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Spectrophotometric Determination of Copper(II) in Natural Waters, Vitamins and Certified Steel Scrap Samples Using Acetophenone-*p*-chlorophenylthiosemicarbazone

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A very simple, highly sensitive and selective spectrophotometric procedure was developed for the determination of copper(II). It is based on the reaction at pH 4-9 between the synthesized acetophenone-*p*-chlorophenylthiosemicarbazone (A-*p*-ClPT) and Cu(II) forming a green complex, Cu(II):A-*p*-ClPT (1:2), that floats quantitatively with oleic acid (HOL) surfactant. It exhibits a constant and maximum absorbance at 600 nm in both aqueous and surfactant layers. Beer's law is obeyed over the concentration range 0.25-6.35 mg l^{-1} with a detection limit of 0.021 mg l^{-1} for a standard aqueous solution of Cu(II) with a concentration of 3.82 mg l^{-1} (calculated on the basis of 3σ) and molar absorptivities of 5.5×10^3 and 1.3×10^4 mol l^{-1} cm^{-1} in aqueous and surfactant layers, respectively. Sandell's sensitivity was calculated to be 0.244 μg cm^{-2} and the relative standard deviation (n = 9) was 0.19%. The different analytical parameters affecting the flotation and determination processes were examined. The proposed procedure has been successfully applied to the analysis of Cu(II) in natural waters, certified scrap steel samples and vitamin samples. The results obtained agree well with those samples analyzed by atomic absorption spectrometry (AAS). Moreover, the flotation mechanism is suggested based on some physical and chemical studies on the solid complexes isolated from aqueous and surfactant layers.

Key words: Copper, Spectrophotometry, Flotation, Natural waters, Vitamins, Certified samples

INTRODUCTION

Many industrial wastewater streams (such as those used in metal works, semiconductor, and copper industries, mining, etc.) contain heavy metals, which are of great environmental concern and must be removed prior to water discharge or water recycling [1-3]. Copper has received considerable attention owing to its uses in metallurgy and chemical industries. Moreover, it is an essential constituent of about thirty enzymes and glycoproteins and is required for the synthesis 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, helps to maintain myelin in the nervous system, is important in the formation of bone and brain tissues and is necessary for other many important functions [4,5].

When levels of Cu exceed certain values, however, defense mechanisms to protect against excess Cu are overcome and toxicity results. The reported list of toxic Cu species [6] often includes $Cu(OH)^+$, $Cu_2(OH)_2^{2+}$, and $CuCO_3$. However, without doubt, Cu^{2+} ions that are present in various aqueous solutions (their presence is a function of pH) are considered to be the most toxic of dissolved copper species [4,6]. Excess copper in water is not only harmful to human beings, but also interferes

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with the self-purification of bulk water [7] and exerts an adverse effect on the microbiological treatment of wastewater [8]. Therefore, from the viewpoints of pollution, environmental chemistry, geochemistry, marine biology and analytical control in industrial, food, agricultural, pharmaceutical and clinical areas, it is necessary to establish a rapid, simple, sensitive and accurate procedure for the selective concentration of Cu^{2+} prior to its determination.

Numerous techniques for the separation and concentration of metal ions including evaporation of solvents, electro-deposition, liquid-liquid extraction, surface adsorption, precipitation, ion exchange, ion exchange impregnated materials, immobilized reagents, electro-osmosis and flotation have been reported [9]. Although some of these techniques may be tedious, having limited concentration factors, lengthy and rigid conditions for the separation of solid adsorbents [10], the flotation technique has many advantages that overcome these drawbacks. It has recently received considerable interest owing to its simplicity, rapidity, economy, good separation yields (R > 95%) for small impurity agent concentrations (10^{-6}-10^{-2} M), a good prospect for application for species having different nature and structure, flexibility and friability of equipment and processing for recovery purpose [11]. It is believed that this process will soon be incorporated as a clean technology to treat water and wastewater [12]. Moreover, flotation is suggested as a method for elimination of interferences [13].

Spectrophotometry still represents an attractive technique for the determination of metal ions in aqueous media because of its simplicity, being inexpensive and is readily available [14]. Therefore, spectrophotometry after selective flotation was chosen for this investigation.

Copper has been removed and/or analyzed in simulated waste solutions, human hair and natural waters by flotation [5,15-24]. Although a vast number of reagents are available for the spectrophotometric determination of copper [5,16,25-32], little work has been done using A-*p*-ClPT and perhaps no trial has been made to float and analyze the analyte with this reagent. Therefore, this work aims to develop a simple and rapid procedure for the selective separation and determination of Cu(II) in natural waters, certified and vitamin samples using HOL as a surfactant and A-*p*-ClPT as a chelating agent. The procedure involves the spectrophotometric determination of Cu(II) in the surfactant layer directly after separation by flotation; thus overcoming the problems of elution.

EXPERIMENTAL

Reagents

Unless otherwise stated, all chemicals used were of analytical-reagent grade. Doubly distilled water was used for preparing aqueous solutions. Acetophenone-*p*-chlorophenyl-thiosemicarbazone, A-*p*-ClPT (Chart 1) was synthesized as has been described elsewhere [33] by condensation of a hot solution of 1:1 4-*p*-chlorophenylthiosemicarbazide with acetophenone. The resulting solution was boiled under reflux for 2h. Then the yellowish-white crystals of A-*p*-ClPT were filtered off, washed with ethanol, recrystallized from absolute ethanol and finally dried in a vacuum desiccator over anhydrous $CaCl_2$. The purity was checked by elemental analysis and spectral (mass and infrared) studies. The product is crystalline (m.p.: 192 °C) sparingly soluble in ethanol but easily soluble in acetone, DMF and DMSO; hence its stock solution (1.0×10^{-3} M) was prepared in acetone. Oleic acid (HOL) stock solution (6.36×10^{-2} M) was prepared by dispersing 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 $CuCl_2.2H_2O$ in doubly distilled water.

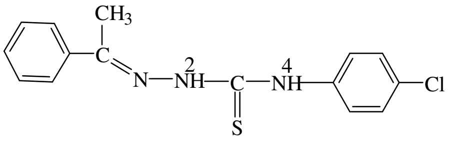

Chart 1

Sample Collection and Pretreatment

One liter of tap, Nile or Seawater samples was filtered, the pH adjusted to 1 with concentrated HCl to prevent losses by sorption or coprecipitation, and preserved in high quality clean plastic containers.

Certified Scrap Steel Sample

The steel sample (#21899), kindly supplied by the

Analytical Chemistry Laboratory Service, at the Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany, had the following characteristics: 0.519% copper (by weight); other main components include Cr, Ni, Mn, Zn, with traces of C, P, Si, S, V, Ti, Mo, and Co.

A weighed amount of the sample (200-300 mg) was digested with 10 ml of aqua regia and heated to near dryness. Then the sample was mixed with 5 ml of concentrated sulfuric acid and heated for 30 min. The solution was then diluted and neutralized with NaOH, evaporated, and the remaining solid was ignited at 850 ^{o}C (for 5-10 min). Sulfates were converted to the corresponding oxides, cooled, and diluted with doubly distilled water in a 100 ml calibrated flask. After adjusting the pH of the sample solution, Cu(II) was floated and determined spectrophotometrically by the recommended procedure.

ICP Certified Multielement Standard Solution

This solution, also kindly supplied by the Analytical Chemistry Laboratory Service at PTB, contained 1011 µg ml^{-1} Cu(II) in addition to Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, and Zn in the same concentration range as copper. Using 50 ml of the sample, after buffering to pH~7, a defined volume of the solution was introduced into the flotation cell to apply the procedure for flotation and determination of copper. Both the steel scrap certified sample and multielement standard solution were used to separate and preconcentrate Mn(II), Ni(II), Cu(II), and Zn(II), as previously described [34].

Theragran Hematinic Sample

Each Theragran-M tablet (Bristol-Myers Squibb Company, New York) supplies: vitamin A (10000 IU), vitamin D (400 IU), vitamin B1 (10 mg), vitamin B2 (10 mg), vitamin B6 (5 mg), vitamin B12 (5 mg), vitamin C (200 mg), vitamin E (15 IU), niacinamide (100 mg), calcium pantothenate (20 mg), iodine (0.15 mg), iron (12 mg), copper (0.67 mg), manganese (1 mg), magnesium (65 mg) and zinc (1.5 mg). As previously described [5], five tablets were crushed, digested using 5 ml of concentrated of HNO_3 and heated to near dryness. After cooling, the residue was dissolved in another 5 ml of concentrated HNO_3 and the solution was gently evaporated using a water bath. The residue was again heated with 50 ml distilled water, filtered off and diluted to 100 ml in a calibrated flask after adjusting the pH to ~7. A defined volume treated by the recommended procedure for the flotation and determination of copper.

Apparatus

The flotation cell (a cylindrical tube with a 15 mm inner diameter and 290 mm length, a stopcock at the bottom and a stopper at the top) was the same type as previously described [16]. The spectral data were recorded on Unicam UV 2100 UV-Vis and MATSON 5000 FTIR spectrophotometers. The pH was adjusted with HCl and/or NaOH and measured with a digital pH meter (Hanna Instruments, model 8519).

Procedure

Separation. All samples used in this investigation were in the form of aqueous solutions after suitable treatment. Therefore, the following procedure was applied to all samples.

A suitable aliquot containing a known amount of Cu(II), specified for each investigation, was mixed with a suitable amount of A-*p*-ClPT followed by the addition of 3 ml of double distilled water. After adjusting with HCl and/or NaOH to the required pH, the solution was transferred to the flotation cell and the total volume was made up to 10 ml with an acetone-water mixture to ensure a final acetone volume fraction of 30%. The cell was shaken well for a few seconds to ensure complexation. To this, 3 ml of HOL (of known concentration) was added. The cell was then inverted upside down twenty times by hand. Bubbles were created inside the cell. Meanwhile, the stopper of the cell was removed to permit air movement. After allowing it to stand for 5 min for complete flotation of the colored complex, the concentration of Cu(II) in the surfactant layer was determined spectrophotometrically.

Determination. The concentration of Cu(II) in the floated layer was determined spectrophotometrically by transferring a suitable volume to the quartz cell and measuring the absorbance at 600 nm against the reagent blank (A-*p*-ClPT).

The analyte concentration was calculated from a calibration curve constructed by taking different concentrations of Cu(II).

The flotation efficiency (%F) was calculated from the relation:

$$\%F = C_s/C_i \times 100$$

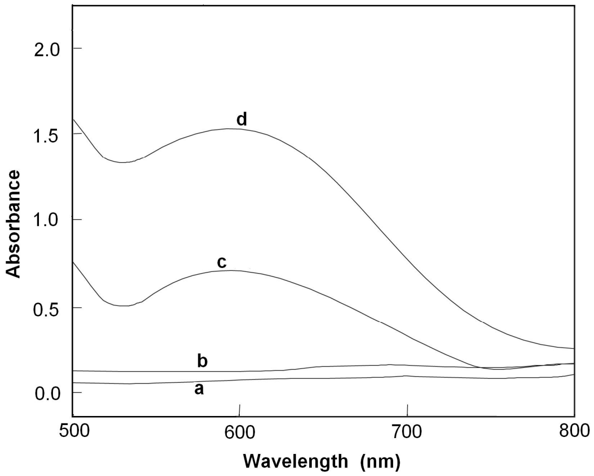

Fig. 1. Absorption spectra of (a) 4 × 10^{-4} M Cu(II), (b) 8 × 10^{-4} M A-*p*-ClPT, (C) Cu-A-*p*-ClPT-H_2O complex and (d) Cu-A-*p*-ClPT-HOL complex.

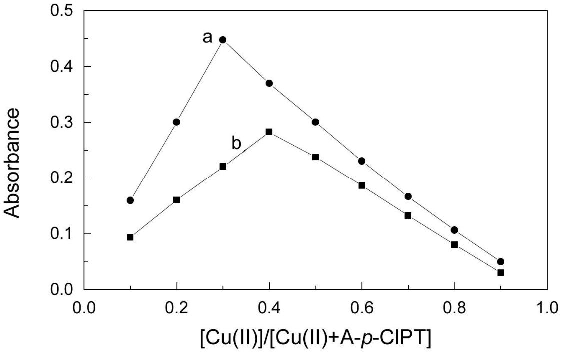

Fig. 2. Composition of Cu(II) complex by the continuous variation methods. (a) Cu(II) complex floated by HOL surfactant. (b) Cu(II) complex in aqueous solution. The measurements were carried out at 600 nm and pH~7, using 1 × 10^{-4} M A-*p*-ClPT as a blank.

where C_i and C_s denote the initial Cu(II) concentration and its concentration in the surfactant layer, respectively. All the experiments were carried out at room temperature, about 25 °C.

RESULTS AND DISCUSSION

In order to obtain the optimum conditions for the maximum flotation efficiency of Cu(II) with the HOL surfactant, the different factors affecting this process have been studied. It should be noted that the maximum absorbance of the complex Cu-A-*p*-ClPT corresponds to its maximum flotation efficiency. So, the maximum absorbance can be expressed by the maximum floatability of the analyte and the inverse is true, as well [14,35].

Absorption Spectra

The absorption spectra of Cu(II), A-*p*-ClPT reagent and of Cu-A-*p*-ClPT complex formed in aqueous acetone solution (30% v/v) and that floated into the HOL layer are given in Fig. 1. Notice that the absorption spectra of the analyte and the ligand (curves a and b) have no absorption bands in the region that corresponds to that of the complexes Cu-A-*p*-ClPT and Cu-A-*p*-ClPT-HOL, curves (c) and (d), having their maximum absorbances at 600 nm. Moreover, it is interesting to note that the floated complex has a higher maximum absorbance value in comparison with that formed in the aqueous solution resulting in an enhancement in the sensitivity of the spectrophotometric determination of Cu(II) after flotation. Hence, subsequent analysis of the colored complex was carried out at 600 nm after flotation.

Composition of the Complex

The composition of the copper complex was studied by the continuous variation method. A typical graph obtained (Fig. 2) by the former method showed that 1:2 and 1:1 (Cu:A-*p*-ClPT) complexes are formed in the surfactant and aqueous solutions, respectively (curves a and b). However, the difference in molar ratio between the floated complex and that formed in the aqueous solution may be attributed to the floatability of a small quantity of free reagent in addition to the complex [26]. Moreover, it must be noted from the data in Fig. 2 that the HOL surfactant intensifies the color of the complex (higher absorbance than in the aqueous solution) which confirms the determination of Cu(II) after floatation of its complex [36].

Effect of pH

Since the pH of the medium is a highly significant factor in flotation processes, pH was the first variable to be optimized. A series of experiments was carried out to study the effect of

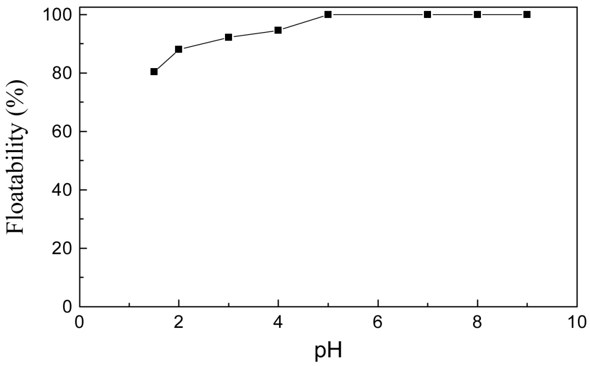

Fig. 3. Floatability of 1.0×10^{-4} M Cu(II) *vs*. pH using 2.0×10^{-4} M A-*p*-ClPT and 1.0×10^{-3} M HOL.

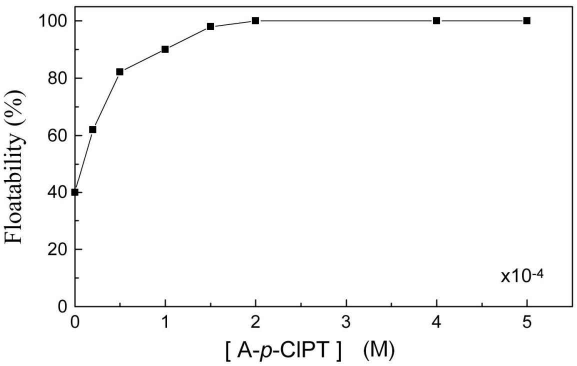

Fig. 4. Floatability of 1.0×10^{-4} M Cu(II) *vs*. A-*p*-ClPT concentration at pH~7 using 1.0×10^{-3} M HOL.

pH on the flotation efficiency of 1.0×10^{-4} M Cu(II) with 1.0×10^{-3} M HOL in the presence of 2.0×10^{-4} M A-*p*-ClPT. The results presented in Fig. 3 show that the floatability of the Cu-A-*p*-ClPT complex increases with increasing pH, reaching its maximum value (maximum and nearly constant absorbance) in the pH range 5-9. Fortunately, pH~7 was attained by direct addition of reagents and, unless otherwise stated, adjustment of the solution pH was not required. Therefore, pH~7 was used as the optimal pH for other experiments.

Effect of Ligand Concentration

Initial experiments were performed to float Cu(II) with HOL surfactant alone. However, the flotation efficiency did not exceed 40%. Therefore, a trial was made to improve this process using different reagents. It was found that the use of some thiosemicarbazone derivatives as collecting agents in this regard, especially acetophenone-*p*-chlorophenylthiosemicarbazone (A-*p*-ClPT), gave optimistic results. The floatability of a series of solutions containing 1.0×10^{-4} M Cu^{2+}, 1.0×10^{-3} M HOL and various amounts of A-*p*-ClPT at pH~7 was investigated. The results are shown in Fig. 4. As can be seen, the flotation efficiency (equivalent to the maximum absorbance) increases with increasing concentration of the ligands, reaching its maximum value (*ca*. 100%) at a 1:2 (Cu:A-*p*-ClPT) ratio. These results agree well with those obtained in Fig. 2. Moreover, the excess of ligands has no adverse effect on the flotation process and so the procedure be applied to real samples containing Cu(II). Accordingly, a concentration of A-*p*-ClPT which equal to twice that of Cu(II) was used in the recommended procedure.

Effect of Surfactant Concentration

Samples of floated Cu(II) were tested with different concentrations of HOL without ligand (Fig. 5, curve a). The flotation efficiency did not exceed 40%. Therefore the floatability of Cu(II) was tried in the presence of A-*p*-ClPT using various concentrations of HOL. The results, graphically presented in Fig. 5 (curve b), show that the maximum floatability of Cu(II), obtained over a wide concentration, may be due to the formation of a stable envelope of surfactant on the surface of air bubbles or a hydrated micelle coating on the surface of analyte-ligand system [8]. As a result, the hydrophobicity of the resulting surface was not satisfactory for flotation. Accordingly, 1.0×10^{-3} M HOL was used throughout the measurements for Cu(II) determination.

Effect of Cu(II) Concentration

To confirm the data obtained in Fig. 4 another series of experiments were carried out to float various amounts of Cu^{2+} ions in the presence of 2.0×10^{-4} M A-*p*-ClPT using 1.0×10^{-3} M HOL at pH~7 (Fig. 6). As can be seen, the floatability reaches 100% at a Cu(II) concentration of 1.0×10^{-4} M, corresponding to 1:2 molar ratio (Cu:A-*p*-ClPT), which agrees well with the data obtained in Fig. 4. At higher concentrations of the analyte, the flotation efficiency decreases. This may be attributed to the fact that the amount of A-*p*-ClPT is insufficient to bind all Cu^{2+} ions that exist in the solution.

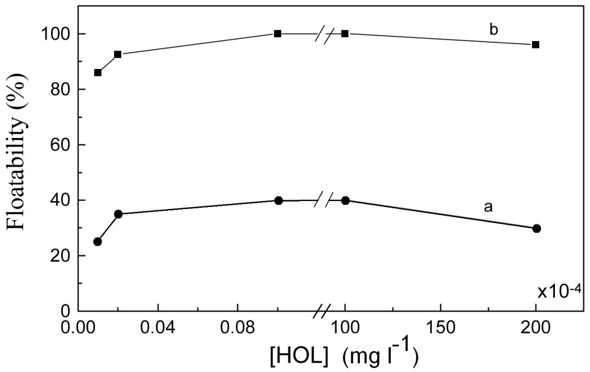

Fig. 5. Floatability of 1.0×10^{-4} M Cu(II) *vs.* HOL concentration at pH~7. (a) In the absence of A-*p*-ClPT and (b) in the presence of 2.0×10^{-4} M A-*p*-ClPT.

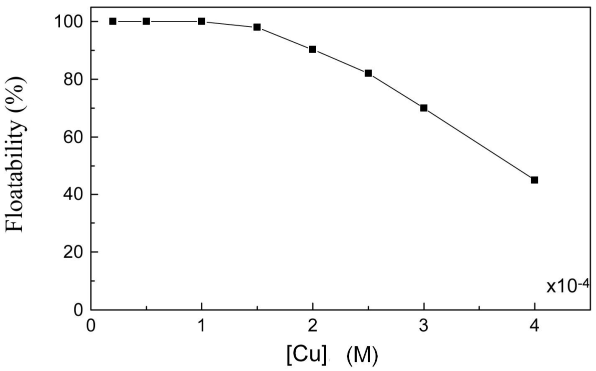

Fig. 6. Floatability of different concentrations of Cu(II) using 2.0×10^{-4} M A-*p*-ClPT and 1.0×10^{-3} M HOL at pH~7.

Consequently, in the analysis of copper in its natural unknown samples, excess ligand can be safely used.

Effect of Temperature

To study the effect of temperature on the flotation efficiency of Cu(II), the solution containing Cu(II) and A-*p*-ClPT and that containing the HOL surfactant were either heated or cooled to the same temperature. Then the solution of HOL was quickly poured into the Cu(II) solution. The mixture was introduced into the flotation cell jacketed with 1 cm thick fiberglass insulation. The flotation and determination procedure was then followed. Since the floatability and absorbance of the complex Cu-A-*p*-ClPT were not markedly affected by raising the temperature from 5 to 80 °C, measurements were carried out at room temperature, ~25 °C. However, given that most industrial influents are usually hot, the simple procedure presented here may find its application in the analysis of Cu(II) ions directly in industrial wastewaters.

Effect of Time

The minimum time required for the color development of the Cu-A-p-ClPT complex was found to be ~2 min at room temperature. The absorbance of the floated complex, measured at 600 nm, was constant for 20 min., after which the color begins to fade. The total time required for one determination was 6-8 min. Therefore, the use of this simple procedure for analysis of Cu(II) may be considered as time saving compared to some another techniques.

Effect of Foreign Ions

Under the optimized conditions determined as above, analysis of copper(II) ions (1.0×10^{-4} M) using A-*p*-ClPT (2.0×10^{-4} M) as the ligand and oleic acid (1.0×10^{-3} M) as the surfactant was studied in the presence of high concentrations of various cations and anions usually found in some water samples. The tolerable amounts of each ion (presented as ion:Cu ratio) giving a maximum error of ±2% in the flotation efficiency (maximum absorbance) are summarized in Table 1. It can be seen that the ions investigated do not interfere. Thus the recommended procedure is fairly selective and can be safely employed for the determination of Cu(II) in various complex materials.

Effect of Ionic Strength

Table 2 summarizes the effect of varying the ionic strength of different salts on the flotation efficiency of 1.0×10^{-4} M Cu(II) ions with 1.0×10^{-3} M HOL in the presence of 2.0×10^{-4} M A-*p*-ClPT at pH~7. The salts used in adjusting the ionic strength generally resemble those present in natural water samples. As can be seen, the ionic strength of the medium has not markedly affected the flotation process nor the determination of Cu(II).

Calibration Curve and Sensitivity

Under the optimum conditions described in the

Table 1. Effect of Some Foreign Ions on the Separation and Determination of 1.0×10^{-4} M Cu(II) Using 2.0×10^{-4} M A-*p*-ClPT in the Presence of 1.0×10^{-3} M HOL at pH~7

Foreign ion added	Foreign ion/Cu(II)	Foreign ion added	Foreign ion/Cu(II)
Na^+	4786.8	Hg^{2+}	698.0
Mn^{2+}	4000.0	Ni^{2+}	681.4
Zn^{2+}	3975.5	Cd^{2+}	400.0
K^+	2813.2	Ba^{2+}	291.3
Mg^{2+}	1646.1	Cl^-	15514.8
Al^{3+}	1481.5	SO_4^{2-}	2708.3
Ca^{2+}	997.5	NO_3^-	1774.2
Cr^{3+} or Cr^{6+}	970.7	SiO_3^{2-}	526.3
Fe^{3+}	716.8	$C_2O_4^{2-}$	430.1

Table 2. Effect of Ionic Strength on the Floatability of Cu(II)[a]

Salt	Concentration (M)	F (%)
NaCl	0.02	100.0
	0.10	100.0
	0.50	99.5
KCl	0.02	100.0
	0.10	100.0
	0.50	99.2
$CaCl_2$	0.02	100.0
	0.03	99.3
	0.05	98.5
$MgSO_4$	0.02	100.0
	0.03	99.0
	0.05	97.5

[a] 1.0×10^{-4} M Cu(II), 2.0×10^{-4} M A-*p*-ClPT, 1.0×10^{-3} M HOL, pH~7.

recommended procedure, the calibration curves (Fig. 7, curves a and b) show good linearity over the range 0.25-6.35 mg l^{-1} of Cu(II). The molar absorptivities are 5.5×10^3 and 1.3×10^4 l mol^{-1} cm^{-1} for the colored complex in the aqueous and scum layers, respectively. The detection limit of a standard aqueous solution of with 3.82 mg l^{-1} Cu(II), calculated on the basis of 3σ [36], was found to have 0.021 mg l^{-1} Cu(II), which corresponds to Sandell's sensitivity of 0.244 μg cm^{-2} and a relative standard deviation (n = 9) of 0.19%. Moreover, close inspection of the calibration curves reveals that the determination of the analyte after flotation enhances the sensitivity of the spectrophotometric procedure [36].

Flotation Mechanism

The suggested flotation mechanism of Cu(II) is based on the following points:

Copper(II) reacts with the thiosemicarbazone derivative (A-*p*-ClPT) to form a 1:1 complex in aqueous solution (Chart 2).

The purity of A-*p*-ClPT (Chart 1) was confirmed by elemental analysis [Found (Calcd.); C = 59.4 (59.3); H = 4.5 (4.6)], spectral (mass, electronic and infrared) studies [34]. The most characteristic features of the IR spectrum of A-*p*-ClPT (Fig. 8a) is that it exhibits two bands at 3292 and 3242 cm^{-1} assigned to ν (N^4H) and ν (N^2H) vibrations, respectively [37]. The bands at 1635 and 797 cm^{-1} are attributed to ν (C=N) and ν (C=S) vibrations, respectively.

Careful comparison of the IR spectrum of the Cu-A-*p*-ClPT complexes, isolated from the aqueous solution and surfactant layer (Figs. 8b and 8c), with that of A-*p*-ClPT shows that the ligand behaves as a bidentate ligand in the thione form and coordinates through the C=N and C-S groups. These bonding sites are suggested based on the following

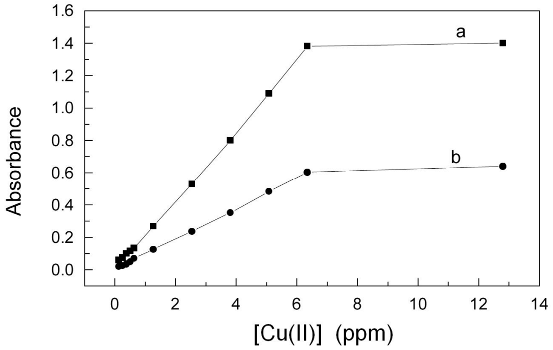

Fig. 7. Calibration curves for the determination of Cu(II) at pH~7. (a) in the floated layer and (b) in aqueous solution using 2.0×10^{-4} M A-*p*-ClPT and 1.0×10^{-3} M HOL.

evidence: i) the disappearance of ν (N^2H); ii) the shift of ν (C=N) to a lower frequency by 41 cm^{-1}; iii) the appearance of a new band at 443 cm^{-1}, assignable to ν (Cu-N) [38,39]; iv) the disappearance of the thioamide band, ν (C=S), with the simultaneous appearance of new bands at 607 and 352, ascribed to ν (C-S) and ν (Cu-S) cm^{-1} vibrations, respectively [40]. The coordinated water gives absorption frequency at 3455, 850, and 550 cm^{-1} due to ν (OH), rocking and wagging, respectively [41]. Also, the appearance of a new band at 292 cm^{-1}, due to (Cu-Cl) vibration [40], is good evidence for the existence of chloride inside the coordination sphere.

Moreover, the electronic spectra of the complexes (as has been presented elsewhere) [42] exhibits one broad band more or less centered at 16600 cm^{-1} which is assigned to a combination of the transitions $^2B_{1g} \rightarrow {}^2E_{1g}$ and $^2B_{1g} \rightarrow {}^2A_{1g}$, associated with a square planar configuration around the Cu(II) ion [41]. In addition to the d-d transition, the band observed at 2197 cm^{-1} is attributed to intraligand charge transfer [41]. All the above observations suggest a square planar structure for the complex [Cu(A-*p*-ClPT)(Cl)(H_2O)] as shown in Chart 2.

Oleic acid begins to dissociate at pH ≥ 5.2 [42]. Therefore, oleic acid can interact with other systems, through hydrogen bonding, either by its undissociated or dissociated form depending on the pH of the medium.

The infrared spectra of the complex isolated from the surfactant layer (after thorough washing) has no absorption bands corresponding to the oleic acid surfactant (Fig. 8c). This means that oleic acid may combine weakly with the complex [Cu(A-*p*-ClPT)(Cl)(H_2O)] perhaps through hydrogen bonds.

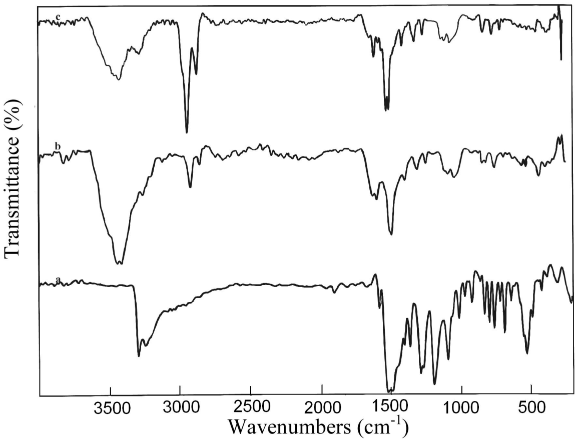

Fig. 8. Calibration curves for the determination of Cu(II) at pH~7 (a) in the floated layer and (b) in aqueous solution using 2.0×10^{-4} M A-*p*-ClPT and 1.0×10^{-3} M HOL.

Oleic acid binds with [Cu(A-*p*-ClPT)(Cl)(H_2O)] giving hydrophobic aggregates that float to the solution surface with aid of air bubbles (created inside the flotation cell by slight shaking) [43].

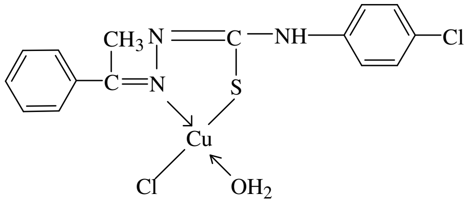

Chart 2

Application

Water samples. To investigate the applicability of the recommended procedure to natural water samples (taken from different locations), the recoveries of known amounts of Cu(II) added to these samples were examined. To 10 ml aliquots of clear uncontaminated, filtered water samples, 0.5 or 1.5 mg l^{-1} of Cu(II) were added and the pH was adjusted to ~7. After flotation, the concentration of Cu(II) was determined either spectrophotometrically in the surfactant layer at 600 nm

Table 3. Determination of Cu(II) Spiked in Natural Water Samples by Spectrophotometric Method[a]

Type of water (location)	Cu(II) added (mg l^{-1})	Spectrophotometric Procedure		AAS Procedure	
		Found (mg l^{-1})	Recovery (%)[b]	Found (mg l^{-1})	Recovery (%)[b]
Distilled water	–	ND	–	ND	–
	0.5	0.499	99.8	0.498	99.6
	1.5	1.5	100.0	1.5	100.0
Tap water	–	ND	–	4.5 ± 0.03[c]	–
(Our laboratory)	0.5	0.493	98.6	0.495	99.0
	1.5	1.490	99.3	1.495	99.7
Nile water	–	ND	–	15.5 ± 0.04[c]	–
(Mansoura City)	0.5	0.494	98.8	0.495	99.0
	1.5	1.495	99.7	1.495	99.7
Sea water					
(Alexandria)	–	ND	–	12.5 ± 0.03[c]	–
	0.5	0.499	99.8	0.498	99.6
	1.5	1.5	100.0	1.499	99.9
(Ras El-Barr)	–	ND	–	17.5 ± 0.02[c]	–
	0.5	0.499	99.8	0.499	99.8
	1.5	1.5	100.0	1.5	100.0
Lake water	–	ND	–	10.5 ± 0.03[c]	–
	0.5	0.499	99.8	0.498	99.6
	1.5	1.5	100.0	1.5	100.0

[a]After flotation using 2.0×10^{-4} M A-*p*-ClPT and 1.0×10^{-3} M HOL at pH~7. ND: not detected. [b]Values calculated for the only added amount of Cu(II). [c]Analysis has been carried out by AAS after preconcentration as reported elsewhere [44] and the values are in ppb.

or by atomic absorption spectrometry (AAS) in the mother liquor at 324.7 nm. The results obtained are given in Table 3. Spectrophotometric determination of Cu(II) after flotation gives satisfactory results compared to those obtained by AAS. Thus the spectrophotometric determination of Cu(II) after flotation makes the procedure highly selective and sensitive.

Certified vitamin and simulated samples. The results of the application of the proposed procedure to the recovery and determination of the analyte in two types of certified samples, vitamin tablets and a simulated solution are tabulated in Table 4. The sensitivity of the proposed procedure for the separation and analysis of Cu(II) was investigated by calculating the relative standard deviation for the different samples. The procedure is highly sensitive and precise with an RSD that does not exceed 2.95% for the analysis of the vitamin tablets.

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Table 4. Analysis of Cu(II) in Certified, Vitamin and Simulated Samples[a]

Sample	Certificate (mg l^{-1})	Spectrophotometric Procedure		AAS Procedure	
		Found (mg l^{-1})	RSD (%)[f]	Found (mg l^{-1})	RSD (%)[f]
Certified 1[b]	1011	1005	0.35	1007	0.34
Certified 2[c]	5.19	5.17	0.98	5.18	0.88
Theragran-M vitamin	0.67[e]	0.66[e]	2.95	0.66[e]	2.25
E Ag 1000 3[d]	1040	1031	1.06	1035	0.99

[a] Using 1.0×10^{-4} M A-*p*-ClPT and 1.0×10^{-3} M HOL at pH~7. [b] Certified sample 1: multielement standard solution. [c] Certified sample 2: Steel scrap sample. [d] E Ag 1000 3: Simulated sample containing different metals such as Cd, Zn, Pb, Ni, Au, Pt, and Ag in addition Cu(II). [e] Values are given in mg/tablet. [f] Calculated for seven replicate analyses.

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