants in analytical chemistry [12]. The method is based on the micelle formation ability of non-ionic surfactants in aqueous solutions. Aqueous solutions of these surfactants possess the property to decrease their solubility and become turbid when heated above a temperature referred to as the cloud-point temperature. At higher temperatures the colloidal system is separated into a small volume of surfactant-rich phase and an aqueous phase. Analyte can be concentrated in the surfactant-rich phase. The mechanism by which this separation occurs is attributed to the rapid increase in the aggregation number of the surfactant's micelles, as a result of the increase in temperature. During their formation, the micelles have proved to entrap several hydrophobic substances, isolating them from the bulk aqueous solution. Centrifugation and decantation of the solution assist easy separation of the two phases.

Simplicity, low capital cost, high efficiency, rapidity and environmental friendliness are the most important advantages of this technique. These advantages provoke CPE to be applied in many studies for preconcentration and subsequent determination of various metal ions [13–17]. The selectivity and effi-

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ciency of the method depend directly on the complexing performance and lipophilic nature of the ligand. Schiff bases were shown to exhibit interesting ionophoric properties, in particular towards heavy metal ions. These properties were investigated by applying these ionophores in a variety of analytical methods and techniques such as liquid-liquid extraction [18], solid phase extraction [19], cloud-point extraction [20], transport across liquid membranes [21] and preparation of ion selective electrodes [22]. Although the cloud-point extraction methodology has been used for preconcentration of copper ions [23–31], the application of Schiff bases in such methods is rarely investigated.

In continuation to our studies on the ion receptor properties and analytical applications of Schiff base ionophores [32–40], this paper concerns on the synthesis and application of bis(2-hydroxynaphthaldehyde)-1,2-propanediimine (Scheme 1) as a complexing agent for the cloud-point extraction of trace copper in water samples and its subsequent determination by flame atomic absorption spectrometry (FAAS).



Scheme 1. Structure of bis(2-hydroxynaphthaldehyde)-1,2-propanediimine.

EXPERIMENTAL

Reagents and solutions. Ethanol (Merck), 2-hydroxynaphthaldehyde (Acros) and 1,2-diaminopropane (Merck) were used for synthesis of the studied Schiff base. Stock copper solution (1000 mg/L) was prepared by dissolving appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck) in double distilled water. This solution was standardized complexometrically by EDTA. Triton X-114 (Merck) stock solution (2%, v/v) was prepared by diluting of concentrated solution in double distilled water. Nitric, phosphoric, acetic and formic acids and sodium hydroxide (Merck) were of the highest purity. All other chemical reagents used were of analytical reagent grade (Fluka or Merck) and were used as received.

Apparatus. ^1H NMR spectrum was recorded on a FT-Bruker (AVC 250MHz) spectrometer and data was referenced relative to residual protonated solvent (7.26 ppm for CDCl_3). FT-IR spectrum was recorded on a Unicam (Matson 1000) spectrometer. A flame atomic absorption spectrometer (Varian 220AA) using air/acetylene flame was used for metal ion determination. Phase separation was assisted by a centrifuge (Heraeus Labofuge 300). A Metrohm digital pH meter (model 780) used for pH adjustments. A thermostated

water bath (Julabo MP-5) was applied for controlling the temperature of the cloud-point extraction experiments.

Synthesis of bis(2-hydroxynaphthaldehyde)-1,2-propanediimine. A solution of 2-hydroxynaphthaldehyde (2 g, 12 mmol) in ethanol (30 mL) was refluxed with 1,2-diaminopropane (0.43 g, 5.8 mmol) for 2 h. The yellow precipitate was filtered off and recrystallized twice from ethanol. The purity of the product was checked by thin layer chromatography. Yield, 1.58 g (71%). UV-Vis (CH_2Cl_2): 274, 310 nm. IR (KBr): $\nu_{\text{O-H}} = 3400 \text{ cm}^{-1}$, $\nu_{\text{C-H}} = 2930 \text{ cm}^{-1}$, $\nu_{\text{C=N}} = 1631 \text{ cm}^{-1}$, $\nu_{\text{C=C}} = 1549 \text{ cm}^{-1}$, $\nu_{\text{C-O}} = 1186 \text{ cm}^{-1}$. ^1H NMR (CDCl_3): δ (ppm) 1.44–1.60 (d, 3H, $\text{NCH}(\text{CH}_3)\text{CH}_2\text{N}$), 3.71–3.78 (d, 2H, $\text{NCH}(\text{CH}_3)\text{CH}_2\text{N}$), 3.88–4.01 (m, 1H, $\text{NCH}(\text{CH}_3)\text{CH}_2\text{N}$), 6.97–7.80 (m, 12H, ArH), 8.80, 8.93 (s, 2H, $\text{CHNCH}_2\text{CH}(\text{CH}_3)\text{N}$), 14.66, 14.75 (s, 2H, OH).

Procedure. An aliquot of 10 mL of the sample or standard solution (pH 5) containing the analyte, 0.3 mL of Triton X-114 (2%, v/v) and 50 μL of the prepared Schiff base dissolved in methanol ($1 \times 10^{-3} \text{ M}$) were heated in a thermostated water bath at 35°C for 15 min. Separation of the phases was achieved by centrifugation for 10 min at 3000 rpm. Then, it was cooled in an ice-bath for 5 min to increase the viscosity of the surfactant-rich phase. The aqueous phases can readily be discarded by inverting the tube. A volume of 300 μL of nitric acid (0.1 M) was added to the surfactant-rich phase (200 μL) to reduce its viscosity and to facilitate sample handling prior to FAAS assay. The final solution (500 μL) was introduced into the nebulizer of the spectrometer by conventional aspiration. This volume allows for achieving two determinations by the FAAS instrument. It is noteworthy that the reported values are the mean values of at least three repeated CPE experiments. Calibration was performed by using different standard solutions of copper, submitted to the same preconcentration and determination procedures. Blank solution was also submitted to a similar procedure and measured parallel to the sample solutions.

RESULTS AND DISCUSSION

Effect of pH. Considering a cation exchange mechanism for the copper ion complexation by the Schiff base, the extraction efficiency depends on the pH of aqueous phase. CPE of copper ions was carried out in the pH range 2–8. Depending on the desired pH, the solutions were buffered by using mixtures of phosphoric, formic or acetic acids with sodium hydroxide. The results are shown in Fig. 1. It is seen that maximum extraction can be achieved at $\text{pH} > 4$. Therefore, pH 5 (acetate buffer) was chosen as the optimum value for further experiments.

Effect of the ligand concentration. The extraction efficiency as a function of the Schiff base concentra-

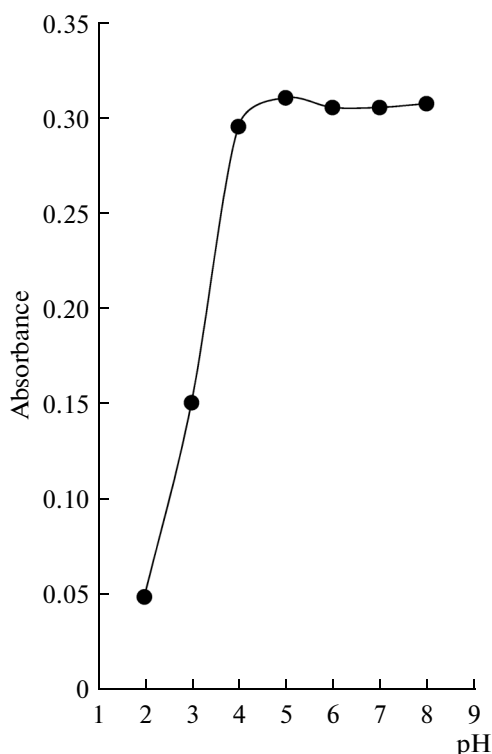


Fig. 1. Effect of pH on the cloud-point extraction of copper. Experimental conditions: 10 mL of aqueous phase containing 5 $\mu\text{g/L}$ Cu^{2+} , 0.1% (v/v) Triton X-114, 2×10^{-6} M Schiff base, 35°C, incubation time 20 min.

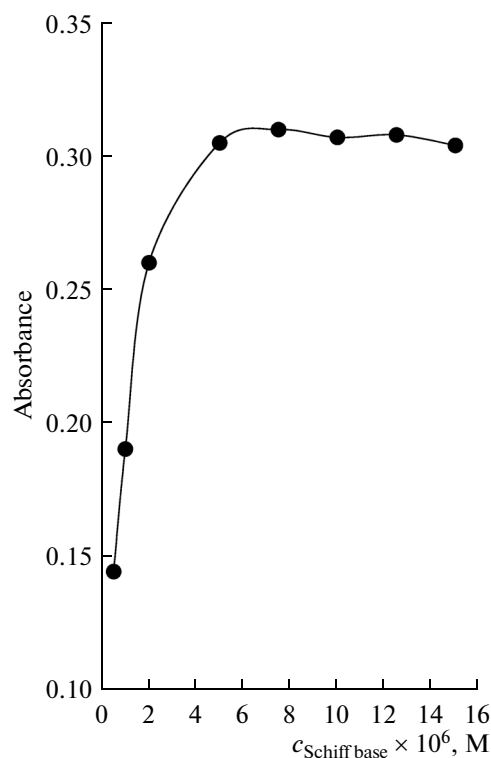


Fig. 2. Effect of the amount of the Schiff base on the cloud-point extraction of copper. Experimental conditions as in Fig. 1.

tion was verified by performing a series of experiments using different amounts of the studied Schiff base (Fig. 2). It was found that the absorption augments by increasing the ligand concentration. This confirms the ligand mediates extraction procedure. However, the signal was not altered by addition the ligand concentration beyond 5×10^{-6} M (50 μL from 1×10^{-3} M of the Schiff base solution). This observation can be interpreted by considering a quantitative extraction of the analyte in such conditions.

Effect of the Triton X-114 concentration. Triton X-114 is a non-ionic surfactant extensively used in CPE. This is due to its advantages such as commercial availability with high purity, low toxicity and cost, high density of the surfactant-rich phase facilitating the phase separation by centrifugation and relatively low cloud-point temperature. Figure 3 shows the effect of the amount of this non-ionic surfactant in the range of 0.02–0.14% (v/v) on the CPE efficiency of copper(II) ions. The results reveal that the amounts of Triton X-114 providing a volume ratio (micelle to aqueous phase) higher than 0.04% cause a quantitative extraction of the copper ions from aqueous samples using a single step extraction procedure. At lower concentrations, the extraction efficiency of complexes is low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively.

Thus, a concentration of 0.06% (v/v) Triton X-114 was used for subsequent experiments.

Incubation time and temperature dependency of the process. Incubation time and temperature are among the most important parameters to be optimized in order to achieve easy phase separation and efficient preconcentration in CPE processes. It is desirable to employ the shortest incubation time and the lowest incubation temperature possible. The phase volume ratio of all non-ionic surfactants decreases as the incubation temperature is raised. Therefore, a greater enrichment factor can be obtained under conditions where the CPE is performed using an incubation temperature above the cloud-point temperature of the surfactant. The dependency of extraction recovery on the incubation temperature and time was studied in the range 25–60°C and 2–30 min, respectively. The results showed that an equilibration time of 15 min and 35°C were adequate to achieve quantitative extraction.

Effects of added electrolyte. The cloud-point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds. Most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency. An increase in the ionic strength in the CPE does not seriously alter the efficiency of extraction of the chemical forms. More-

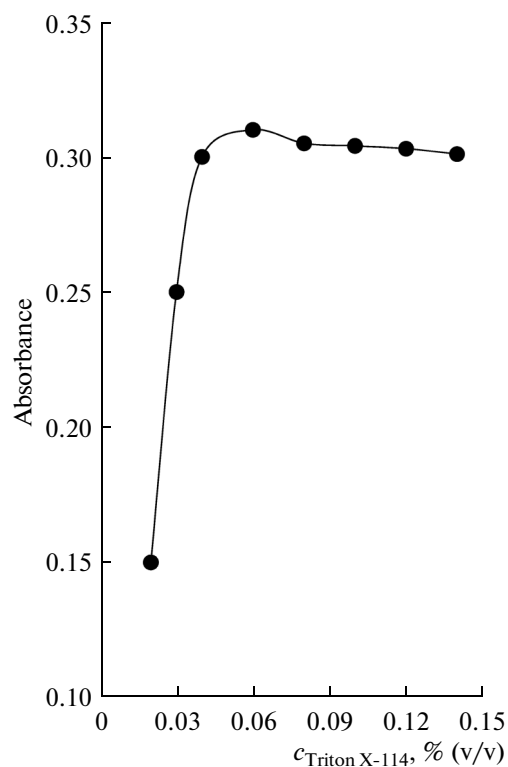


Fig. 3. Effect of the amount of Triton X-114 on the cloud-point extraction of copper. Experimental conditions as in Fig. 1, except for the ligand concentration which was 5×10^{-6} M.

over, the addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some non-ionic surfactant systems, since it alters the density of the bulk aqueous phase [12]. It was observed that the addition of NaCl within 0–0.5 M had no significant effect on the CPE efficiency in the present study.

Interferences study. To perform this study, 10 mL of solution containing 50 $\mu\text{g/L}$ Cu(II) and interfering ion in different interfering-to-analyte ratios was subjected to the extraction procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recoveries of Cu(II) less than 95%, are given in Table 1.

Analytical figures of merit. Using the optimized conditions for the proposed CPE method, the obtained calibration graph was linear from 1–400 $\mu\text{g/L}$. Preconcentration factor was equal to 20. It was calculated as the ratio of the aqueous solution volume (10 mL) to that of the surfactant-rich volume after dilution with nitric acid (0.5 mL). The RSD of the method was calculated to be 1.0% (copper concentration 50 $\mu\text{g/L}$ and 5 replicate experiments). The limit of detection, defined as $3s_b/m$ (where s_b and m are the standard deviation of the blank and the slope of calibration graph, respectively), was found to be 0.3 $\mu\text{g/L}$.

Applications. In order to validate the proposed methodology, the developed procedure was applied to the determination of copper in six water samples including two samples of tap water (Qom city and Zanjan city), three samples of well water (Qom, Zanjan and Kurdistan provinces) and a sample of river water (Abhar, Zanjan province). The results (Table 2) show that the proposed procedure is applicable to demonstrate recovery, preconcentration and determination of copper ions in water samples.

The Schiff base bis(2-hydroxynaphthaldehyde)-1,2-propanediimine is successfully used in a CPE procedure for preconcentration of copper in water samples by FAAS. This study presents the development of a low cost, rapid, easy to use, safe and environmentally friendly method for the determination of trace amounts of copper. Table 3 shows a comparison of the proposed procedure with some other reported CPE methods for determination of copper. It is seen that, the linear range and corresponding dynamic range and the limit of detection of the proposed method is superior to those reported in the literature. However, a comparison of the parameters shown in Table 3 with those reported by using

Table 1. Tolerance limits of interfering ions in the determination of 50 µg/L of Cu(II)

Added cation (M^{n+})	M/Cu molar ratio	Copper recovery, %	Added anion (A^{m-})	A/Cu molar ratio	Copper recovery, %
Na ⁺	1000	100.4	Cl ⁻	800	97.8
K ⁺	1000	98.2	Br ⁻	300	100.3
Ca ²⁺	1000	98.4	I ⁻	1000	100.0
Mg ²⁺	1000	97.6	ClO ₃ ⁻	1000	97.5
Ag ⁺	800	103.2	SCN ⁻	800	100.2
Cd ²⁺	1000	101.2	SO ₄ ²⁻	1000	100.4
Co ²⁺	1000	98.9	Cr ₂ O ₇ ²⁻	1000	97.2
Pb ²⁺	700	97.3	S ₂ O ₃ ²⁻	200	100.6
Ni ²⁺	500	104.2	C ₂ O ₄ ²⁻	1000	101.0
Zn ²⁺	400	101.0			
Mn ²⁺	400	103.6			
Eu ³⁺	700	96.9			
Th ⁴⁺	1000	93.0			

Table 2. Determination of copper in the water samples by the proposed method

Sample	Added, µg/L	Found*, µg/L	Recovery, %
Tap water (Zanjan City, Feb. 2009)	0	ND**	—
	5	4.96 ± 0.05	99.2
	10	9.93 ± 0.03	99.3
Tap water (Qom City, Mar. 2009)	0	ND	—
	5	4.75 ± 0.04	95.0
	10	10.21 ± 0.03	102.1
Well water (Dizjoun, Qom Province, Apr. 2009)	0	2.83 ± 0.03	—
	5	7.23 ± 0.05	92.3
	10	13.04 ± 0.07	101.6
Well water (Vistan, Zanjan Province, Apr. 2009)	0	3.23 ± 0.04	—
	5	8.55 ± 0.06	103.9
	10	13.02 ± 0.04	98.4
Well water (Paveh, Kurdistan Province, Apr. 2009)	0	2.97	—
	5	8.07 ± 0.09	101.2
	10	13.03 ± 0.07	100.4
River water (Abhar, Zanjan Province, Apr. 2009)	0	2.10	—
	5	7.01 ± 0.05	98.7
	10	12.39 ± 0.03	102.4

* Mean ± SD, $n = 3$.

** ND—not detectable.

Table 3. Analytical parameters and conditions for the cloud-point extraction of copper in this and other works

Linear range, µg/L	LOD, µg/L	Incubation time, min	Incubation temperature, °C	Concentration factor	Reference
1–250	0.3	10	40	10	[24]
1–100	0.4	15	40	29	[25]
1–260	0.6	15	45	30	[26]
1–250	1.6	25	45	30	[27]
250–500	0.7	20	50	25	[29]
10–1000	5	10	65	22	[30]
1–400	0.3	15	35	20	This work

another Schiff base ionophore [30] reveals the important role of lipophilic nature of an ionophore on the analytical characteristics of a CPE.

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