

Separation via Flotation and Spectrometric Determination of Copper(II) in Environmental Samples using a Newly Synthesized Girard T Derivative

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Abstract

A simple, highly sensitive and selective spectrophotometric procedure was developed for the determination of copper(II) ions. The procedure is based on the reaction at pH 4-7 between the newly synthesized Girard T derivative N-[[[(phenylamino)thioxo methyl] hydrazino carbonyl methyl] trimethyl ammonium chloride (PTHAC) and Cu(II) to form an intense green Cu(II):PTHAC (1:1) complex that floats quantitatively with oleic acid (HOL) surfactant. The different analytical factors affecting the flotation and determination processes were examined viz. pH, temperature, concentration of metal, ligand and HOL, etc. The Cu-PTHAC complexes were characterized by elemental analysis, infrared, mass and electronic spectral studies. The formed Cu(II)-PTHAC complex shows a constant and maximum absorbance at 650 nm in the aqueous and scum layers. Beers' law is obeyed over the concentration range 0.1-6 mg l⁻¹ with a detection limit of 0.03 mg l⁻¹ and molar absorptivities (at λ_{max} 650 nm) of 0.27×10^4 and 0.20×10^5 l mol⁻¹ cm⁻¹ in aqueous and surfactant layers, respectively. Sandell's sensitivity is calculated to be 3.2×10^{-3} μ g cm² and the relative standard deviation (n=5) is <3.72%. The suggested procedure has been successfully applied to the analysis of copper in different natural waters and ore samples. Moreover, the flotation mechanism is recommended based on some physical and chemical studies of the solid complex isolated from the aqueous and scum layers.

Keywords: Copper; Spectrophotometry; Flotation; Natural waters; Ore samples; Girard T

Introduction

Numerous manufacturing wastewater streams (such as those used in metal works, semiconductor, and copper industries, mining, etc.) contain heavy metals which are of excessive environmental worry and must be removed previous to water discharge or water recycling [1-3]. Copper has received substantial attention owing to its uses in metallurgy and chemical industries. Moreover, it is an important constituent of about thirty enzymes and glycoproteins and is essential for the manufacture of hemoglobin and for some biological processes. It also promotes iron absorption from the gastrointestinal system, is involved in the transport of iron from tissues into plasma, aids to maintain myelin in the nervous system, is necessary to the formation of bone and brain tissues and is needed for other many important functions [4,5].

When levels of Cu(II) exceed certain values, however, defense mechanisms to keep against excess Cu are overawed and toxicity results. The reported list of toxic Cu species [6] often includes Cu(OH)⁺, Cu₂(OH)₂²⁺ and CuCO₃. However, without uncertainty, Cu²⁺ ions that are present in several aqueous solutions are measured to be the most toxic of dissolved copper species [4,6]. Therefore, from the viewpoints of pollution, environmental chemistry, geochemistry, marine biology and analytical control in industrial, food, agricultural, pharmaceutical and clinical areas, it is essential to establish a rapid, simple, sensitive and exact procedure for the selective concentration of Cu²⁺.

Flotation has been extensively used for determination of trace heavy metals in media of diverse origin [7-14]. Spectrophotometry still characterizes an attractive technique for the determination of metal ions in aqueous media because of its simplicity, being low-cost and is readily available [15].

Copper has been removed and/or analyzed in virtual waste solutions and natural waters by flotation [16-20]. Though a vast number

of reagents are presented for the spectrophotometric determination of copper [21-25], little work has been done using the newly synthesized Girard T derivative N-[[[(phenylamino) thioxo methyl] hydrazino carbonyl methyl] trimethyl ammonium chloride (PTHAC) and perhaps no trial has been made to float and analyze the analyte with this reagent.

So, the aim of this work is to develop a simple and rapid procedure for the selective separation and determination of copper in natural waters using oleic acid (HOL) as a surfactant and (PTHAC) as a chelating agent. The procedure entails the spectrophotometric determination of copper in the surfactant layer directly after separation by flotation; thus overcoming the problems of elution. The proposed procedure is applied to the analysis of Cu(II) in different environmental samples.

Experimental

Chemicals and solutions

Unless else stated, all chemicals used were of analytical-reagent grade. Doubly distilled water (DDW) was used for preparing aqueous solutions. Oleic acid (HOL) stock solution (6.36×10^{-2} M) was prepared by dissolving 20 ml of HOL (food grade with sp. gr. 0.895, provided by J.T. Baker Chemical Co.) in 1 L of kerosene. Copper stock solution was prepared by dissolving the requisite amount of CuCl₂·2H₂O in doubly distilled water.

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Received July 18, 2014; Accepted August 18, 2014; Published August 26, 2014

Citation: Akl MA, Mostafa MM, Elbadrawy Z (2014) Separation via Flotation and Spectrometric Determination of Copper(II) in Environmental Samples using a Newly Synthesized Girard T Derivative. Chem Sci J 5: 087. doi: 10.4172/2150-3494.1000087

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Preparation of N-[(phenylamino) thioxo methyl] hydrazino carbonyl methyl} trimethyl ammonium chloride (PTHAC)

N-[(phenylamino) thioxo methyl] hydrazino carbonyl methyl} trimethyl ammonium chloride (PTHAC) (Chart 1) was synthesized by boiling, under reflux, a solution of G.T trimethyl ammonium-acethydrazide (16.8 gm, 0.1 M) and phenyl isothiocyanate (12 ml, 0.1 M) in absolute ethanol for 2 hours. The white product was filtered off hot and washed thoroughly with cold solution of absolute ethanol and dry diethyl ether, respectively. The isolated product was dried in an oven at 90°C, crystallized from absolute ethanol and finally dried in a vacuum desiccator over silica gel. The purity of the isolated compound was checked by m.p., TLC and molecular weight measurements. The product is crystalline (m.p.: 215°C) soluble in ethanol and easily soluble in water, DMF and DMSO; therefore its stock solution (1×10^{-3} M) was prepared in DDW.

Apparatus

The flotation cell (a cylindrical tube with 15 mm inner diameter and 290 mm length, a stopcock at the lowest and a stopper at the top) was the same type as previously defined [26]. The spectral data were recorded on Unicam UV 2100 UV-Vis spectrophotometer and were confirmed by flame AAS measurements at 324.7 nm with Perkin-Elmer 2380 atomic absorption spectrometer. The pH was controlled with HCl and/or NaOH and measured with a digital pH meter (Hanna Instruments, model 8519).

Characterization

Elemental analyses (C, H, N) were performed with a Perkin-Elmer 2400 series II analyzer at the Micro Analytical Center at Cairo University, Egypt. Infrared spectra of the studied BMGT and its isolated Cu (II) complex were recorded as KBr discs on Mattson 5000 FTIR spectrophotometer ($400-4000\text{ cm}^{-1}$). Mass spectra were recorded on MS 70 ev EIGC, MS QP-1000 EX Shimadzu (Japan) mass spectrometer at Cairo University.

Analytical procedure

Separation: A suitable aliquot containing a known amount of copper, specified for each investigation, was added to a suitable amount of PTHAC followed by the addition of 3 ml of double distilled water. After modifying with HCl and/or NaOH to the required pH, the solution was transferred to the flotation cell and the total volume was completed to 10 ml with double distilled water. The cell was shaken for a few seconds to confirm complexation. 3 ml of 2×10^{-4} mol/l HOL were added. The cell was then reversed upside down twenty times by hand. Bubbles were shaped inside the cell. The scum layer was separated and the concentration of copper in the surfactant layer was determined spectrophotometrically. The mother liquor was aspirated directly to the flame to determine Cu(II) by flame AAS.

Determination: The concentration of copper in the floated layer was determined spectrophotometrically by transferring a certain

volume to the quartz cell and measuring the absorbance at 650 nm versus the reagent blank (PTHAC). The separation efficiency (%F) was calculated from the relation: $\%F = (C_s/C_i) \times 100\%$

Here, C_s and C_i denote the scum and the initial concentrations of Cu(II), respectively.

The mother liquor was separated from the flotation cell and then introduced directly into the AAS flame for measurement of Cu(II) at 324.8 nm. The floatability of Cu(II) was obtained from the relationship:

$$\%F = (C_i - C_f/C_i) \times 100\%$$

Where C_i and C_f denote the initial and final concentrations of Cu(II).

Analysis of samples

Analysis of water samples: Water samples were obtained as follows: distilled, tap water, river Nile, and sea water from Mansoura City. All samples were filtered through G4 sintered glass. The samples were heated at $<90^\circ\text{C}$ for 30 min, allowed to cool and then 4 ml of 10% $\text{NH}_4\text{OH.HCl}$ was added to reduce excess oxidant immediately before the flotation procedure was carried out. To large flotation cells, five water samples (1 L each) containing a defined amount of Cu(II) and 5 ml of 10^{-3} M PTHAC were added and the pH was adjusted to 7. The reaction mixture was shaken to ensure complete complexation. Then, 8 ml 10^{-3} M HOL was added to each flotation cell and the cells are shaken upside down for five minutes. The scum layer was separated and eluted with 1 mol/l HCl. The final volume was 10 ml.

Analysis of real samples: Lead-zinc sulfide and stream sediment ores were provided from National Center of Metrology, Cairo, Egypt. Accurately 0.5 g solid sample was completely dissolved in Teflon beaker with mixture of acids (45 ml HF, 15 ml H_2SO_4 and 5 ml HNO_3). After complete dissolution, the solution was evaporated till dryness. The residue was then dissolved in 20 ml HCl (1:1) and completed to 100 ml in a measuring flask with bidistilled water. The procedures of flotation, separation, elution and spectrophotometric and or flame AAS determination of Cu(II), were carried out.

Results and Discussion

Absorption spectra

The absorption spectra of Cu-PTHAC in the aqueous and organic layers are completely different from that of PTHAC reagent. PTHAC reagent exhibits a maximum absorbance at 570 nm. The absorption spectra of the Cu-PTHAC in the aqueous and in the scum layer are shown in Figure 1b and 1c, respectively. It is evident that the maximum absorption of the Cu-PTHAC is at 650 nm (with a red shift of 80 nm) at which the ligand does not have any absorption. Moreover, comparing the absorption spectra of Cu-PTHAC in the aqueous, Figure 1b, and in the scum layer, Figure 1c, revealed that only a single complex is formed, the extraction of which into the scum layer enhanced markedly the absorbance and hence the sensitivity of the method.

Effect of Experimental variables

Effect of pH: The pH of a solution is a very important factor for metal chelate formation and for the flotation process. Therefore, the effect of pH on the flotation of 5×10^{-5} M Cu(II) with 1×10^{-4} M HOL in the absence and presence of 1×10^{-4} M PTHAC was studied in the pH values ranging from 2.0 to 9.0. The results are shown in Figure 2. In the absence of PTHAC (graph a) the flotation efficiency of Cu(II) is very low over the pH range tested. On the addition of the ligand,

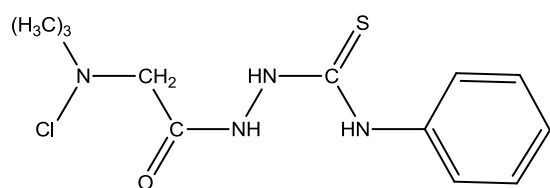


Chart 1: PTHAC.

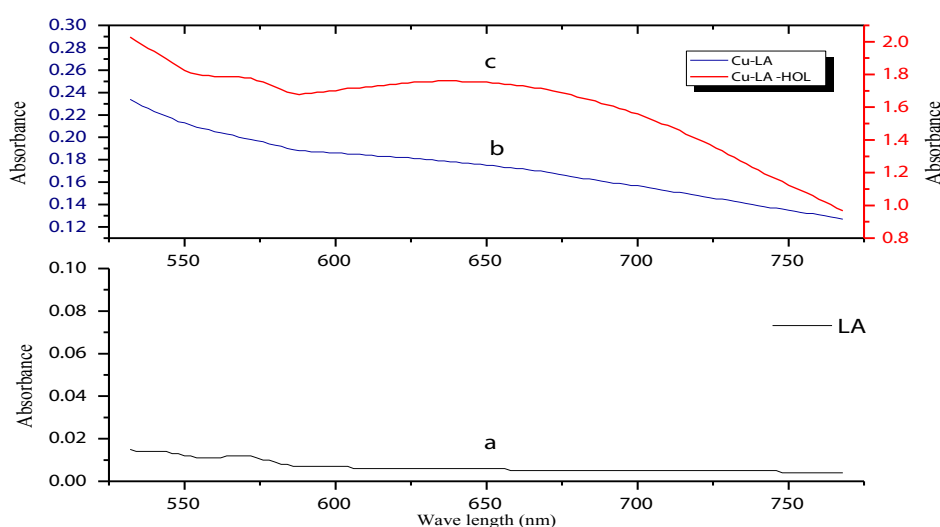


Figure 1: Absorption spectra of (a) 8×10^{-4} M PTHAC, (b) Cu-PTHAC- H_2O complex and (c) Cu-PTHAC-HOL complex.

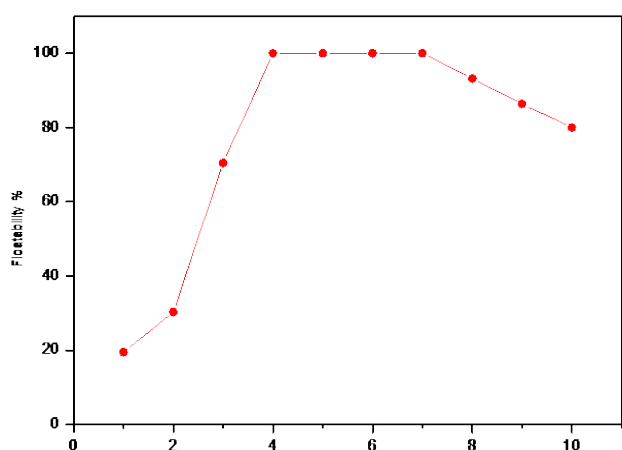


Figure 2: Floatability of 5×10^{-5} M Cu(II) vs. pH using 2×10^{-4} M PTHAC and 1×10^{-4} M HOL.

the flotation efficiency reached its maximum ($\sim 100\%$) over pH values ranging from 4.5 to 7.0. According to graphs (a) and (b), the effective role of the ligand is clear; it forms a complex with Cu(II) ions rendering them more hydrophobic and easily separated from the solution bulk using the HOL surfactant. At higher pH values, the decrease in the flotation efficiency may be attributed to the formation of a white emulsion and due to the formation of excessive foams of sodium oleate. This will hinder the reaction to complete.

Effect of surfactant concentration: Samples of floated Cu(II) were mixed with different concentrations of HOL without ligand (Figure 3: curve a). The flotation efficiency did not exceed 40%. Hence the floatability of Cu(II) was tried in the presence of PTHAC using various concentrations of HOL. The results, graphically presented in Figure 3 (curve b), show that the maximum floatability of Cu(II) is attained over a wide concentration range of HOL (1×10^{-4} to 0.5×10^{-2} M). At higher HOL concentration, the flotation efficiency decreased. At a higher HOL concentration the surfactant molecules will gather together to form a

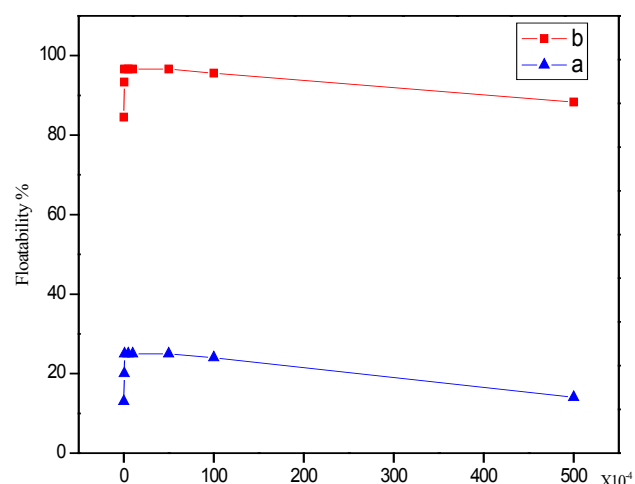
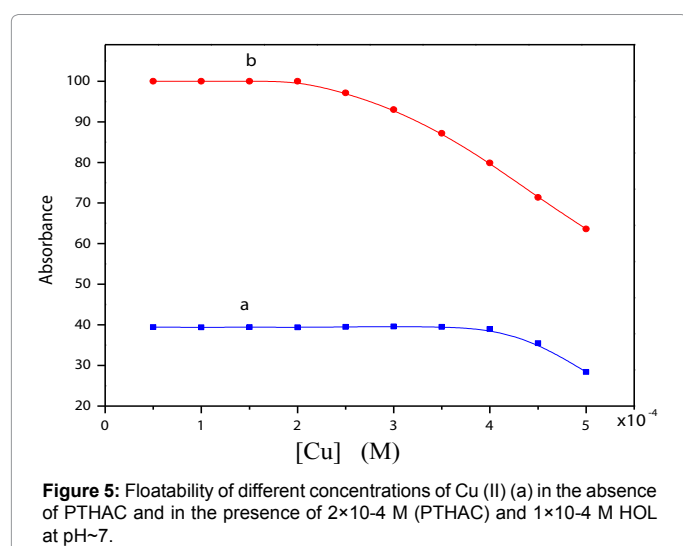
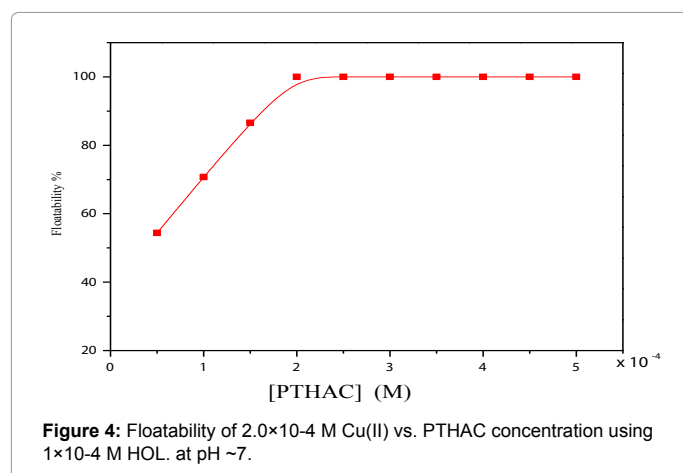


Figure 3: Floatability of 7.8×10^{-5} M Cu(II) vs. HOL concentration at pH ~ 7 . (a) In the absence of PTHAC and (b) in the presence of 1×10^{-4} M PTHA.

microball called a micelle. Micelles compete with the colligend molecule (M-PHTAC complex) and since they stay in solution, they reduce the effectiveness of separation. Also, the concentration of surfactant changes the bubble size with the size getting smaller as the surfactant increases. This makes creamier foam. A suitable concentration of HOL (1×10^{-4} M) was used throughout this work.

Effect of ligand concentration: Initial experiments were made to float Cu(II) with HOL surfactant alone. The flotation efficiency did not exceed 40%. Therefore, a trial was made to progress this process using different reagents. It was found that the use of PTHAC as a collecting agent in this respect, gave expectant results. The floatability of a series of solutions containing 2.0×10^{-4} M Cu(II), 1.0×10^{-4} M HOL and various amount of PTHAC, at pH ~ 7 was investigated. The results are shown in Figure 4. As can be seen, the flotation efficiency (equivalent to the maximum absorbance) increases with increasing concentration of PTHAC, reaching its maximum value (ca.100%) at a 1:1 (Cu: PTHAC)



ratio. The excess of ligand has no opposing effect on the flotation process and so the procedure be applied to real samples containing unknown amounts of copper.

Effect of Cu(II) concentration: To check the data obtained in Figure 4 another series of experiments were carried out to float various amounts of Cu^{2+} ions in the presence of 2×10^{-4} M PTHAC using 1×10^{-4} M HOL at pH ~7 (Figure 5). As can be realized, the floatability reaches 100% at a Cu(II) concentration of 2.0×10^{-4} M, corresponding to 1:1 molar ratio (Cu:PTHAC), which agrees well with the data attained in Figure 4. At higher concentrations of the analyte, the flotation efficiency decreases. This may be credited to the fact that the amount of PTHAC is unsatisfactory to bind all Cu^{2+} ions the solution. Therefore, in the analysis of copper in its natural unknown samples, excess ligand can be safely used.

Effect of temperature: Solutions of Cu (II), HOL and PTHCA were either heated or cooled. The PTHCA and HOL are quickly poured into the Cu (II) solution at zero time. The solution was introduced into flotation cell jacked with 1 cm thick fiberglass insulation at pH ~ 7. The data indicated that temperature up to 60°C has no effect on the flotation process. Hence, subsequent experiments were carried out at

($25 \pm 2^\circ\text{C}$).

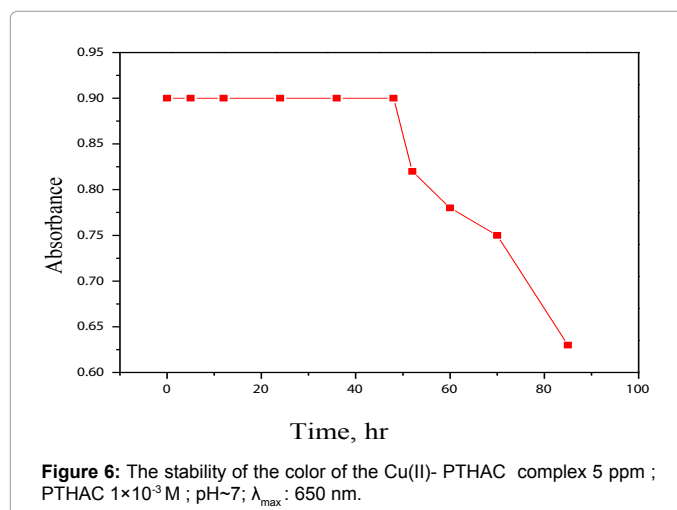
Effect of time: Cu(II)-(PTHAC) complex is olive green with a maximum absorbance value at 650 nm. This absorbance is measured repeatedly at different intervals of time to establish the time stability of the complex. It was observed that the color improvement was instantaneous and stable for more than 48 hours (Figure 6).

Effect of volume: A Series of experiments was conducted to float different quantities of Cu(II) in a fixed volume (10 mL) under the recommended conditions. It was found that the smallest amount of the analyte which can be safely and quantitatively separated from 10 ml is 2×10^{-5} mol/l. Another series of experiments were conducted to float a fixed concentration of the analyte (2×10^{-3} mol/l) from different aqueous volumes using suitable large flotation cells under the recommended conditions. The data showed that 1×10^{-3} mol/l of Cu(II) can be quantitatively separated from different aqueous volumes up to 2 L to 10 ml HOL with a pre concentration factor of 200. After that, the floatability decreases by 30% at 2.5 L.

Effect of foreign ions: In order to study the tendency of PTHCA to form complexes with a great number of metal ions, the effect of foreign metal ions on the flotation of Cu(II) ion using the optimum conditions was examined. These foreign ions were selected on the basis that they are normally present in fresh and saline waters. The tolerable amounts of each ion giving a maximum error $\pm 5\%$ in the flotation efficiency are summarized in Table 1. The experimental data showed that most of the investigated foreign cations did not interfere in the recovery of Cu(II) ions using the optimum conditions whereas other foreign ions have little interfering effects (~12%). All of these interferences were completely removed by increasing the concentration of PTHCA.

Effect of ionic strength: Table 2 illustrates the effect of changing the ionic strength of different salts on the flotation efficiency of 1.0×10^{-4} M Cu(II) ions with 1.0×10^{-4} M HOL in the presence of 1.0×10^{-4} M PTHAC at pH 4-7. The salts used in modifying the ionic strength usually looks like individuals present in natural water samples. As can be seen, the ionic strength of the medium has not evidently affected the flotation process or the determination of copper.

Validity of Beer's law and reproducibility



Floatability, (%)	Added ion 5×10^{-6} mol l ⁻¹
98.1	Mg ²⁺
96.3	Ca ²⁺
98.1	Al ³⁺
96.3	Pb ²⁺
98.0	Mn ²⁺
100.0	Cr ³⁺
96.3	Cd ²⁺
93.0	Hg ²⁺
98.1	Zn ²⁺
69.4	EDTA
90.0	KSCN

Table 1: Effect of different ions on the floatability of 1.0×10^{-4} M of Cu(II) using 1.0×10^{-4} M of PTHAC, 1.0×10^{-4} M HOL at pH 4-7.

Salt	Concentration (M)	F (%)
NaCl	0.1	100
	0.01	100
	0.001	100
KCl	0.1	98.1
	0.01	100
	0.001	100
CaCl ₂	0.1	92.5
	0.05	94.5
	0.001	96.3

Table 2: Effect of Ionic Strength on the Floatability of 1.0×10^{-4} M of Cu(II) using 1.0×10^{-4} M of PTHAC, 1.0×10^{-4} M HOL at pH 4-7.

Under optimum conditions that are described in the suggested procedure, the calibration curves show good linearity over the range 0.1-6 mg l⁻¹ of Cu (II). The molar absorptivities (at λ max. 650 nm) are 0.2699×10^4 and 0.19716×10^5 l mol⁻¹ cm⁻¹ for the colored complex in the aqueous and scum layers, correspondingly. The detection limit of a standard aqueous solution is 0.03 mg l⁻¹ Cu(II), calculated on the basis of 3 σ , with a relative standard deviation (n=5) of 3.72% and Sandell's sensitivity of 3.2×10^{-3} μ g cm⁻². The regression equation of the calibration graph obtained by $A = \log(p_o/p_t) = 19716 [Cu^{II}] + 0.1415$.

Flotation mechanism

In the studies concerning the separation via flotation, the role of surfactant is very important. The nature of interaction between oleic acid surfactant and the complex formed must be studied to approach the actual mechanism of flotation. The proposed mechanism may proceed by forming physical force. Van Der Waal or by forming a hydrogen bond between the hydrophilic part of HOL and the active sites in the ligand complex or by interaction between oleic acid and the complex, formed in solution, through a coordinate bond forming a self-floatable species (Analyte-Ligand-HOL).

Many experimental studies were carried out to approach the flotation mechanism. The data obtained can be summarized in the following points:

- Copper(II) reacts with the PTHAC to form a 1:1 complex in aqueous solution
- The elemental analysis and the mass spectrum (Figure 7) of the complex isolated in aqueous layer indicate that the complex has the formula $[Cu(PTHAC)Cl EtOH H_2O] \cdot \frac{1}{2} (EtOH.H_2O)$ (Chart 2).
- The floated species have the same colour (green) as that isolated in aqueous solution.

(iii) The isolated complexes have the same melting points (215°C).

(iv) The complexes have $\mu_{eff} \approx 2.0$ BM confirming an octahedral structure around the Cu(II) ion. This geometry is also confirmed by reading the electronic spectra of the complexes. The spectra show a band 640 nm).

(v) The flotation process is not affected by increasing the temperature up to 60°C indicating that the floated complex is not easily destroyed by heat.

(vii) The IR spectral studies of the ligand and its Cu (II)-PTHAC complexes in the aqueous and scum layer reveal the following findings:

1. Careful comparison of the IR spectra of the of the Cu-PTHAC complexes, isolated from the aqueous solution and scum layer (Figure 8b and 8c), with that of PTHAC (Figure 8a) displays that the ligand behaves as a tridentate ligand and coordinates through the C=N, C=S and C=O groups. These bonding sites are recommended based on the following evidence: i) the disappearance of $\nu(N_2H)$; ii) the appearance of $\nu(C=N)$ to a new band at 1623 cm⁻¹; iii) the appearance of a new band at 380 cm⁻¹, assignable to $\nu(Cu-N)$ [27,28] and appearance of $\nu(N-N)$ band at 953 cm⁻¹; iv) the disappearance of the thioamide band, $\nu(C=S)$, with the simultaneous appearance of new bands at 687, 566 and 446, ascribed

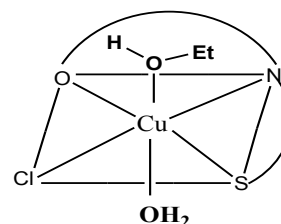
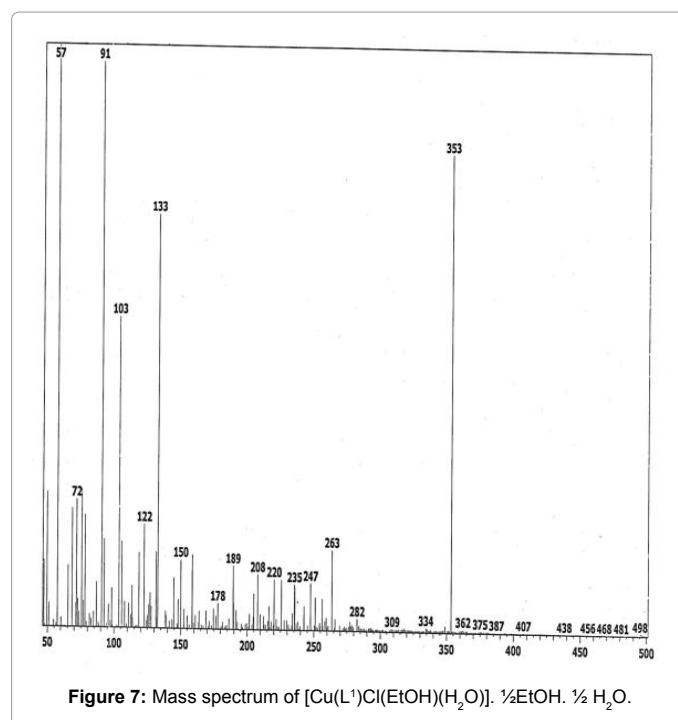


Chart 2: $[Cu(PTHAC)Cl EtOH H_2O] \cdot \frac{1}{2} (EtOH.H_2O)$

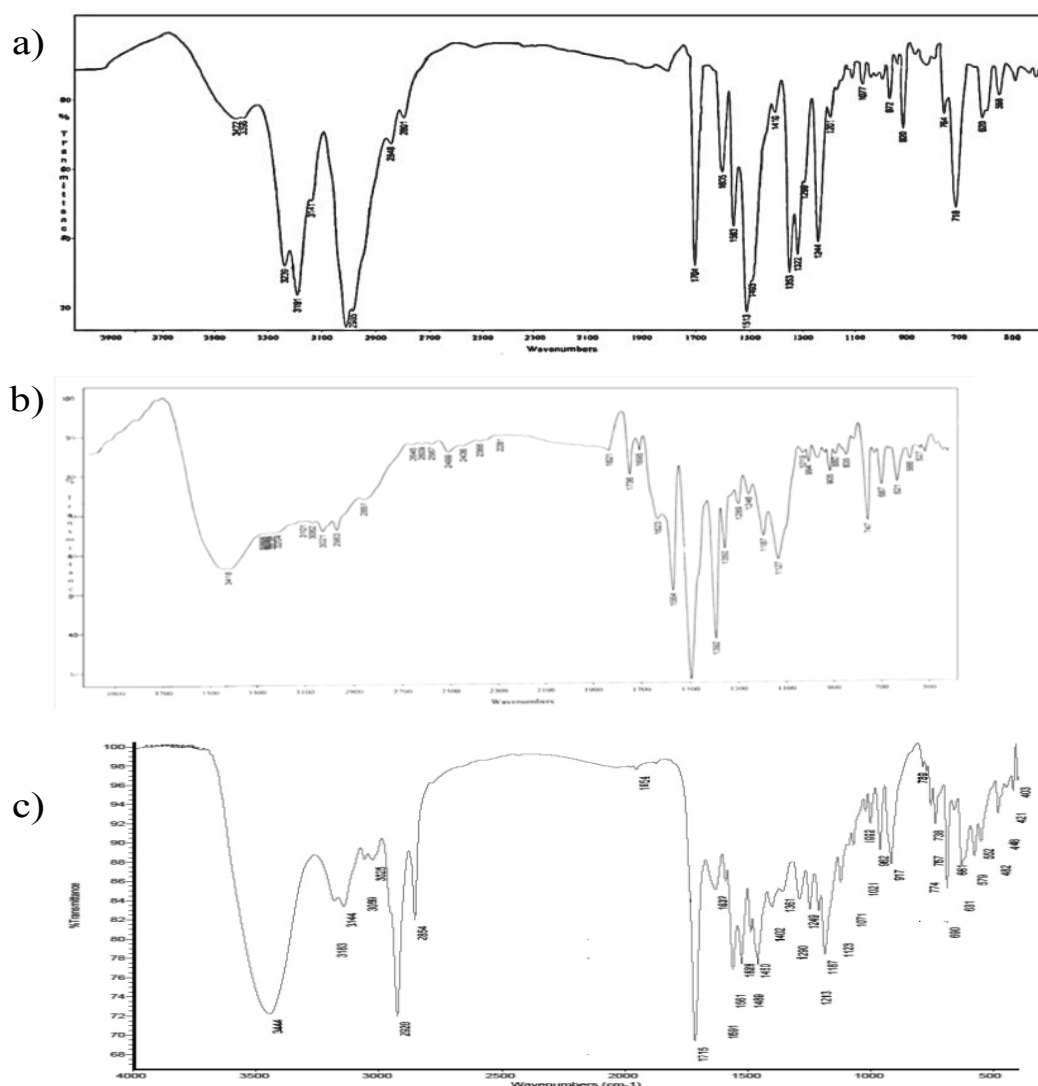


Figure 7: Mass spectrum of $[\text{Cu}(\text{L}')\text{Cl}(\text{EtOH})(\text{H}_2\text{O})] \cdot \frac{1}{2}\text{EtOH} \cdot \frac{1}{2}\text{H}_2\text{O}$.

to $\nu(\text{C-S})$, (Cu-O) and $\nu(\text{Cu-S})$ cm^{-1} vibrations, respectively [28]. The coordinated water gives absorption frequency at 3418, 880 and 835 cm^{-1} due to $\nu(\text{OH})$, rocking and wagging, respectively. Also, the appearance of a new band at 290 cm^{-1} , due to (Cu-Cl) vibration [28], is good indication for the existence of chloride inside the coordination sphere. 3. The infrared spectra of the complex isolated in the scum layer is completely different from the PHTAC and from the Cu-PTHAC isolated in the aqueous layer. The Cu-PTHCA isolated in the scum layer has absorption bands corresponding to the oleic acid surfactant at 1715 cm^{-1} due to $\nu(\text{C=O})$ vibration of carboxylate ion of oleic acid. Another band is also observed at 1460 cm^{-1} assigned to $\nu_s \text{COO}^-$ vibration [29].

The mechanism of flotation is proposed to be due to hydrogen bond formation between the COOH group of HOL and the free NH_2 of $[\text{Cu}(\text{PTHAC})\text{ClEtOH H}_2\text{O}] \cdot \frac{1}{2}(\text{EtOH} \cdot \text{H}_2\text{O})$. Therefore, the system Cu-PTHAC-HOL becomes hydrophobic and floated with air bubbles to the scum layer (generated inside the flotation cell by slight shaking) as represented in Chart 3.

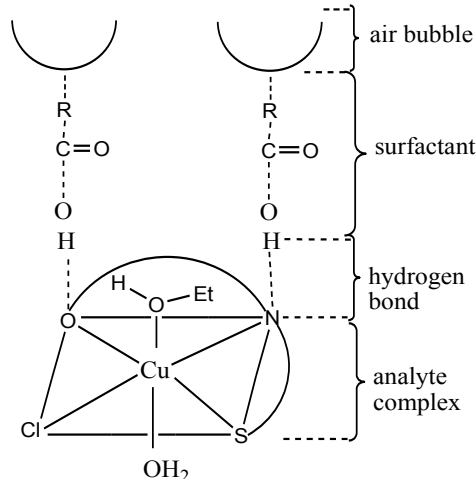


Chart 3: Cu-PTHCA-HOL system.

Application

Water samples

The recovery of certain amounts of Cu (II) added to different water samples was studied. To 30 ml aliquots of pure uncontaminated and filtered water samples definite concentrations of Cu(II) were added and the pH was adjusted to ~7. After flotation, the concentration of Cu (II) was determined spectrophotometrically and confirmed by atomic absorption spectrometry (AAS). The recovery% is >95%, Table 3.

Ore samples

Analysis of Cu (II) in real samples under the recommended conditions is shown in Table 4 with a relative standard deviation, RSD, <1.0%.

Type of water (location)	Cu(II) added (mg l ⁻¹)	Recovery (%)	
		Spectrophoto.	AAS
Distilled water	5	99.8	99.6
	10	100	100
	15	100	100
Tap water	0	0	0
(Our laboratory)	5	99.6	99
	10	99.8	100
	15	100	99.8
Nile water	0	0	0
(Mansoura City)	5	99	99
	10	100	100
	15	99.8	99.7
Sea water	0	0	0
(Demiate City)	5	99.9	99.6
	10	99.4	99.8
	15	99.6	100
(Ras El-Barr)	0	0	0
	5	99.6	99.9
	10	100	99.4
	15	100	99.6

Table 3: Recovery of Cu(II) spiked in natural water samples after flotation using 1.0×10^{-2} M PTHAC and 1.0×10^{-4} M HOL at pH ~7 at room temperature (n=3).

Ore name	Cu(II), ppm		Abs. error	R. error	SD	RSD, %
	found	certified				
Lead-Zinc sulfide ore	9.718	9.7	0.18	0.018	0.013	0.13
Steel scrap sample	5.223	5.2	0.23	0.044	0.02	0.38

Table 4: Analysis of Cu(II) in some ore samples after flotation using 1×10^{-2} mol L⁻¹ PTHAC and 1×10^{-4} mol L⁻¹ HOL at pH 7.

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