

Flotation–Spectrophotometric Method for Separation and Determination of Trace Amounts of Copper

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Summary: A flotation–spectrophotometric method for the determination of Cu^{2+} has been developed. The flotation process is based on the formation of a ternary ion-associate between Cu^{2+} , methylthymol blue (MTB) and cetyltrimethylammonium bromide (CTAB) which is floated at the interface of aqueous phase and n-hexane by shaking in a separating funnel. The aqueous solution is discarded and the adsorbed ion associate ($\text{Cu}^{2+}\text{-MTB-CTA}^+$) on to the wall of a separating funnel is dissolved in a small volume of methanol solvent and its absorbance is measured at 556 nm. The apparent molar absorptivity (ϵ) of the ion associate was determined to be $6.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The calibration curve was linear in the concentration range of 10-400 ng mL^{-1} of Cu^{2+} with a correlation coefficient of 0.9994. The limit of detection (LOD) was 6.7 ng mL^{-1} . The relative standard deviation (RSD) for 50 and 300 ng mL^{-1} of Cu^{2+} was 3.9% and 1.3% ($n=7$), respectively. The method was successfully applied to the determination of Cu in water samples from water treatment process of Ramin power plant, Iran.

Keywords: Flotation–spectrophotometry; copper; methylthymol blue; cetyltrimethyl ammonium bromide.

Introduction

Flame atomic absorption spectrometry (AAS) provides a simple and rapid method for the determination of many heavy metals in different samples. Nevertheless, for extremely low concentration of heavy metals in water samples, a direct determination can not be applied without their previous separation and preconcentration. Today very modern expensive separation instrumentation is available, but many labs can not provide them because of their high cost. Therefore classical preconcentration methods such as ion exchange, solvent-solvent extraction, coprecipitation and flotation are frequently used methods for this purpose [1]. Ternary ion-association complexes wherein central ion reacts with two different ligands, have aroused considerable interest in the past two decades. Flotation–spectrophotometry of such colored ternary complexes probably provides the most sensitive, relatively simple and fast approach to trace metal analysis [2]. It should be mentioned that the term “flotation-spectrophotometric” is based on the fact that some ion associations are not soluble in polar organic solvents, and when an aqueous phase is shaken with an organic solvent, a precipitate originates in the interface or on the extraction funnel walls. Once both phases have been separated the precipitate is dissolved in an appropriate solvent, and the corresponding measurements are made by the spectrophotometry [3, 4]. Different preconcentration-spectrophotometric methods [5-12], solvent-extraction-spectrofluorimetry [13] and chromatographic [14] methods are used for trace quantitative determination of Cu^{2+} .

This paper presents a flotation–spectrophotometric method for quantitative determination of Cu^{2+} . The method is based on the formation of a ternary ion-associate between Cu^{2+} with methylthymol blue (MTB), an anionic dye, and cation of cetyltrimethylammonium bromide (CTAB) surfactant, and extraction of ($\text{Cu}^{2+}\text{-MTB-CTA}^+$) ternary ion-associate into the interface between aqueous and n-hexane phase by flotation method. The proposed method has been successfully applied to the determination of Cu^{2+} in water samples.

Results and discussion

The preliminary investigations showed that Cu^{2+} interacts with MTB and CTAB to form a solid ion-associate which is soluble in some polar organic solvents such as methanol. The absorption spectra of the dissolved ($\text{Cu}^{2+}\text{-MTB-CTA}^+$) ion associate in methanol showed a maximum absorbance at 556 nm. Thus all the absorbance measurements were made at this wavelength.

Various organic solvents such as methyl ethyl ketone, dimethyl formamide, carbon tetrachloride, benzene and n-hexane were tested as a dissolvent and n-hexane was found to show good characteristics as a floating solvent. The solid ion associate floats at the interface of n-hexane-water and adheres on the funnel wall. The aqueous phase is discarded completely. The effect of n-hexane volume on the flotation process was examined in the range of 3-10 mL. The results showed that by increasing the volume of n-hexane up to 7 mL the flotation process

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proceeds more effectively and larger volumes of n-hexane have no significant improvement on the flotation of Cu^{2+} . Therefore, 7 mL was used as optimum n-hexane volume.

Different organic solvents such as acetone, ethanol, methyl ethyl ketone, THF and methanol were examined to dissolve the adhered solid from the wall of the separating funnel. The dissolution of the ion associate with methanol was complete when 2.5 mL of methanol was used as extracting solvent.

The effect of pH on the flotation of $(\text{Cu}^{2+}\text{-MTB})\text{-CTA}^+$ ion-associate was studied by varying the pH of the aqueous phase in the range of 4-11 before adding the organic phase. The pH was adjusted to the desired value using acetate, borate, phosphate and ammonia buffers. The results of this study are presented in Fig. 1. The maximum flotation was observed at pH 6.5, using borate buffer and was selected as optimum pH value. It must be mentioned that the protonation of carbonate groups of the dye in pH values lower than 7 causes low $(\text{Cu}^{2+}\text{-MTB})\text{-CTA}^+$ ion-associate formation and also competition of borate anion with dye anion to form ion associate with Cu^{2+} causes low ion-associate formation at pH values greater than 7. The optimum buffer volume of borate buffer was chosen to be 3 mL.

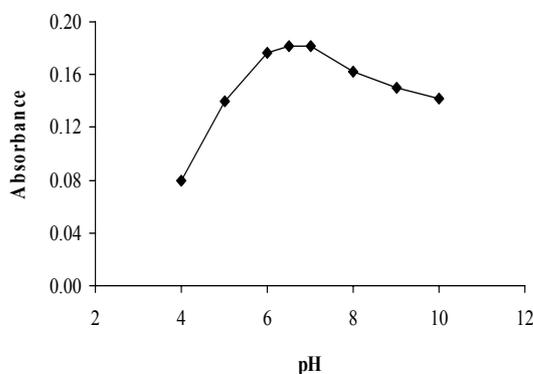


Fig. 1: The influence of pH on the flotation of $(\text{Cu}^{2+}\text{-MTB})\text{-CTA}^+$ ion-associate.

The effect of MTB concentration on the flotation of Cu^{2+} was also examined by applying various concentration of MTB. The absorbance of the dissolved solid was increased by increasing MTB concentration up to $6.0 \times 10^{-6} \text{ mol L}^{-1}$ of MTB in the final solution and remained constant above this concentrations. The results are shown in Fig. 2. Thus, $6.0 \times 10^{-6} \text{ mol L}^{-1}$ of MTB in the final solution was selected as the optimum concentration of MTB for Cu^{2+} flotation process.

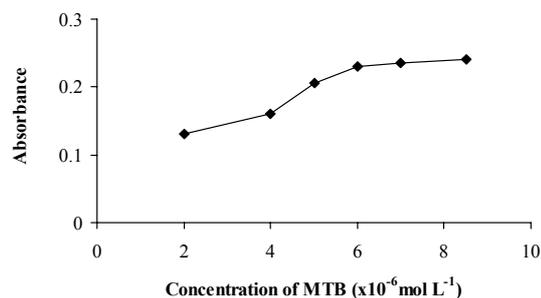


Fig. 2: The effect of MTB dye concentration used for the flotation of Cu^{2+} .

The influence of CTAB concentration on the flotation of Cu^{2+} was also examined by using different concentration of CTAB as a surfactant. The absorbance was increased with increasing CTAB concentration up to $4.0 \times 10^{-5} \text{ mol L}^{-1}$ of CTAB in the final solution and decreased at higher concentrations (Fig. 3). Thus $4.0 \times 10^{-5} \text{ mol L}^{-1}$ of CTAB in the final solution was chosen as the optimum concentration of CTAB for Cu^{2+} flotation process. It should also be mentioned that higher concentrations than $4.0 \times 10^{-5} \text{ mol L}^{-1}$ of CTAB in the final solution causes an increase in the blank absorbance and decreases the absorbance of ternary ion associate.

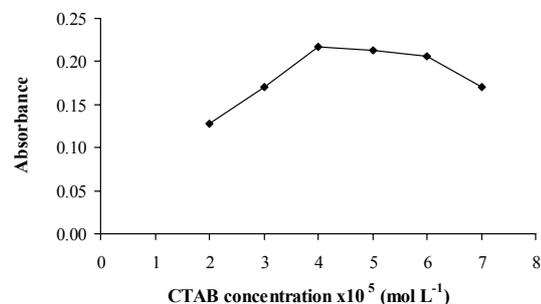


Fig. 3: The effect of CTAB concentration used for the flotation of Cu^{2+} .

The effect of standing time on the formation of $(\text{Cu}^{2+}\text{-MTB})\text{-CTA}^+$ ternary ion-associate was studied over the time period of 2-15 min for 25 ng mL^{-1} of Cu^{2+} , $6.0 \times 10^{-6} \text{ mol L}^{-1}$ of MTB and $4.0 \times 10^{-5} \text{ mol L}^{-1}$ of CTAB concentrations at optimum pH (6.5). and measuring the absorbance at 556 nm after flotation. The maximum absorbance was obtained for 10 min standing time.

The influence of electrolyte concentration on the formation of $(\text{Cu}^{2+}\text{-MTB})\text{-CTA}^+$ ternary ion associate was investigated at different concentration

of NaCl. The results indicated that the absorbance of ion-associate increases with increasing NaCl concentration up to 9.0×10^{-3} mol L⁻¹ of NaCl in the final solution and remains constant at higher concentrations of electrolyte. A constant concentration of 1.0×10^{-2} mol L⁻¹ of NaCl was used throughout.

The flotation of the ion associate may also be influenced by the shaking time, because of increase in the active surface of the gas-liquid interface. Maximum absorbance was obtained at 60 s shaking time. Therefore, a shaking time of 60 s was applied for further experiments.

Quantitative Results

A linear calibration graph was obtained over the concentration range of 10–400 ng mL⁻¹ of Cu²⁺. The regression equation was $A = 2.5 \times 10^{-3}C + 0.1004$ with a correlation coefficient of 0.9995, where A is the absorbance and C shows the concentration of Cu²⁺ in ng mL⁻¹. With regard to the preconcentration factor of the process (40 fold, i.e., from 100 mL aqueous solution to 2.5 mL of methanol), and a path length of 1 cm, the conditional molar absorptivity was 1.85×10^5 L mol⁻¹ cm⁻¹ at the above wavelength. The relative standard deviation (R.S.D) for 50 and 300 ng mL⁻¹ of Cu²⁺ were 3.8% and 1.4% (n=7), respectively. The limit of detection (LOD) based on $3S_b$ [15] was 6.7 ng mL⁻¹.

Effect of Interferences

The influence of various cations and anions on the determination of Cu²⁺ was studied. A fixed concentration of Cu²⁺, 20 ng mL⁻¹, was taken with different concentration of possible interfering ions and the recommended procedure was followed. A relative error of 5% with respect to the absorbance difference for the Cu²⁺ solution was considered tolerable. Tolerance limits are as follows: F⁻, SCN⁻, Br⁻, S₂O₃²⁻, NO₃⁻, K⁺, CO₃²⁻, Li⁺ (1000 folds); SO₄²⁻, Ca²⁺, Ba²⁺, Mg²⁺, Pb²⁺, NH₄⁺, Hg²⁺, NO₂⁻ (500 folds); Sr²⁺, Cd²⁺, Hg²⁺, Ni²⁺, Fe³⁺, (50 folds); Mn²⁺, Bi³⁺, Mo(VI), Ag⁺ (10 folds) and Co²⁺, Zn²⁺, (1 folds).

Application

In order to evaluate the applicability of the method it was applied to the determination of Cu²⁺ in water samples of water treatment unit of Ramin power plant. The results are shown in Table-1. As it is seen, the recovery values show the validity and accuracy of the proposed method.

Table-1: Determination of Cu in Ramin power plant cooling water samples.

Sample number	Cu ²⁺ (ng mL ⁻¹) ^a		
	added	found	%Recovery
1	-	35.5±1.7	-
1	25	60.1±2.9	99.3
1	100	138.9±4.5	102.5
2	-	ND ^b	-
2	30	29.0±1.4	96.7

a. $\bar{x} \pm ts / \sqrt{n}$ at 95 % confidence (n=3), b. Not detected

Experimental

Apparatus

The absorption spectra and absorbance measurements were made by a JASCO model 7850 UV-Visible spectrophotometer. A Metrohm model 632 pH-meter with a combined glass electrode was used for pH measurements.

Reagents

All chemicals used were of analytical grade and used without further purification. 1000 µg mL⁻¹ stock solution of Cu²⁺ was prepared by dissolving 0.7812 g of CuSO₄·5H₂O (Merck) in freshly distilled water and diluting to the mark in a 200 mL volumetric flask. Stock solution of MTB (5×10^{-5} mol L⁻¹) was prepared by dissolving 0.0105 g of MTB (Merck) in distilled water and diluting to 250 mL in a flask. 1×10^{-3} mol L⁻¹. Stock solution of CTAB was prepared by dissolving 0.0364 g of CTAB (Merck) in distilled water and diluting to 100 mL in a flask. Different buffer solutions (acetate, phosphate, borate and ammonia) in the pH range of 5-9 were made by mixing 100 mL of 0.2 mol L⁻¹ solution of acids or salts with appropriate volumes of 0.2 mol L⁻¹ solutions of sodium hydroxide or hydrochloric acid and using a pH meter to adjust the pH to exact value.

Recommended Procedure

Transfer an aliquot of a sample solution containing not more than 40 µg of Cu²⁺ into a 100 mL volumetric flask, containing 12 mL of 5×10^{-5} mol L⁻¹ of MTB, 3 mL of borate buffer of pH=7 and 4 mL of 1×10^{-3} mol L⁻¹ of CTAB, dilute to the mark with distilled water and let stand for about 10 min. Then transfer the flask content to a 100 mL separating funnel containing 7 mL of n-hexane and shake the mixture vigorously for 60 s and then allow standing for 5 min for separation of organic phase from aqueous phase. The (Cu²⁺-MTB)-CTA⁺ ion-associate (color solid) floats on the interface. After discarding the aqueous phase (lower layer) add 2.5 mL of methanol to n-hexane solution containing adsorbed ion associate. The methanol phase extracts

the solid ion associate from n-hexane phase and dissolves it completely. The absorbance of extracted colored ion associate is measured at 556 nm using 1 cm cells against a reagent blank. All the experiments were carried out at room temperature.

The proposed procedure was applied to the determination of Cu^{2+} in water samples. A portion of the water solution containing up to 40 μg of Cu^{2+} was transferred into a 100 mL volumetric flask and the procedures was followed under optimum conditions.

Conclusion

The proposed method is simple, reproducible and sensitive and can be applied for quality control of Cu^{2+} in water samples in any water treatment unit. The method shows good sensitivity due to high molar absorptivity and gives a wide linear dynamic range with respect to some of the reported methods. A forty fold preconcentration factor was achieved and the limit of detection of the proposed method is comparable or better than some of the previously published methods (3-14) for the determination of Cu^{2+} .

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