Determination of Trace Copper in Natural Waters after Selective Separation by Flotation

Shaban E. GHAZY* and Mohamed A. KABIL
Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

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Microgram amounts of copper(II) in one liter of water are quantitatively separated selectively as copper(II) acetate with oleic acid surfactant at pH range 6.5—7.5. The floated scum is separated, after shaking for few seconds, and measured colorimetrically at 700 nm. Beer's law is obeyed in the concentration range $(0.5—5)\times10^{-4}$ mol dm^{-3}, {3.18—31.8 ppm of copper(II)}. Alternatively, the copper in the scum is eluted by nitric acid 0.1 mol dm^{-3}, completed to the suitable volume required for copper atomic absorption measurement at 324.7 nm with 1 ppm detection limit. The different factors affecting the selective flotation of copper(II) have been studied. It has been found that iron(III) seriously depresses the flotation efficiency. The flotation mechanism is discussed. The method of the separation and determination is rapid and applicable to 50 ppb copper(II) concentration level in natural waters.

Enriching techniques for the determination of trace elements in water and sea water commonly include liquid- liquid extraction, ion exchange and coprecipitation.[1] Calhoum and Hurley[2] have reported that traces of copper can be preconcentrated from zinc chloride solution by plating out onto zinc dust. Tarafdar and Rahman[3] have suggested zinc dust for preconcentration of 50 ppb of Cu(II) from 250 cm^3 water with recovery of 95%. Copper has been removed from simulated waste solutions,[4,5] sea water,[6] and human hair[7,8] by coprecipitation on $In(OH)_3$,[6] $Fe(OH)_3$,[9] or $Al(OH)_3$.[10,11] Most of the previously mentioned procedures have low recovery in restoring copper especially from a large volume of aqueous phase[7,8] and also time consuming.[3]

It is well known that copper is one of the most seriously interfering elements in the determination of selenium by hydride-generation/atomic absorption technique.[12—14] Moreover, copper is the adverse interfering element in the determination of mercury(II) complexometrically.[15—17] Hence, our procedure is succeeded to separate selectively copper as copper(II) acetate from mixtures containing selenium and/or mercury.

The aims of the procedure are, quantitative separation of trace amounts of copper at the pH of sea water, absence of salt effect and rapidity. Moreover, the final solution aspirating in atomic absorption instrument for copper determination is an aqueous copper solution. Thence, the complications of back-ground effects of organic solvents, generally used for dissolving the separated copper complex, in the flame can be avoided. The advantages of this proposed procedure may be its application for separation and determination of copper(II) from some alloys, glasses, soils, and copper allied materials. Also, the procedure can be used successfully as a new test during the qualitative chemistry course for sophomore students.

Experimental

Reagents: All reagents, unless specified otherwise, were of analytical-reagent grade.

Stock copper solutions (0.01 mol dm^{-3}≡635.4 ppm Cu) were prepared, by dissolving the appropriate weight of each of $Cu(CH_3COO)_2\cdot H_2O$, $CuCl_2\cdot 2H_2O$, $CuSO_4\cdot 5H_2O$ or $Cu(NO_3)_2$ in 1 dm^3 of bidistilled water.

Stock ammonium, cobalt(II), lead(II), and zinc(II) acetates (1 mol dm^{-3}) were prepared by dissolving the requisite weight of each salt in 1 dm^3 of water.

Oleic acid (HOL) stock solution (6.36×10^{-2} mol dm^{-3}). 20 cm^3 of HOL, food grade (*d* 0.895) were dispersed in 1 dm^3 of kerosene.

Apparatus: The atomic absorption data were measured on Perkin–Elmer Model 2380 atomic-absorption spectrometer using an air-acetylene flame at 324.7 nm. Colorimetric data were recorded by Griffin Model 40 colorimeter.

All pH measurements were carried out with a Hanna Instruments 8519 digital pH meter.

Flotation Cells: Two types of flotation cells were used throughout. Flotation cell (a) was a test tube of 1.2 cm inner diameter and 29 cm length with a stopcock at the bottom. Such cell was used to study the factors affecting the efficiency of flotation. Flotation cell (b) was a cylindrical tube of 6 cm inner diameter and 45 cm length with a stopcock at the bottom and a quick-fit stopper at the top. This cell was used to separate copper from 1 dm^3 of natural water.

Procedure: To study the factors affecting the process of flotation: 20 cm^3 of a solution containing defined amounts of copper(II), HNO_3 or NaOH (for controlling pH) and HOL were introduced into flotation cell (a). The cell was slowly and repeatedly turned upside down about 20 times by hand. Few seconds are required for flotation. The rest of copper in the mother liquor was determined by atomic absorption at 324.7 nm. The scum was taken and directly measured colorimetrically at 700 nm or eluted with 10 cm^3 of 0.1 mol dm^{-3} HNO_3 for atomic absorption measurements. It is noteworthy that, the data obtained colorimetrically were checked by atomic absorption.

The flotation efficiency *F* (%) of copper(II) is conventionally expressed by:

$$F = (1 - C_f/C_i) \times 100\%,$$

where C_i and C_f denote the concentration of copper(II) ions before and after flotation.[18]

Results and Discussion

Effect of pH: Data in Fig. 1 show the changes in the flotation efficiency of different copper(II) salts as a function of pH. It can be seen that, below pH 4 there is no flotation of any of copper(II) salts. This may be attributed to the fact that, oleic acid begins to dissociate at $pH \geq 5.2$[19] to oleate ions which may combine with Cu^{2+} and floated. Moreover, copper(II) acetate may give partly acetic acid at $pH < 4$ and hence changes to the corresponding copper salt uncapable of flotation. Above pH 4, the floatability increases reaching its maximum value (35—40%) for copper(II) chloride, copper(II) nitrate and copper(II) sulfate around pH 7.5 and then decreases. In the case of copper acetate the flotation reaches 100% at pH range from 6.5 to 7.5. At higher pH the floatability of the copper salts decreases due to the formation of excessive foams, turbidity and sodium oleate. In this study, pH 7 was selected for all subsequent experiments.

Effect of HOL Concentration: Varying concentrations of oleic acid surfactant were added to copper(II) solutions (chloride, nitrate, sulfate, and acetate) containing 2.5×10^{-5} mol dm^{-3} copper(II). The results are shown in Fig. 2. It can be seen that, only copper(II) acetate is completely floated at a wide range of HOL concentration level. It is also observed that, the flotation was complete (100%) at a molar ratio of 1 : 2 for HOL : Copper(II) acetate. Such foundation, may be attributed to that one mole of oleic acid surfactant can float two moles of copper(II) acetate which may present in the dimer form,[20] $[Cu_2(CH_3COO)_4(H_2O)_2]$.

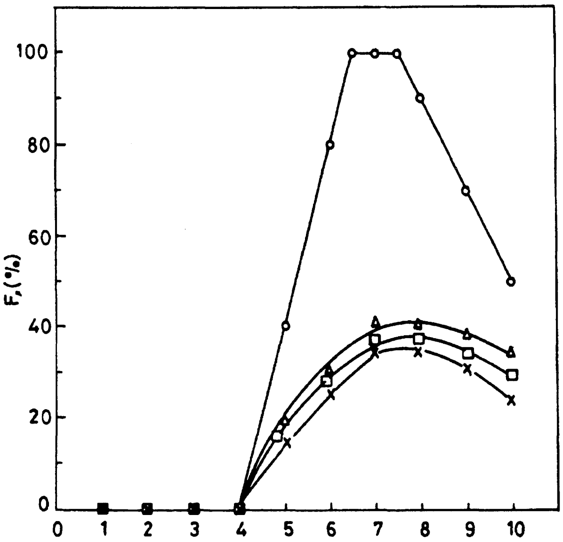

Fig. 1. Floatability of Cu^{2+} vs. pH. Cu^{2+}, 2.5×10^{-5} mol dm^{-3}; HOL, 2.0×10^{-3} mol dm^{-3}. ○ $Cu(CH_3COO)_2 \cdot H_2O$; △ $CuSO_4 \cdot 5H_2O$; □ $Cu(NO_3)_2$; × $CuCl_2 \cdot 2H_2O$.

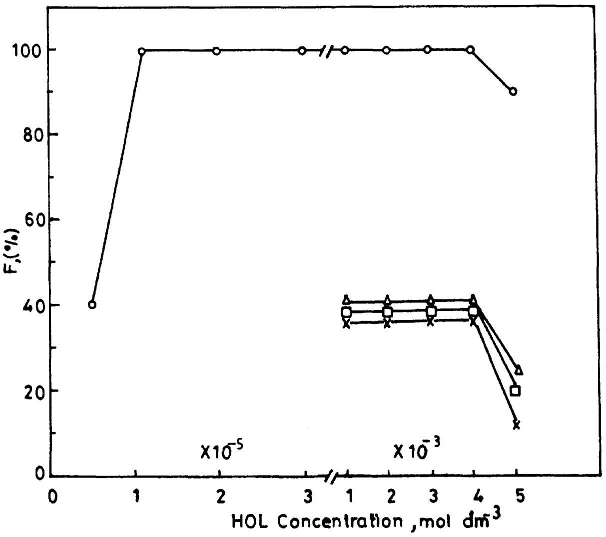

Fig. 2. Floatability of Cu^{2+} vs. HOL concentration. Cu^{2+}, 2.5×10^{-5} mol dm^{-3}; pH 7. ○ $Cu(CH_3COO)_2 \cdot H_2O$; △ $CuSO_4 \cdot 5H_2O$; □ $Cu(NO_3)_2$; × $CuCl_2 \cdot 2H_2O$.

Comparing Figs. 1 and 2, it is evident that copper(II) (chloride, nitrate, or sulfate) floats to a limited extent (35—40%). This proves that the flotation mechanism of copper(II) salts can be discussed on the same basis, perhaps as copper oleate formation. This is in agreement with formation of oleate ions at $pH \geq 5.2$[19] which reacts with copper(II) and floats.

Effect of Copper Concentration: To asses the previous argument, a series of solutions was prepared containing 2×10^{-4} mol dm^{-3} HOL and copper(II) acetate in various concentrations. Data in Fig. 3 show that the curve acquires plateau for 100% flotation recovery of copper(II) acetate. After the molar ratio is attained at 1 : 2 for HOL to copper(II) acetate, the floatability decreases by the same ratio as copper(II) acetate increases with respect to HOL.

Effect of Some Acetate Salts: The flotation of copper(II) salts was carried out in the presence of different concentrations of acetate salts (Table 1). It was found that, copper(II) floats completely (100%) at a molar ratio 1 : 1 in the case of divalent metal acetates (Co, Pb, and Zn), whereas copper(II) restores its full recovery at a molar ratio 1 : 2 for copper salt : ammonium acetate. Accordingly, copper(II) floats completely as copper(II) acetate by oleic acid surfactant. For assured functioning, relatively high concentration of HOL was selected.

Effect of Some Acids: To confirm that the process of flotation of copper(II) acetate depends mainly on hydrogen ion concentration, the effect of different acids and their corresponding salts on the flotation efficiency was carried out. It has been found that HCl, H_2SO_4, HNO_3, or CH_3COOH diminishes completely

Table 1. Floatability of Different Copper(II) Salts (Each in 5×10^{-5} mol dm^{-3}) as Copper(II) Acetate Using HOL (5×10^{-4} mol dm^{-3}) at pH 7

[Copper]/ [acetate] molar ratio	Acetate salt 5×10^{-5} mol dm^{-3}	Flotation %		
		$CuCl_2\cdot2H_2O$	$CuSO_4\cdot5H_2O$	$Cu(NO_3)_2$
2 : 1	CH_3COONH_4	25	25	24
1 : 1		50	50	50
1 : 2		100	100	100
1 : 3		100	100	100
1 : 10		100	100	100
2 : 1	$Co(CH_3COO)_2$	50	50	50
1 : 1		100	100	100
1 : 2		100	100	100
1 : 3		100	100	100
1 : 10		100	100	100
2 : 1	$Pb(CH_3COO)_2$	50	50	50
1 : 1		100	100	100
1 : 2		100	100	100
1 : 3		100	100	100
1 : 10		100	100	100
2 : 1	$Zn(CH_3COO)_2$	50	50	50
1 : 1		100	100	100
1 : 2		100	100	100
1 : 3		100	100	100
1 : 10		100	100	100

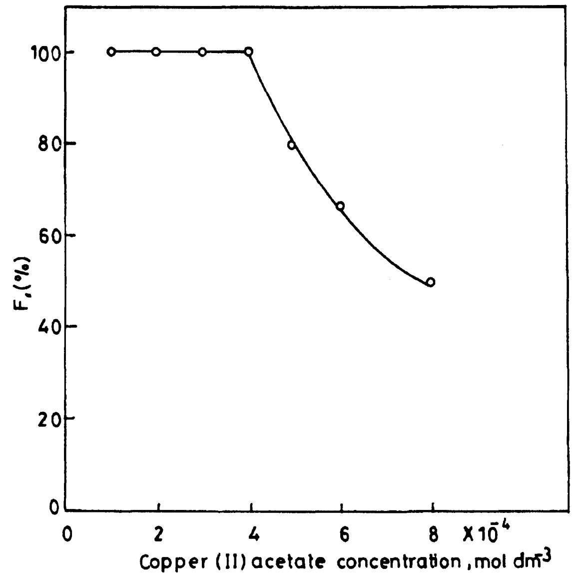

Fig. 3. Floatability of copper(II) acetate using HOL (2×10^{-4} mol dm^{-3}) at pH 7.

the flotation efficiency of copper(II) acetate. This may be attributed to the decrease of pH to less than 4 at which there is no flotation of copper(II), as shown in Fig. 1. Also, the copper(II) acetate may change to the corresponding salt uncapable of flotation with HOL. Whereas, the sodium or potassium salts of the perviously mentioned acids have no effect on the process of copper(II) acetate flotation.

Effect of Foreign Ions: Sample solutions containing 5×10^{-5} mol dm^{-3} of copper(II) as chloride, nitrate or sulfate and various amounts of different ions were introduced into flotation cell (a). The recommended procedure for the flotation, followed by the determination of copper(II), was carried out in presence and absence of 0.1 mol dm^{-3} ammonium acetate. It was observed that in the absence of acetate the flotation does not exceed 10%. Whereas, in the presence of ammonium acetate (Table 2) large number of foreign ions do not interfere. Even in presence of 0.1 mol dm^{-3} ammonium acetate, iron(III) depresses completely the flotation process of copper(II) acetate. Fortunately, such effect can be eliminated by masking iron(III) with thiocyanate. The iron(III) thiocyanate complex can be separated completely by flotation with HOL surfactant in acidic medium. On the other hand, Ag(I) suppresses the flotation efficiency of copper(II) acetate by 20% when Cu(II) was added as chloride or sulfate, whereas the flotation restored its maximum (100%) in case of adding Cu(II) as nitrate. Such effect of Ag(I) may be due to the formation of AgCl or Ag_2SO_4 which float in competition with copper(II) acetate under the optimum conditions. The most interesting point in Table 2 is that Hg(II) and Se(VI) do not interfere. The tolerance limit of the investigated ions (Table 2) is 0.1 mol dm^{-3}, which shows that the method is fairly selective and can be safely applied to selective separation and determina-

Table 2. Effect of Foreign Ions (0.1 mol dm^{-3}) on the Flotation Efficiency of Cu^{2+} (5×10^{-5} mol dm^{-3}) in the Presence of Ammonium Acetate (0.1 mol dm^{-3}) Using HOL (5×10^{-4} mol dm^{-3}) at pH 7

Foreign ion	Flotation %		
(0.1 mol dm^{-3})	$CuCl_2\cdot2H_2O$	$Cu(NO_3)_2$	$CuSO_4\cdot5H_2O$
Fe(III)	0	0	0
Fe(III)[a]	100	100	100
Se(VI), Hg(II), Mg(II), Ca(II) Pb(II), Co(II), Ni(II), K, Na	100	100	100
Ag	80	100	80

a) The interfering effect of Fe(III) was eliminated by preliminary flotation-separation as iron(III) thiocyanate at pH 2 using 5×10^{-4} mol dm^{-3} HOL surfactant in the presence of potassium thiocyanate (0.8 mol dm^{-3}).

Table 3. Separation of Cu(II) from 1 dm^3 of Different Types of Water Using HOL (3.18×10^{-4} mol dm^{-3}) at pH 7 after Adding Ammonium Acetate (0.01 mol dm^{-3})

No.	Type of water	Added copper(II)	Recovery
		µg	%
1	Distilled water	50	99.9
		100	100
		200	100
2	Fresh water	50	99
		100	99.5
		200	100
3	River Nile water	50	99.8
		100	99.9
		200	100
4	Sea Water	50	100
		100	100
		200	100
5	Saline water	50	100
		100	100.1
		200	100.3

tion of copper(II) in various complex matrices.

Effect of Temperature: The flotation of copper(II) acetate was carried out at a temperature range of 10—80 °C. It was found that, up to 40 °C, the flotation efficiency gives 100% recovery under the optimum conditions. Whereas, raising temperature above 40 °C slightly decreases the floatability which may be due to the decomposition of the formed hydrogen bonds between copper(II) acetate dimer and oleic acid surfactant.

Application: Into three flotation cells (b) 1, 2, and 4 cm^3 of copper(II) chloride stock solution (50 ppm of Cu) were added to obtain 50, 100, and 200 µg of copper(II) content in 1 dm^3. To it, 10 cm^3 of ammonium acetate (1 mol dm^{-3}) and 5 cm^3 of HOL (6.36×10^{-2} mol dm^{-3}) were introduced. Water samples from different locations were added to make the total volume 1 dm^3. The flotation cells were turned upside down, by hands twenty times until a blue color appears, for complete flotation. The scum (5 cm^3) was taken and measured colorimetrically for copper determination after constructing a calibration curve, in which Beer's law is obeyed over a concentration range of $(0.5—5)\times10^{-4}$ mol dm^{-3} for copper(II). At low concentration, no color was observed in the scum, it is preferable to elute the copper(II) from the scum by 0.1 mol dm^{-3} HNO_3 and dilute with water to the appropriate volume and then measure the copper(II) concentration using atomic absorption at 324.7 nm. The results are given in Table 3.

Proposed Mechanism for Flotation: Comparing Figs. 2 and 3 with Table 1, it is obvious that the maximum floatability (100%) of copper(II), as copper(II) acetate, was obtained at Cu : HOL molar ratio of 2 : 1. This ratio confirms that one mole of HOL floats one mole of copper(II) acetate dimer[20] may be as $[Cu_2(CH_3COO)_4(H_2O)_2]$, through hydrogen bonding or as $[(H_2O)Cu_2(CH_3COO)_4(HOL)]$ through coordination of oxygen in HOL to the dimeric copper acetate.

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