LIQUID- LIQUID EXTRACTION OF COPPER (II) WITH 1-NAPHTHYL BENZOHYDROXAMIC ACID

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ABSTRACT

The extraction of copper(II) ion from aqueous solution of pH 5 was studied by using 1-naphthylbenzo hydroxamic acid (NBHA). Quantitative extraction was obtained after 25 min. The extract is colorless having maximum absorbance at 320 nm with molar absorptivity of 1.2×10^3 L mol^{-1} cm^{-1}. The amount of copper was determined in the raffinate by absorption spectrophotometry at 510 nm using PAR as chromogenic reagent. The molar absorptivity of the solution is 7×10^4 L mol^{-1} cm^{-1}.

The selectivity of copper extraction was investigated in the presence of diverse ions and the results showed that iron(III) and citrate are the main interfering ions in the procedure. The thermodynamic functions associated with the extraction process are evaluated from the distribution measurements.

Key Words: Extraction; Copper(II); Hydroxamic acid; Thermodynamics.

1. INTRODUCTION

The presence of copper is both vital and toxic for biological systems /1,2/, hence its separation and determination from different mixtures is important.

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There are many different methods for separation and determination of copper at various levels in the literature such as ion exchange using Dowex 1 /3/, Dowex 50W-X_2 /4/ and Chelex-100 /5,6/.

Dithizone is used for extractive spectrophotometric determination of copper but the intensity of solution color and the sensitivity depends upon the acidity of the solution. Complex formation is slow, necessitating prolonged shaking time. Noble metals such as Pt, Pd, Au, Hg are co-extracted with copper, the anions citrate and tartrate inhibit the extraction by complexing copper ion. The interference of noble metals can be eliminated by the difference of extraction rates. Excess dithizone should be removed with dilute ammonia to prevent the conversion of primary complex (violet) to the secondary complex (yellow) /7,8/.

Dithiocarbamates have been used too /9,10/. However, many metals such as Fe, Bi, Mn, Ni, Co, Cr, Mo, U, Cd, Pb, Zn and In interfere which necessitates long procedural masking and stripping. Some of these dithio-carbamates are insoluble in organic solvents or decompose easily /11/.

Liquid-liquid extraction technique is widely used for preconcentration and separation of metal ions /12,13/. Different methods have been used and reported for the extraction of copper such as: 50% extraction with D_2EHPA from HCl solution /14, 15/, diethyldithio phosphoric acid (HDEDTP) in CCl_4 /16/, tri-n-butyl phosphate (TBP) /17,18/, tri-n-octyl phosphine oxide (Topo) from 7M HCl /19/, methyl-di-n-octylamine in trichloro ethylene with 80% extraction /20/, as ion- association with SCN^- by diethyl ether (3% extraction) /21/, triphenyl methyl arsonium chloride into o-dichloro benzene /22/, cuproine and neocuproine /23,24/, potassium ethylxantate into chloroform /25/, acetylacetone and benzoylacetone into benzene /26/, thenoyltrifluroacetone in benzene /27/. Hydroxamic acids which are known as versatile chelating agents are used for extractive determination of Be /28/, La /29/ and Copper /30/.

The separation system bearing a dissociable proton is an effective one and there is no need for a counter anion to counterbalance the positive charge of a metal ion /31/.

The development of effective and selective systems for studying the extraction of Cu(II) is a remarkable task from both a practical and a theoretical viewpoint.

1-Naphthyl benzohydroxamic acid has been reported to transport copper ions /32/. However the maximum transport of 70% is achieved after 35 hours and the influence of experimental parameters on the efficiency of extraction

has not been evaluated, which is an important task for the method development. With this viewpoint we decided to determine the optimum conditions for extraction of copper. In the present paper we describe the ability of 1-naphthyl benzohydroxamic acid to extract copper (II) by taking into account the influence of different experimental parameters such as: pH, equilibration time, ligand concentration, solvent type and temperature.

In order to establish the selectivity of the method, copper was extracted from its mixtures with different ions.

2. EXPERIMENTAL

2-1. Apparatus

A Julabo model Mp-5 circulatory thermostated water bath for temperature control (± 0.1°C),a Heraeus model labofuge 300 centrifuge were used for complete separation of aqueous and organic phases after extraction, and a Shimadzu 240 uv-vis, spectrophotometer with matched 10 mm quartz cells was employed for spectral measurements.

Interference measurement was performed by using a Perkin-Elmer 2100 atomic absorption spectrometer. Elemental analysis was done with a Perkin-Elmer 2400; IR spectra were recorded on a UNICAM- Matson 1000 FTIR spectrometer with KBr pelets. NMR spectra were obtained by a JEOL EX-90A spectrometer in $CDCl_3$ with TMS as internal standard. The melting point was obtained with an Electro thermal 9100 apparatus.

2-2. Reagents

All chemicals used were of analytical reagent grade from Merck or Fluka. Buffer solutions of pH 3-6, 6-9 were prepared by mixing appropriate ratios of 0.5 M acetic acid and 0.5 M sodium acetate, 0.1 M sodium dihydrogen phosphate and 0.1M dipotassium hydrogen phosphate. Copper stock standard solution was prepared by dissolving 0.695 g copper nitrate pentahydrate in water and diluting up to 250 ml with deionized glass double distilled water. Its final concentration (1.15×10^{-2} *M*) was determined titrimetrically in the presence of fast sulphon black F with standard EDTA solution (0.01 M) /33/. Working solutions were obtained by appropriate dilution. 4(2-pyridylazo) resorcinol (PAR) from Fluka was used as received and a stock solution of 2.7 $\times 10^{3}$ M in deionized glass double distilled water was prepared for

spectrophotometric determination of copper /34/.

2-3. Hydroxamic acid

1-Naphthyl benzohydroxamic acid was synthesized as follows :

a) Reduction of 1-nitronaphthalene by 80% hydrazine hydrate in the presence of Raney nickel at low temperature to 1-naphthylhydroxylamine /32/.

b) Reaction of 1-naphthylhydroxylamine with an equimolar amount of benzoylchloride in benzene at low temperature (0-5°C) in the presence of 5% aqeuous sodium hydrogen carbonate drop by drop within 2 hours.

The produced residue was recrystallized from water-ethanol mixture and then the colorless crystals characterized by mp, NMR, IR and elemental analysis.

The results obtained were in good agreement with those reported /32/. A stock solution of NBHA (2.5×10^{-2} mol/L) was prepared by dissolving 0.65 g of the reagent in chloroform and diluting up to 100ml.

2-4. Extraction procedure

A 5 ml aliquot of sample solution containing 10-50 μg/ml copper (II) ions was transferred into a 10ml calibrated flask. The solution was made up to the mark with 5ml buffer solution of pH5. The content of the flask was transferred into an extraction cell placed in a thermostated water bath. 10ml of 2×10^{-2} mol/L ligand solution in chloroform was added (equal vol. of aq. and org. phases). The extraction equilibrium was reached after 25 min. under magnetic stirring. After the phase separation and collection of the organic layer, the extraction was repeated with another 5ml of ligand solution to ensure the complete recovery of copper. The concentration of copper remaining in the rafinate was measured spectrophotometrically using PAR.

For this procedure, 5 ml of aqeuous phase was mixed with 1 ml PAR solution in a 10 ml calibrated flask and made up to the mark by adding buffer solution of pH 10 and KNO_3 solution to adjust the final ionic strength at 0.7M. The absorbance was measured against the reagent blank at 510 nm.

The values of percentage extraction (%E) and distribution ratio (D) of copper were calculated at different pH and ligand concentrations from the absorbance of aqueous phase before and after equilibration by the equations 1 and 2.

$$\%E = \left(\frac{A_0 - A_{eq}}{A_0}\right)100 \tag{1}$$

$$D_M = \frac{A_0 - A_{eq}}{A_{eq}} \tag{2}$$

where A_0 and A_{eq} are absorbances of aqueous solution before and after extraction respectively.

3- RESULTS AND DISCUSSION

3-1. Effect of pH and equilibration time

The percentage of extraction is influenced by the pH of aqueous solution.

Maximum extraction of copper was obtained in a pH range of 4.5-5.5 (Fig. 1); at the lower and higher pH the extraction is incomplete, which may be due to the protonation of the reagent at lower pH than 4.5 and hydrolysis of copper ion at higher pH than 5.5.

In order to establish the optimum equilibration time, the extraction was performed at various time intervals. Since the percentage of extraction depends upon pH, constant pH of 5 was maintained. The results revealed that the quantitative extraction was achieved after 25 min. (Fig. 2). The slow rate of equilibration may be attributed to the steric effect of 1-naphthyl group.
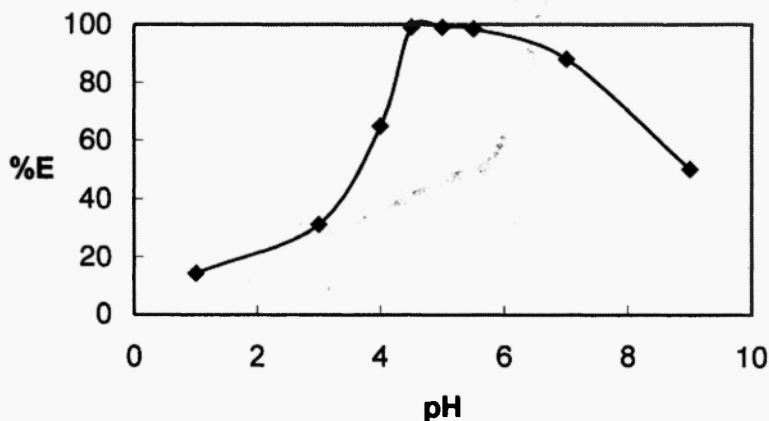

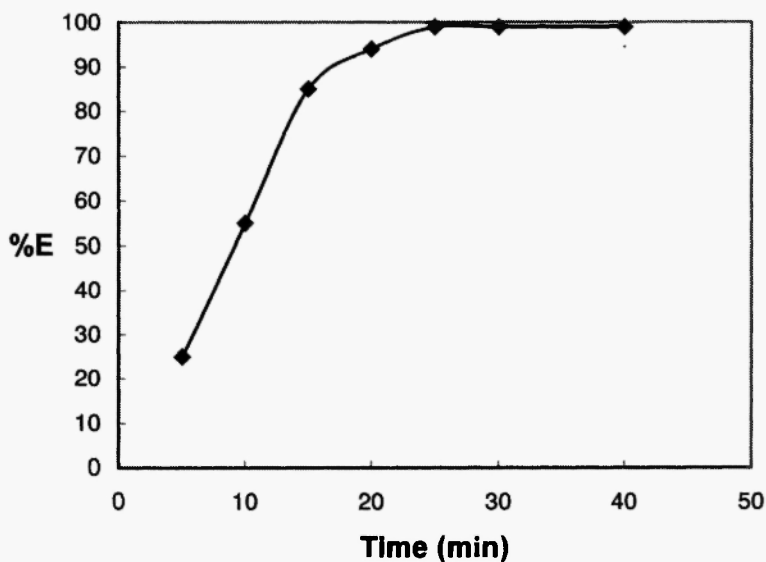**Fig. 1:** Effect of varying pH on the extraction of copper(II).

Fig. 2: Effect of varying equilibration time on extraction of Cu(II).

3-2. Effect of ligand concentration

The effect of ligand concentration was studied by extracting copper $(1 \times 10^{-3}\,M)$ with different amounts of ligand. It was observed that 10ml of $2 \times 10^{-2}\,M$ ligand is adequate for complete extraction of copper. The lower concentration of NBHA reduces the percentage of extraction while an excess of reagent can be used without any difficulty (Table 1).

Table 1

Effect of varying concentration of ligand on the extraction of copper(II).

NBHA $(M \times 10^{-2})$	-log[NBHA]	%E	log D_M
0.5	3.30	71.0	0.39
0.75	3.12	84.9	0.75
1.0	3.0	90.90	1.0
1.5	2.82	94.67	1.25
2.0	2.69	99.0	1.99
2.5	2.6	99.0	1.99

Copper: $1 \times 10^{-3}\,M$, Solvent: Chloroform, pH: 5.0

3-3. Stoichiometry of the complex

The composition of the copper(II)-NBHA complex extracted into chloroform is studied by log-log analysis, i.e. by plotting a graph of the logarithm of the distribution ratio of the metal against the logarithm of ligand concentration, while keeping the initial concentration and pH constant and varying the amount of ligand (equation 5). The plot of log D_M against log [ligand] gave a straight line of slope 1.8 (Fig. 3) indicating the metal/ligand ratio is 1:2.

$$M_{aq}^{n+} + nHL_{org} \Leftrightarrow ML_{n\,org} + nH_{aq}^+ \tag{3}$$

$$K_{ex} = \frac{[ML_n]_{org}[H^+]_{aq}^n}{[M^{n+}]_{aq}[HL]_{org}^n} \tag{4}$$
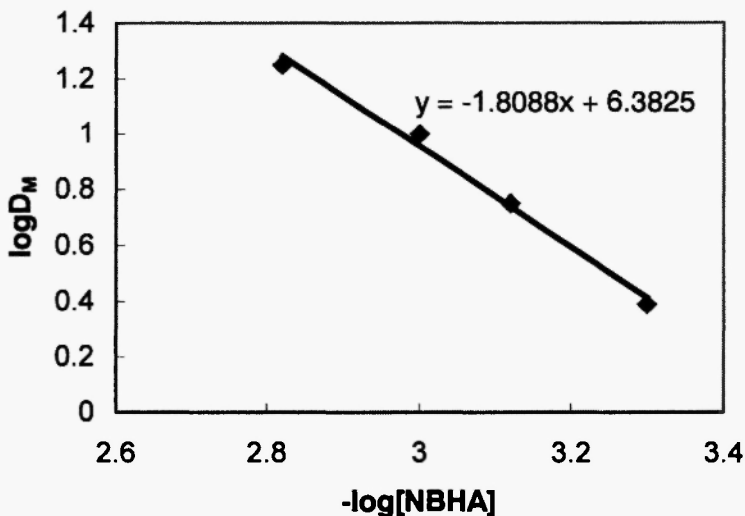

Fig. 3: Plot of distribution of cupper[D_M] against hydoxamic acid[NBHA] in solvent extraction of copper(II).

By introducing $D = \dfrac{[M]_{org}}{[M]_{aq}}$ and taking the log of both sides we obtain

$$\log D_M = \log K_{ex} + n\log[HL]_{org} + npH \tag{5}$$

3-4. Effect of solvent

The extraction was carried out with different solvents like chloroform, benzene, dichloromethane and 1,2-dichloroethane. The results are given in Table 2, and they show that chloroform is the most appropriate solvent for quantitative extraction.

Table 2
Effect of varying solvent on the extraction of copper(II).

Solvent	Extraction (%)
Chloroform	99.0
Benzene	90.0
Dichloroformethane	68.4
1,2-Dichloroethane	57.0

Copper : 1×10^{-3} M ; NBHA : 2×10^{-2} M; pH : 5.0

3-5. Effect of temperature and determination of thermodynamic functions

In order to study the effect of temperature on the extraction of copper by NBHA, a series of extraction experiments was carried out in the range of 283-298 K.

It was observed that the distribution of copper ion decreases with increasing temperature (Table 3). The enthalpy (ΔH°) and entropy (ΔS°) changes were obtained by using van't Holf's equation (6) and from the slope and intercept of the plot of log K_{ex} vs. 1/T (Fig. 4) /35-37/. The free-energy change (ΔG°)was calculated by the Gibbs-Halmholtz equation (7).

$$\log K_{ex} = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} \tag{6}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{7}$$

The calculated thermodynamic functions are presented in Table 3. It should be mentioned that the functions are calculated using concentrations rather than activities, and hence do not represent the real thermodynamic

quantities. However at constant pH (activity of H$^+$), the contribution of activity coefficients must be constant. So the values in Table 3 can be reliable for relative comparison. The data show that the extraction process is exothermic associated with negative entropy changes $(\Delta H^\circ_{ex}\rangle T\Delta s^\circ_{ex})$, i.e enthalpy has a greater influence on the extraction equilibrium and the extraction process is enthalpy driven /38/.

Table 3
Variation of extraction constants with temperature, and thermodynamic functions of Cu(II) extraction

Temperature (K)	log K$_{ex}$	ΔH°(KJmol^{-1})	ΔS°(KJmol^{-1})	ΔG°(KJmol^{-1})
283	1.46			
288	1.43	-15.28	-0.026	-7.63
293	1.38			
298	1.34			

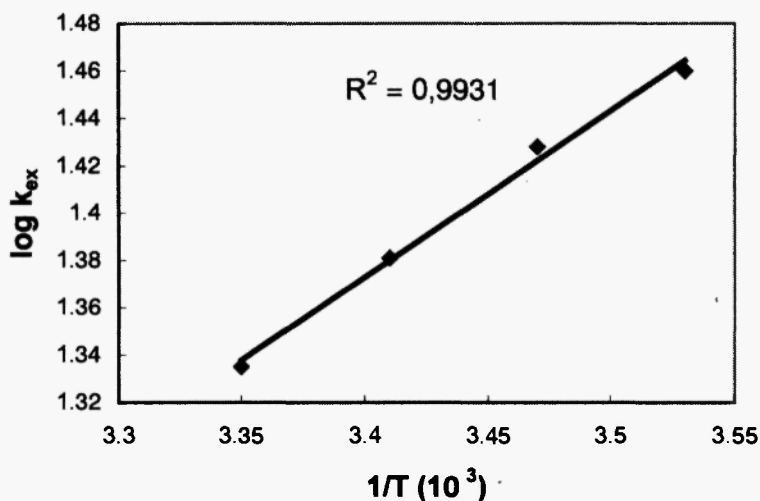Copper: 1×10^{-3} M , NBHA: 2×10^{-2} M, pH: 5.0

Fig. 4: Variation of logK$_{ex}$ with inverse temperature.

3-6. Selectivity of the method

The selectivity of the present method was investigated by separating copper ion from its binary mixtures with several ions. The results are given in Table 4, where Fe(III), I^- and citrate interfered seriously reducing the percentage of extraction by more than 8%. Interference of Fe (III) was eliminated by 2×10^{-3}M oxalate; moreover, it was observed that the interference minimized at lower NBHA concentration ($<3 \times 10^{-3}$M). Addition of oxalate also prevented the precipitation of cations such as Cr(III), Ti(IV) and Fe(III). Mo (VI), which is in the form of MoO_4^{2-} under the experimental conditions, does not interfere. I^- can be removed in the presence of 1ml of 20% hydrogen peroxide solution prior to NBHA addition; citrate should be removed before extraction.

Table 4

Separation of copper from its binary mixtures

Diverse ion	Recovery of copper (%)"
Ag^+	96.8 ($\pm$ 1.2)
Na^+	99.0 ($\pm$ 1.1)
K^+	99.0 ($\pm$ 1.0)
Ca^{2+}	99.0 ($\pm$ 1.0)
Mg^{2+}	99.0 ($\pm$ 0.9)
Fe^{3+*}	93.5 ($\pm$ 1.0)
Co^{2+}	98.5 ($\pm$ 0.7)
Ni^{2+}	97.75 ($\pm$ 1.0)
Zn^{2+}	97.0 ($\pm$ 1.2)
Mn^{2+}	98.5 ($\pm$ 1.1)
V(V)	99.0 ($\pm$ 0.9)
Ti (IV)	98.9 ($\pm$ 1.0)
Mo(VI)	97.8 ($\pm$ 0.9)
I^-**,	99.0 ($\pm$ 0.8)
Citrate	45.0 ($\pm$ 1.0)
Hg^{2+}	94.0 ($\pm$ 0.8)
Pb^{2+}	93.0 ($\pm$ 1.1)

* after masking by 2×10^{-3} mol/L oxalate

** after removal in presence of 20% H_2O_2

Conditions: aqueous phase, 1×10^{-3} mol/L of each ion.

organic phase, 2×10^{-2} mol/L of NBHA in chloroform.

[a] The values in parentheses are the relative standard deviation of three independent analyses.

3-7. Separation and determination of copper in alloy samples

In order to investigate the applicability and the accuracy of the proposed method, it was applied to the standard alloy samples (NIST SRM 629 and NKK 1021). 0.5 g of each sample was dissolved in 15 ml of hot hydrochloric acid (1:1) on a water bath, then 5 ml of hydrogen peroxide (20%) was added to the hot solution, cooled and filtered the solution. The filtrate was diluted in a 250 ml calibrated flask with deionized double distilled water. An aliquot of this solution was taken for extraction and determination of copper. The results are presented in Table 5 and show that the extraction is almost quantitative.

Table 5

Determination of copper in standard alloys

		Copper found (%)	
Sample	**Copper present (%)**	**Spectrophotometry***	**AAS***
NISTSRM 629	1.50	1.45 (±0.1)	1.48 (±0.05)
NKK 1021	2.72	2.64 (±0.1)	2.69 (±0.04)

* The results are average of three analysis, the values in paranteses are relative standard deviation.

4. CONCLUSION

NBHA can extract Cu^{2+} as CuL_2 chelate almost quantitatively at pH range of 4.5-5.5 and at constant temperature of 25°C.

At lower pH than 4.5 the ligand protonates, causing lower extraction. The equilibration time of 25 min. suggests that the chelate formation and rate of

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extraction is influenced by the steric effect of the ligand. Copper ion can be separated from its mixtures with various cations selectively in the presence of oxalate.

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