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# Preconcentration and separation of copper (II) with solvent extraction using *N,N'*-bis(2-hydroxy-5-bromo-benzyl) 1,2-diaminopropane

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## Abstract

Preconcentration and separation with solvent extraction of Cu(II) from aqueous solution using *N,N'*-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane ( $H_2L$ ) as the new extractant has been studied. Separation of Cu(II) from other metal ions such as Cd(II), Ni(II), Zn(II), Pb(II), Cr(III), Co(II) and Mn(II) at aqueous solutions of various pH values and complexing agent  $H_2L$ , has been described. The possible extraction mechanism and the compositions of the extracted species have been determined. The separation factors for these metals using this reagent are reported while efficient methods for the separation of Cu(II) from other metal ions are proposed. From the loaded organic phase, Cu(II) stripping was carried out in one stage with different mineral acid solutions. The stripping efficiency was found to be quantitative in case of  $HNO_3$  and HCl. From quantitative evaluation of the extraction equilibrium data, it has been deduced that the complex extracted is the simple 1:1 chelate,  $CuL$ . The extraction constant has a value of  $\log K_{ex} = -4.05 \pm 0.04$ . © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Solvent extraction; Separation; Preconcentration; Copper(II); *N,N'*-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane

## 1. Introduction

Copper is both vital and toxic for many biological systems [1,2]. Thus, the determination of trace amounts of Cu is becoming increasingly impor-

tant because of the increased interest in environmental pollution [3]. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provides accurate and rapid determination of copper in natural waters and wastewaters [4]. Nevertheless, very frequently for the extremely low concentration copper in waters, a direct determination cannot be applied without their previous preconcentration and separation.

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The most widely used techniques for the separation and preconcentration of trace amounts of Cu are liquid–liquid extraction [4], precipitation [5,6] and chelating resins [7]. The large distribution ratios possible in solvent extraction systems allow the analytical determination of substances present in otherwise non-detectable concentrations. A proper choice of extractant may lead to an increase in concentration by several orders of magnitude. In other words, a large increase in sensitivity is obtained in the analytical method, even when the analyte is analytically detectable in the original sample; its preconcentration by means of solvent extraction permits use of smaller samples, simplification of the procedure, and increased accuracy of the samples. Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained in the same step [8].

Solvent extraction of metal chelate complexes has been used as a separation method for a long time. Recovery of metals from an aqueous phase by solvent extraction is achieved by contacting the aqueous phase with an organic phase that contains a metal selective chelating agent dissolved in a diluent [9]. For extraction of metal ions, it is preferable that the chelating reagent used has a high distribution coefficient and pH dependence in the system chosen [10].

Solvent extraction of copper has become an important process and is used in several hydrometallurgical plants to recover and to separate copper from wastewaters [11]. The commercial reagents designed specifically for copper extraction were a ketoxime-based reagent (LIX 87QN) [12], 8-alkarylsulphonamidoquinoline (LIX 34)

[13], anti-2-hydroxy-5-nonylacetophenone oxime (SME 529) [14], a hydroxyoxime (LIX 64N) [15], aliphatic- $\alpha$ -hydroxyoxime (LIX 63) [8], etc.

A more characteristic combination of solvent extraction with spectrophotometric analysis is found in cases for which the latter is performed on the extracting phase. This historically is also the first instance in which solvent extraction was used in spectrophotometry or, in fact, in chemical analysis in general. Numerous metal ions are extractable by a solution of dithizone in chloroform or in carbon tetrachloride. Organic solutions are obtained in which the metaldithizonate complexes can be determined by spectrophotometry at different wavelengths [8]. Many extractants such as acetyl acetone, 8-hydroxy quinoline, dimethyl glyoxime, cupferron, dithizone and sodium diethyl dithiocarbamate are used for spectrophotometric determination of copper.

In this work a newly synthesized ligand *N,N'*-bis(2-hydroxy-5-bromo-benzyl)] 1,2 diaminopropane ( $H_2L$ , shown in Fig. 1) is studied as an extractant for Cu(II). Extraction and preconcentration of copper(II) from wastewater samples and determination by atomic absorption spectrometry have been reported. However, the separation of Cu(II) from other metal ions and the solvent extraction spectrophotometric method of Cu(II) have been reported.

## 2. Experimental

### 2.1. Reagents

All reagents and solvents were of analytical

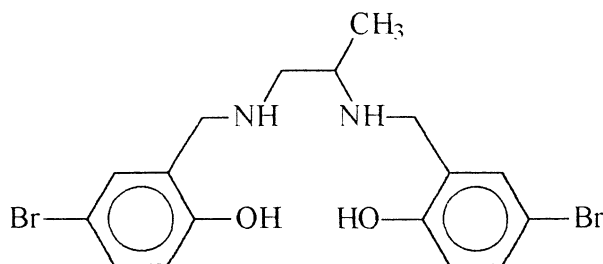


Fig. 1. Structure of *N,N'*-bis(2-hydroxy-5-bromo-benzyl)]1,2 diaminopropane ( $H_2L$ ).

reagent grade.  $H_2L$  was prepared by refluxing 2 eq. of 5-bromo-2-hydroxybenzaldehyde (40 mmol) with 1 eq. (20 mmol) of 1,2-diaminopropane in 100 ml of ethanol for 4 h. The solution turned bright yellow and on cooling the yellow Schiff base solid appeared. The EtOH was removed by rotary evaporation and the solid recrystallized from hot EtOH. Approximately 10 mmol of the Schiff base was dissolved in 100 ml of ethanol and 2 g (52 mmol) of sodium borohydride added in two portions. The mixture was stirred for 2 h, and approximately 40 ml of double-distilled water was added to this. The product precipitated, was filtered out, and recrystallized from hot ethanol.

The structure of the compound was confirmed by FT-IR and NMR spectrometry. Stock solutions of  $Cu^{2+}$  was prepared from  $CuCl_2 \cdot 2H_2O$  and standardized titrimetrically with EDTA [16]. Adjustment of pH of the aqueous phase was made with buffers (acetic, phosphoric and boric acids and their potassium salts). Potassium chloride was added to give a constant ionic strength of 0.1 M.

## 2.2. Apparatus

AA 929 Unicam Spectrometer was used for FAAS measurements with an air–acetylene flame. Absorbance measurements were made using a Cary 1-E UV-Vis Spectrophotometer with 1.0-cm quartz cells. A pH meter (Metrohm 691 pH Meter) was also used. All extractions were performed by using a mechanical flask agitator in 50 cm<sup>3</sup> stoppered glass flasks.

## 2.3. Procedures

### 2.3.1. Extraction procedure

Aqueous solutions containing  $1.0 \times 10^{-4}$ – $1.0 \times 10^{-3}$  mol l<sup>-1</sup> copper (II) chloride in appropriate buffer were equilibrated with equal volumes of the chloroform solution of the ligand ( $1.0 \times 10^{-3}$ – $1.0 \times 10^{-2}$  mol l<sup>-1</sup>) by shaking in a mechanical shaker at 25°C. Optimum equilibration time was determined for this system. In most cases distribution equilibrium was attained in less than 15 min and a shaking time of 30 min was sufficient to obtain reproducible results. The ionic

strength of the aqueous solution was 0.1 M KCl in all experiments except those in which the effect of ionic strength was studied. After agitation, the solutions were allowed to stand for 10 min. The copper concentration of the aqueous phase was determined by FAAS, and that of the organic phase from the difference by considering the mass balance. The pH of the aqueous phase was recorded as equilibrium pH. The absorption of the organic phase after extraction equilibrium had been established was measured spectrophotometrically at 401 nm.

### 2.3.2. Preconcentration procedure

These experiments were carried out in two stages. First, after extraction of the aqueous phase (100 ml) containing 60 µg Cu(II), a 30-ml portion of the organic phase ( $10^{-3}$  M  $H_2L$  in chloroform) was stripped with 15 ml of aqueous acid solutions, including HCl,  $H_2SO_4$ , and  $HNO_3$ . At the second stage, 100 ml of aqueous solution containing 6 µg Cu(II) was extracted with 30 ml of organic phase ( $10^{-3}$  M in chloroform), then stripped by 5 ml of 10% M  $HNO_3$ . The amount of copper in aqueous phase after stripping the organic phase was determined by FAAS, and then the recovery percentage (R%) was calculated.

## 3. Results and discussion

### 3.1. Extraction of copper from aqueous solutions into organic phase

#### 3.1.1. Choice of agitation time and solvent

The effect of the agitation time on the degree of extraction was studied at pH 6.7 with  $[H_2L] = 1 \times 10^{-3}$  M in  $CHCl_3$  and  $[Cu^{2+}] = 1 \times 10^{-3}$  M. In all cases equilibrium was attained in less than 15 min. A shaking period of 30 min was therefore chosen for safety. Various solvents, such as chloroform, dichloromethane, nitrobenzene, isobutyl methyl ketone, toluene, were investigated. Of these, chloroform was found to be the most suitable solvent as the extractability of the complex was very high. Therefore, chloroform was used in subsequent experiments.

### 3.1.2. Effect of pH on the extraction of Cu(II) and other metal ions

Fig. 2 shows the effect of pH on the extraction of Cu(II) into chloroform with  $H_2L$ . As shown in Fig. 2, the copper extraction is quantitative within the pH range of 3.5–10.

### 3.1.3. Effect of ionic strength of the aqueous phase

The influence of KCl in the concentration range of 0.1–1.0 M on the extraction efficiency of copper (II) was studied in solutions containing  $1 \times 10^{-3}$  M  $Cu^{2+}$  with  $10^{-3}$  M  $H_2L$  in the organic phase. The extraction efficiency decreases with increase in ionic strength of the aqueous medium. Taking into account Eq. (5), which will be discussed later, the extraction constant ( $K_{ext}^0$ ) at zero ionic strength for this reaction can be correlated with the ionic strength ( $I$ ) by

$$K_{ext}^0 = K_{ext} \frac{\gamma_{H^+}^2}{\gamma_{Cu^{2+}}} \quad (1)$$

$$K_{ext} = K_{ext}^0 \frac{\gamma_{Cu^{2+}}}{\gamma_{H^+}^2} \quad (2)$$

According to the Debye–Huckel limiting law given by

$$\log \gamma_{\pm} = -0.5z_{\pm}^2 \sqrt{I} \quad (3)$$

the activity coefficient ( $\gamma_{\pm}$ ) decreases with increase in ionic strength. At the constant pH, the activity coefficient of  $Cu^{2+}$  decreases as the ionic strength increases, hence  $K_{ext}$  decreases.

### 3.1.4. Effect of aqueous to organic phase ratio

Phase ratio ( $A/O$ ) is one of the factors that affect the extraction efficiency. The extraction efficiency,  $E\%$  can be represented by [17]

$$E\% = \frac{D}{D + A/O} \times 100 \quad (4)$$

where  $D$  is the distribution ratio,  $A$  and  $O$  are the volumes of the aqueous and organic phases, respectively. Equation indicates that the extraction efficiency decreases with increasing  $A/O$  ratio. Fig. 3 shows the effect of  $A/O$  on percentage extraction which was satisfied by Eq. (4).

### 3.1.5. Effect of temperature

The influence of temperature on the extraction of copper (II) by  $H_2L$  was studied using  $1 \times 10^{-3}$  M  $Cu^{2+}$  and  $1 \times 10^{-3}$  M ligand concentration. Results showed that there is a slight decrease in copper extraction as the temperature increased.

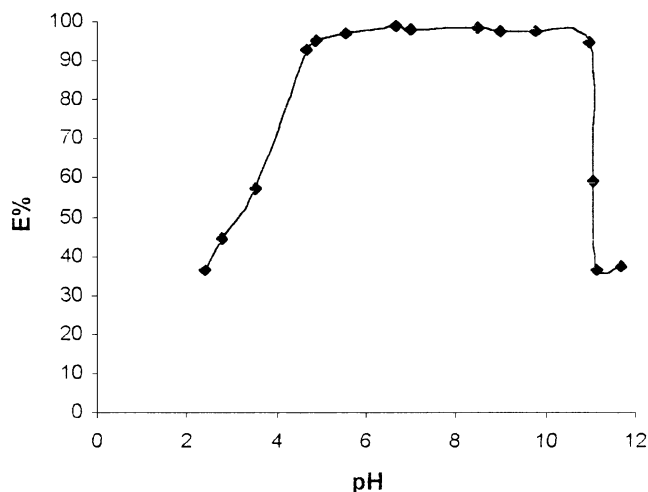


Fig. 2. Effect of pH on the extraction of Cu(II) and other metal ions.

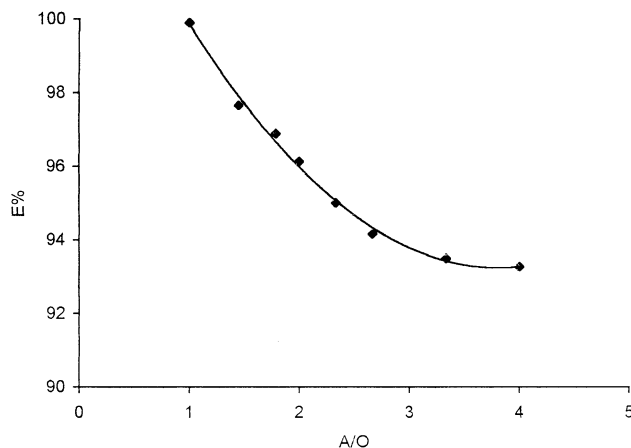


Fig. 3. Effect of the  $A/O$  ratio on the extraction of Cu(II) with  $H_2L$  in chloroform.

### 3.2. Spectrophotometric determination method of Cu(II)

The absorption spectra of the ligand ( $H_2L$ ) and  $CuL$  complex are shown in Fig. 4. As seen, the spectra of  $CuL$  complex have two maxima, one of which overlaps with the maximum of ligand at 285 nm. The other maximum appears at 401 nm at which the ligand has no absorbance. Therefore, wavelength 401 nm has been used in all subsequent measurements of absorbance.

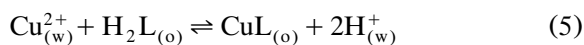
#### 3.2.1. Extractability of the complex

The aqueous phase (15 ml) containing  $10^{-4}$  M Cu(II), buffer and 0.1 M KCl were extracted with successive 15 ml portions of  $10^{-3}$  M  $H_2L$  in chloroform. The absorbance of the organic phase after each extraction was measured at 401 nm using chloroform as a reference. The results are given in Table 1. Each absorbance of the second to fourth extract for Cu(II) was in complete agreement with that of the second to fourth reagent blank. This result indicates that extraction with 15 ml portion of chloroform containing  $10^{-3}$  M  $H_2L$  at only one stage is sufficient for complete extraction of the complex.

#### 3.2.2. Composition of the extracted species

If only mononuclear species are extracted, under the conditions in which chloride does not take

part in the distribution equilibrium, the extraction process may be represented by the equation,



where  $H_2L$  represents the extractant reagent and subscripts (w) and (o) denote the aqueous and organic phases, respectively. The extraction constant of the species  $CuL$  is given by

$$K_{ext} = \frac{[CuL]_o [H^+]_w^2}{[Cu^{2+}]_w [H_2L]_o} \quad (6)$$

When  $CuL$  is the only extractable species and the metal is present in the aqueous phase predominantly as the cation  $Cu^{2+}$ , the metal distribution ratio ( $D$ ) and the extraction constant are related by

$$\log D = \log K_{ext} + 2pH + \log [H_2L]_o \quad (7)$$

where

$$D = \frac{[Cu]_o}{[Cu]_w} = \frac{[CuL]_o}{[Cu]_w} \quad (8)$$

According to Eq. (7) a plot of  $\log D$  against pH at constant  $5 \times 10^{-3}$  M of  $[H_2L]$  will give straight line of slope is two and intercept  $\log [H_2L]_o + \log K_{ext}$  (Fig. 5). A plot of  $\log D - 2 \text{ pH}$  against  $\log [H_2L]_o$  (Fig. 6) will give a straight line of slope

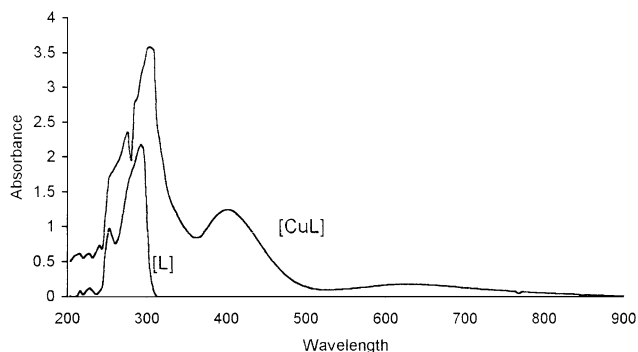


Fig. 4. The absorption spectra of the ligand ( $H_2L$ ) and CuL complex.

Table 1  
Extraction of copper(II) as CuL

No. of extractions	Absorbance	
	Reagent blank	$1 \times 10^{-4}$ M $Cu^{2+}$
1	0.0151	0.1886
2	0.0149	0.0151
3	0.0150	0.0149
4	0.0152	0.0150

and intercept  $\log K_{\text{ext}}$ ; hence, from the graphs shown in Figs. 5 and 6 the extraction constant ( $\log K_{\text{ext}}$ ) has been calculated as  $-4.05$ .

In order to confirm the stoichiometry of the CuL complex additional spectrophotometric measurements were performed by using Job and slope-ratio method [17]. Both Job's method and the slope ratio method confirm the 1:1 stoichiometry of the CuL complex.

### 3.2.3. Determination of Cu(II)

The applicability of the  $H_2L$  for determination of Cu(II) spectrophotometrically was studied in the range of  $5 \times 10^{-6}$ – $7 \times 10^{-4}$  M Cu(II) solutions buffered at pH 4.75. The concentration of  $H_2L$  in chloroform was  $10^{-3}$  M. The effective molar absorption was calculated after from the data obtained by the measurements of organic phase absorbance at the conditions extraction was completed. The calibration graph obtained was a straight line passing through the origin over the range of mentioned above. The molar absorptivity at 401 nm was  $1.511 \times 10^3 \text{ mol}^{-1} \text{ l cm}^{-1}$ . The complex obeys Beer's law from 0.32 to  $44.5 \mu\text{g ml}^{-1}$  with an optimum range. The relative standard deviations were 0.16% (11 samples, each containing  $31.77 \mu\text{g ml}^{-1}$  copper). The precision was determined from 30 results obtained for  $5 \times 10^{-4}$  M Cu(II); the mean value of a copper(II)

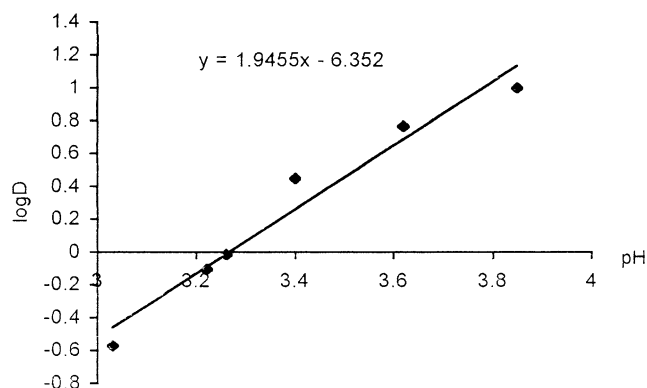
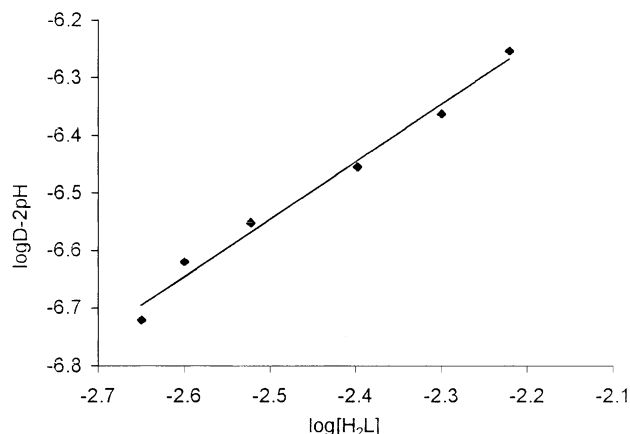


Fig. 5. The plot of  $\log D$  vs. pH at constant  $[H_2L]$ .

Fig. 6. The plot of  $\log D - 2pH$  vs.  $\log H_2L$ .

was  $5.06 \times 10^{-4}$  M with a standard deviation of  $8.27 \times 10^{-7}$  M copper(II).

There were no measurable changes in the absorbance of the extracts even after standing for 5 days in a glass-stoppered tube at room temperature.

The proposed method was applied for the analysis of different samples containing copper (Table 2). The obtained results which was compared with those obtained by FAAS, indicate that the proposed procedures provide very good precision. The comparison of the copper contents of samples obtained by proposed and FAAS methods were made by using *t*-test [14]. The test results shown in Table 2 indicate that there is no significant difference between two methods. In different ores and wastewater samples, one of the ions

interfering the determination was  $Fe^{3+}$  for which NaF was used as a masking agent. The results of the six replicate determination of copper in samples are tabulated in Table 2.

#### 3.2.4. Effect of foreign ions

The effect of foreign ions on the spectrophotometric determinations of Cu(II) was studied. A 15-ml solution containing  $9.74 \text{ mg l}^{-1}$  Cu(II) and various amounts of foreign ions extracted with organic phase containing  $10^{-3}$  M  $H_2L$ , and the amount of copper(II) was calculated from the absorbance of organic phase after extraction. The results are given in Table 3,  $10 \text{ mg l}^{-1}$  concentration Fe(III) interfered to the absorbance of the complex. The interference from Fe(III) was eliminated by using excess  $F^-$ . The interference from

Table 2  
Analysis of samples for copper

Sample	Proposed method	FAAS method	<i>t</i> -Test	
			$ \bar{X}_1 - \bar{X}_2 $	$\pm ts \sqrt{\frac{N_1 + N_2}{N_1 N_2}}$
Lead ore	$43.054 \pm 1.2 \text{ g/kg}$	$44.074 \pm 1.6 \text{ g/kg}$	1.016	1.62
Copper ore	$121.23 \pm 5.9 \text{ g/kg}$	$121.26 \pm 5.3 \text{ g/kg}$	0.03	3.1
Magnetit	$2.510 \pm 0.05 \text{ g/kg}$	$2.429 \pm 0.023 \text{ g/kg}$	0.081	0.124
Wastewater	$17.08 \pm 0.06 \text{ mg/l}$	$17.70 \pm 0.9 \text{ mg/l}$	0.62	0.81

If the experiment difference  $|\bar{X}_1 - \bar{X}_2|$  is smaller than the computed value  $(\pm ts \sqrt{(N_1 + N_2)/(N_1 N_2)})$ , no significant difference between the means has been accepted at 95% CI.

Table 3  
Effect of foreign ions on the determination 9.74 mg l<sup>-1</sup> of Cu(II)

Ion	Amount added (mg/l)	Cu <sup>2+</sup> found (mg/l)	Error%
None	–	9.74	–
Cr <sup>3+</sup>	1000	9.60	–1.4
Fe <sup>3+</sup>	10	10.29	5.7
Al <sup>3+</sup>	1000	9.73	–0.1
Ni <sup>2+</sup>	1000	9.73	–0.1
Zn <sup>2+</sup>	1000	9.40	–3.5
Co <sup>2+</sup>	100	9.90	1.6
Mn <sup>2+</sup>	1000	9.79	0.5
Cd <sup>2+</sup>	1000	9.50	–2.5
Pb <sup>2+</sup>	1000	9.43	–3.2
Ca <sup>2+</sup>	1000	9.60	–1.4
Mg <sup>2+</sup>	1000	9.65	–0.9
Ba <sup>2+</sup>	1000	9.71	–0.3
Na <sup>+</sup>	1000	9.74	–
K <sup>+</sup>	1000	9.74	–
CO <sub>3</sub> <sup>2-</sup>	1000	9.70	–0.4
SCN <sup>-</sup>	100	9.71	–0.3
PO <sub>4</sub> <sup>3-</sup>	1000	9.75	0.1
NO <sub>3</sub> <sup>-</sup>	1000	9.73	–0.1
CH <sub>3</sub> COO <sup>-</sup>	1000	9.74	–
Cl <sup>-</sup>	1000	9.74	–
Br <sup>-</sup>	1000	9.73	–0.1
F <sup>-</sup>	1000	9.66	–0.8
I <sup>-</sup>	1000	9.70	–0.4
NH <sub>4</sub> <sup>+</sup>	1000	9.84	1.0
SO <sub>4</sub> <sup>2-</sup>	1000	9.72	–0.2
C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> <sup>2-</sup>	1000	9.50	–2.5

Co(II) and SCN<sup>-</sup> were observed after 100 mg l<sup>-1</sup>. The other ions listed in Table 3 did not interfere in amounts up to 1000 mg with an error below 4%. The interference from Fe(III) and Co(II) is due to the spectral interference.

### 3.3. Separation of Cu(II) from other metal ions

The separation of the metal ions based on the pH adjustment was assisted by the observation that some of the metals were quantitatively extracted at certain pH values at which others were extracted minimally or not at all. This means that it was possible to predict the separability of Cu(II) from other metal ions. The degree of separation was determined in terms of 'separation factor',  $S_f$  defined as the ratio of  $D_1$  for the desired metal ion  $M_1$  to  $D_2$  for the contaminant metal ion  $M_2$ .

$$S_f = D_1/D_2 = \frac{[M_1]_{(org)}/[M_1]_{(aq)}}{[M_2]_{(org)}/[M_2]_{(aq)}} \quad (9)$$

At certain pH values, Cu(II) is quantitatively extracted with 0.01 M H<sub>2</sub>L in chloroform alone from synthetic binary mixtures of Cu(II) with other metal ions (Table 4). All of these separations are based upon the magnitude of the separation factor ( $S_f$ ). Only those separations indicating a large separation factor ( $S_f = \infty$ ) was preferred while selecting optimum conditions for separations. As shown in Table 4, the separation of Cu(II) is possible from Ni(II), Cr(III), Co(II), Cd(II), Mn(II), Zn(II), Pb(II) at pH 3.5. Furthermore, the separation of Cu(II) from Fe(III) is difficult because the separation factors are in the range of 0.7–1.5. This separation factor can be increased by masking Fe(III) in the presence of



Table 4  
The separation factor for the separation of Cu(II) from other metals

Metal ion	pH = 3.5	pH = 4.8	pH = 5.8
Cr(III)	∞	475	265
Ni(II)	∞	153	406
Fe(III)	0.7	0.4	1.5
Co(II)	∞	1628	101
Mn(II)	∞	∞	∞
Zn(II)	∞	26572	4508
Pb(II)	∞	35908	518
Cd(II)	∞	∞	∞

NaF, so Cu(II) was quantitatively extracted in organic phase.

#### 3.4. Preconcentration of Cu(II) and determination with FAAS

The effect of various acids on the stripping of the aqueous solution containing 0.6 ppm Cu(II) has been given in Table 5 for the preconcentration purpose. The highest recovery values, almost quantitatively have been obtained with 3% HCl and 10% HNO<sub>3</sub>. The results obtained by using 10% HNO<sub>3</sub> for preconcentration of 0.06 ppm Cu(II) solutions have been shown in Table 6, indicating that the recovery is 99.8%. The proposed procedure has been applied to the wastewater samples obtained from different plants before and after the addition of 0.4 ppm Cu(II) to the sample. As can be seen from the data given in Table 7, it has been concluded that the amount of Cu(II) can be determined by using FAAS after the proposed preconcentration procedure.

By following the proposed procedure, the effect of various ions on the preconcentration of Cu(II)

and on the determination by FAAS was investigated. For the determination by FAAS of 75 µg of Cu(II) in 100 ml, no interference was caused by 1000 mg/l of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, Ba<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, I<sup>-</sup>, F<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, tartarat ion, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup> and 100 ppm SCN.

#### 4. Conclusions

The results indicate that H<sub>2</sub>L in organic phase extracts efficiently copper(II) in aqueous phase containing 0.1 mol l<sup>-1</sup> KCl in the pH range of approximately 4.5–10 at 25°C. The extraction mechanism corresponds to a cation exchange, in which a complex of stoichiometric formula (CuL) is formed in the organic phase liberating at the same time 2 mol H<sup>+</sup> ions in the aqueous phase. The extraction reaction is exothermic and logK<sub>ex</sub> = -4.05 ± 0.04.

Although the effective molar absorption coefficient found for H<sub>2</sub>L seems to be lower than other ligands proposed for the determination of copper by solvent extraction method, the suggested procedure has some additional advantages that proposed method may be interfered only by a few ions (Fe<sup>3+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup> and SCN<sup>-</sup>) and also that it has a high precision and a low standard deviation. The developed procedure was also applies on environmental samples of ore and wastewater samples.

The separation of Cu(II) from other metal ions by an extraction process is investigated by using *N,N'*-bis(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane. A single extraction and stripping gave a good separation and preconcentration of Cu(II)

Table 5  
The effect of acids on stripping

Acid%	HCl			H <sub>2</sub> SO <sub>4</sub>			HNO <sub>3</sub>		
	3%	5%	10%	5%	10%	20%	5%	10%	20%
Found	60	58.8	58.2	59.3	52.3	34.0	57.0	60.0	58.2
R%	100	98	97	98.7	87.2	56.7	95	100	97

Table 7  
The application of the preconcentration procedure on wastewater samples

Wastewater samples	Amount added μg/ml	Found μg/ml	Recovered	R%	R.S.D.%
Sulfuric acid factory	–	35.78	–	–	1.1
	0.4	36.2	0.42	105	2.1
Boric acid factory	–	0.14	–	–	2.0
	0.4	0.54	0.4	100	2.4
Leather factory I	–	0.15	–	–	1.5
	0.4	0.54	0.39	97.5	3.1
Leather factory II	–	0.117	–	–	2.5
	0.4	0.511	0.394	99	0.8

from other metal ions in aqueous solutions. The separation of Cu(II) can be accomplished quantitatively from other metal ions except Fe(III) at pH 3.5. This separation factor for Fe(III) can be increased in the presence of NaF, by masking Fe(III); by this way Cu(II) quantitatively extracted into organic phase. From the loaded organic, Cu(II) stripping efficiency was found to be quantitative.

A preconcentration process has been proposed for the determination of Cu(II) in water samples which contain so trace concentrations of Cu(II) that they cannot be measured directly by FAAS. It has been shown that the extraction of aqueous phase containing Cu(II) with organic phase containing H<sub>2</sub>L and then stripping the organic phase with 10% HNO<sub>3</sub> give a solution Cu(II) which can directly be analyzed by FAAS. In this determination procedure, the foreign ions in the solution has been found not to interfere the absorbances.

As a result it can be concluded that the proposed procedure can satisfactorily be considered as an alternative application for preconcentration and separation of copper in various samples.

Table 6  
The effect of initial concentration of Cu(II) on the preconcentration procedure

	Initial concentrations of copper (II)	
	0.6 ppm	0.06 ppm
Found	0.6	0.0594
R%	100	99.8
R.S.D.%	1.1	0.85

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