

EXTRACTION-FLUORIMETRIC DETERMINATION OF LOW LEVELS OF COPPER BY 1,7- DIAZA-15- CROWN-5 AND ROSE BENGAL

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ABSTRACT : *A simple and sensitive extraction- fluorimetric method for the determination of copper is reported. The 1,7- diaza-15- crown-5- copper- rose bengal (DA15C5-Cu-RB) ternary complex is quantitatively extracted into chloroform, diluted with ammoniacal acetone and its fluorescence intensity is measured at 570nm with excitation at 540nm. A linear calibration graph was obtained over the copper concentration range of 0.05-0.50 μ g/mL. The relative standard deviation for 0.35 μ g/mL copper is 3.9%. The interfering effect of a large number of diverse ions on the determination of copper was studied. The method was applied to the determination of copper in tap water.*

KEY WORDS : *Copper, Low Level Determination, 1,7-Diaza-15-crown-5, Rose bengal, Extraction, Fluorimetry.*

INTRODUCTION :

Macrocyclic crown ethers are well known as selective ligands for various metal ions [1]. Some such complexes can be extracted from aqueous solutions into an organic phase. Although the extraction properties of crown ether complexes has been widely studied [2-9], their applications to the determination of metal ions are still

rather limited [10-14]. Application of highly fluorescent anionic dyes or counter anions with large molar absorptivities could lead to sensitive methods for trace metal determinations.

Compared with numerous spectrophotometric [15,16] and fluorimetric [17,18] methods available for the determination of copper, the

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use of macrocyclic ligands in such analyses is quite sparse. To the best of our knowledge, there is only one literature report on the determination of copper with a cyclic tetrathio ether and bromocresol green in the concentration range of 0.6-3.2 $\mu\text{g/mL}$ [19]. In this paper we report a simple and sensitive method for the quantitative extraction of DA15C5-Cu-RB ternary complex into chloroform, followed by fluorimetric measurements at 570nm. Structures of the crown ether and the dyestuff used are shown in Fig. 1.

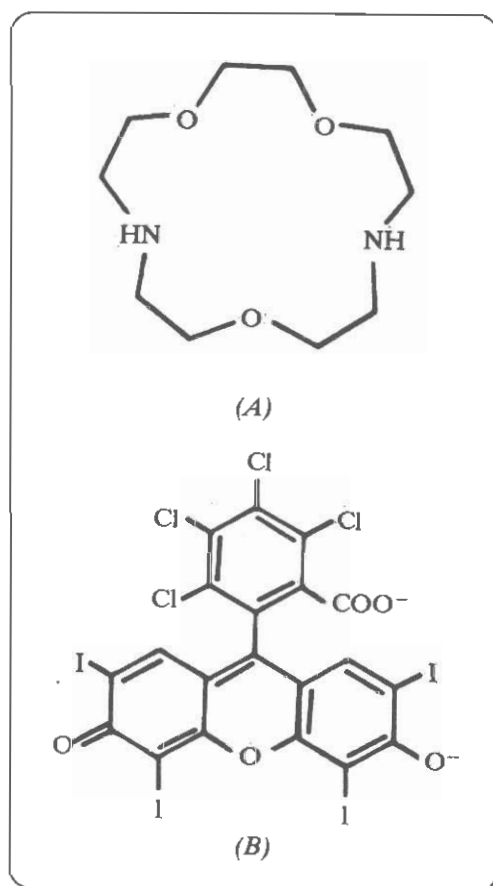


Fig. 1: Structure of DA15C5 (A) and rose bengal (B).

EXPERIMENTAL :

Reagents

All of the chemicals used were of the highest purity available and used without further purification except for vacuum drying over P_2O_5 . Triply distilled deionized water was used throughout.

A stock solution of copper (1000 $\mu\text{g/mL}$) was prepared by dissolving 1.8108g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck, Darmstadt, Germany) in water and diluting to the mark in a 500mL volumetric flask. The solution was standardized complexometrically with EDTA solution [20]. Working solutions were prepared by appropriate dilution of the stock solution with water.

A buffer solution of pH 9.0 was prepared by mixing 8.3mL of concentrated acetic acid and 16.7mL of 25% ammonia in a 500mL volumetric flask and diluting to the mark with distilled water.

Rose bengal(RB)stock solution ($7.2 \times 10^{-4}\text{M}$) was prepared by dissolving 0.1465g of the dyestuff (Fluka) in water and diluting to the mark in a 200mL volumetric flask.

1,7- Diaza-15-crown-5 (DA15C5) stock solution ($1.35 \times 10^{-3}\text{M}$) was prepared by dissolving the appropriate amount of the crown ether (Merck) in chloroform.

Apparatus

All fluorescence spectra were recorded on a Shimadzu RF-5000 spectrofluorometer. The fluorescence intensity measurements were made with a LS-2B Perkin-Elmer filter fluorimeter. Measurements of pH were made with a Corning 113pH meter using a combined electrode.

Procedure

An aliquot of sample containing 0.5-5.0 μg of copper was placed in a 10mL volumetric flask. Five mL of rose bengal solution ($7.2 \times 10^{-4}\text{M}$) and 2mL of buffer pH9.0 were added and then the solution was diluted to the mark with distilled water. The solution was transferred into a 50mL separatory funnel and 5mL of DA15C5 solution in chloroform was added. The solution was shaken vigorously for 5min. The phases were allowed to separate. Then a 1.0mL portion of the organic phase was diluted to 10mL with 2% (v/v) ammoniacal acetone in a volumetric flask and then its fluorescence intensity was measured at 570nm, with excitation at 540nm, against a reagent blank.

RESULTS AND DISCUSSION :

Since Cu^{2+} ion forms a fairly stable 1:1 complex with DA15C5 in aqueous solution [21], application of a highly fluorescent anionic dye such as rose bengal [22] as counter ion was expected to result in a sensitive and useful method for trace copper ion determination.

In preliminary experiments it was found that, despite the quantitative extraction of the DA15C5-Cu-RB ternary complex under appropriate experimental conditions into chloroform, the extract shows a low fluorescent property. However, it was observed that the fluorescence intensity of the complex was increased by addition of acetone, presumably due to the increased dissociation of the ternary complex with increasing dielectric constant of the solvent mixture [23]. A 10-fold dilution of the extract with 2% (v/v) ammoniacal acetone showed an even more marked effect; the fluorescence intensity was enhanced by a factor of 20. It seems reasonable to assume that, in this case, the dissociation of ternary complex is complete and the resulting fluorescence is entirely due to free RB.

The excitation and emission spectra of rose bengal are shown in Fig.2. Based on the resulting spectra, the excitation and emission wavelengths selected for further experiments were 540 and 570nm, respectively.

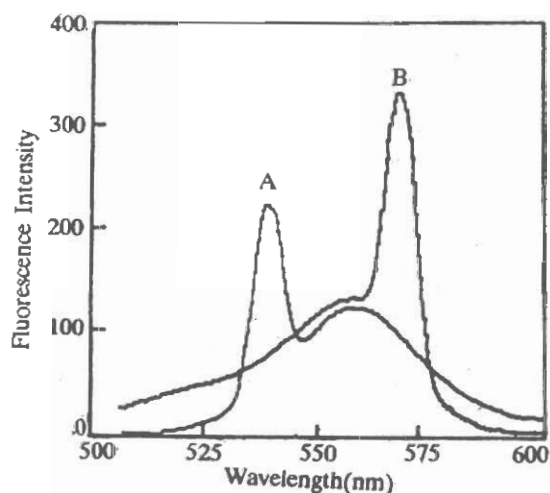


Fig. 2: Excitation (A) and emission (B) spectra of rose bengal.

Effect of Variables

The influence of pH on the extraction of DA15C5-Cu-RB complex was studied over the pH range 4-13 and the results are shown in Fig.3. As it is seen, maximum extraction of copper occurs within the pH range 8-9. In this range, the dyestuff is mainly in the form RB^{2-} which is suitable for ion pair formation with Cu^{2+} -DA15C5 complex. At lower pH values, the fraction of RB^{2-} in solution decreases and, consequently, a gradual decrease in the extent of extraction is observed. On the other hand, the drastic decrease in the extent of extraction observed at higher pH values could be related to a relatively strong competitive effect of hydroxyl ion with RB^{2-} for copper which, in turn, reduces the efficiency of the copper extraction. A pH of 9.0 was chosen as the optimum working pH. It was found that, addition of 2mL of buffer, pH 9.0, is adequate to reach the maximum extraction efficiency.

The effect of rose bengal and DA15C5 concentrations on the extraction of DA15C5-Cu-RB complex was investigated and the results are shown in Figs. 4 and 5, respectively. As it is

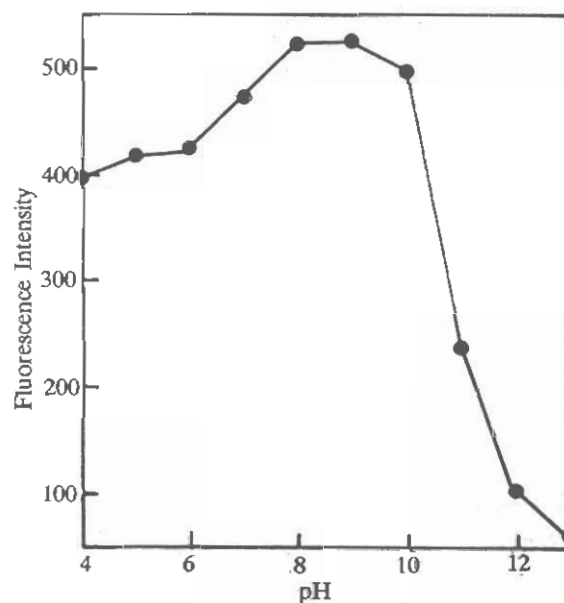


Fig. 3: Effect of pH on the extraction of copper. Conditions: Cu^{2+} , $0.6\mu\text{g/mL}$; rose bengal, $3.6 \times 10^{-4}\text{M}$; DA15C5, $1.5 \times 10^{-4}\text{M}$.

seen, the fluorescence intensity of the organic phase increases with increasing both rose bengal and DA15C5 concentrations in the aqueous and organic phases, respectively. Maximum extraction of copper occurs when the reagent to metal ion mole ratio is about 8, for rose bengal, and about 30, in the case of DA15C5. A further excess of both reagents has no considerable effect on the measured fluorescence intensity, except that in the case of rose bengal the intensity of the blank solution tends to increase gradually.

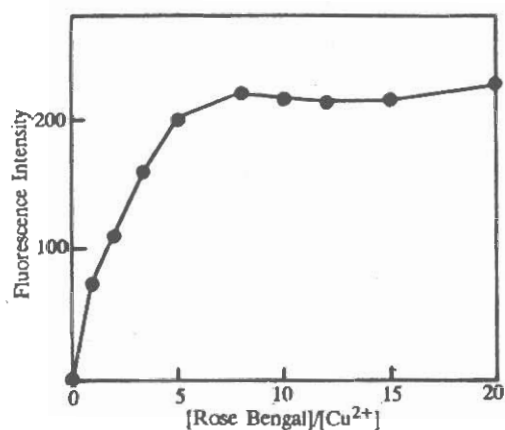


Fig. 4: Effect of rose bengal concentration on the extraction of copper. Conditions: Cu^{2+} , $0.3\mu\text{g/mL}$; DA15C5, $1.5 \times 10^{-4}\text{M}$; pH 9.0.

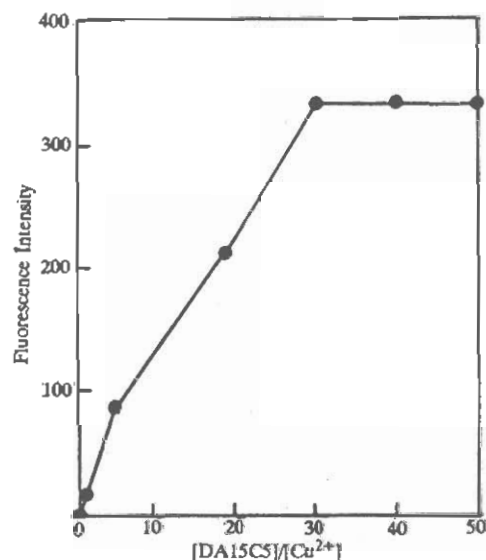


Fig. 5: Effect of DA15C5 concentration on the extraction of copper. Conditions: Cu^{2+} , $0.4\mu\text{g/mL}$, rose bengal, $6.0 \times 10^{-5}\text{M}$; pH 9.0.

The ionic strength of the aqueous solution, adjusted by cesium chloride, was found to affect the extraction of DA15C5-Cu-RB complex into chloroform. There is an inverse relationship between the extent of extraction and the ionic strength of the aqueous phase. Similar results have already been reported in the literature [14,24].

The extraction of DA15C5-Cu-RB ternary complex under the conditions recommended in the procedure is rapid. A shaking time of 3-5min was found sufficient for the extraction of copper.

The extraction process was performed under optimal conditions with some common organic solvents such as chloroform, carbon tetrachloride, benzene, methyl isobutyl ketone and 1,2-dichloromethane. It was found that the DA15C5-Cu-RB ternary complex is readily extractable in chloroform. While, in other solvents used, the colored complex could not be extracted into the organic phase completely and some of that remained between the two phases as a precipitate.

Quantitative extraction of copper as DA15C5-Cu-RB complex was confirmed by observing no further enhancement in the fluorescence intensity of the mixture of two 2.5mL portions of the organic phase, obtained from two successive extraction of an aqueous copper solution, compared with that of a 5mL organic phase obtained from a single stage extraction of the same copper solution, under optimal experimental conditions.

Calibration

Under the optimum conditions described above, a linear calibration graph of ΔI vs. $[\text{Cu}^{2+}]$ was obtained in the concentration range of $0.05\text{-}5.0\mu\text{g/mL}$ with a regression equation of $\Delta I = -38.1 + 951.0 [\text{Cu}^{2+}]$ and a correlation coefficient of 0.9988 (Fig. 6). The relative standard deviation of nine replicate measurements is 3.9% for a $0.35\mu\text{g/mL}$ copper solution.

Effect of Diverse Ions

In order to study the influence of various

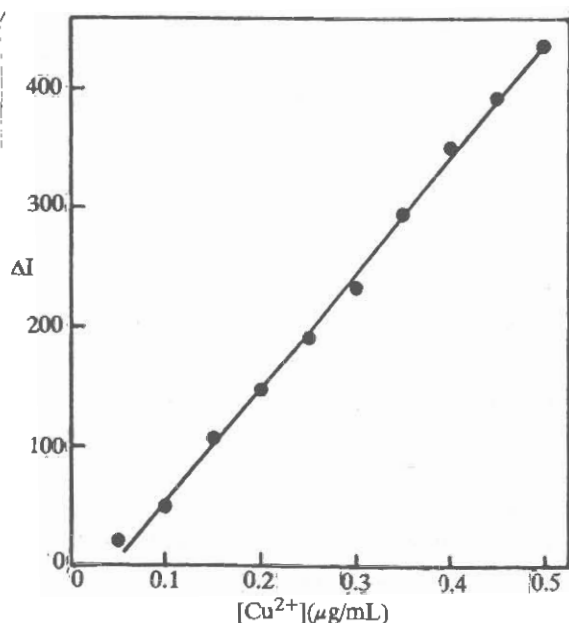


Fig. 6: Calibration graph. Conditions: rose bengal, $3.6 \times 10^{-4} M$; DA15C5, $1.35 \times 10^{-3} M$; pH 9.0.

cations and anions on the determination of copper ion, a fixed concentration of copper ($0.5 \mu\text{g/mL}$) was taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of twice the standard deviation of measurements was considered tolerable. The results are summarized in Table 1. As it is seen, most of the cations and anions used have no considerable effect on the determination of copper ion. However, palladium and oxalate ions were found to interfere with the copper determination to some extent.

Application

The proposed method was applied to the determination of copper in tap water using the standard addition method. The amount of copper in tap water obtained from three different sample solutions according to the proposed method was found to be $0.10 \pm 0.01 \mu\text{g/mL}$ which is in satisfactory agreement with that obtained by atomic absorption spectroscopy ($0.11 \pm 0.02 \mu\text{g/mL}$).

CONCLUSIONS :

The method described provides a simple and

reliable means of determination of trace amounts of copper. It is free from interference from many cations and anions. Although the linear range of the proposed method is not much improved, compared with some previously reported methods [15-19], it compares favorably in sensitivity and selectivity with most of the published methods for the determination of copper by use of ion- association compounds, and it can certainly be placed among the most sensitive ones.

Table 1 : Tolerance limits of diverse ions on the determination of $0.5 \mu\text{g/mL}$ copper.

| Ion | Tolerated ration of foreign ion to copper |
|---|---|
| CH_3COO^- | 6200 |
| K^+ | 3200 ^a |
| Cs^+ | 2800 ^a |
| NH_4^+ | 1890 |
| MoO_4^{2-} | 1340 |
| $\text{Na}^+, \text{NO}_3^-$ | 1000 ^a |
| WO_4^{2-} | 483 |
| VO_3^- | 416 |
| $\text{Li}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Al}^{3+}, \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{IO}_3^-, \text{BrO}_3^-, \text{IO}_4^-, \text{S}_2\text{O}_8^{2-}, \text{NO}_2^-, \text{OCN}^-, \text{SO}_4^{2-}, \text{HAsO}_4^{2-}$ | 200 ^a |
| $\text{Zn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{In}^{3+}, \text{Hf}^{4+}$ | 200 |
| $\text{ClO}_4^-, \text{I}^-$ | 100 |
| $\text{La}^{3+}, \text{SeO}_3^{2-}$ | 52 |
| $\text{PtCl}_4^{2-}, \text{S}_2\text{O}_3^{2-}$ | 48 |
| $\text{Ti}^+, \text{V}^{3+}, \text{TeO}_6^{6-}, \text{PO}_4^{3-}$ | 20 |
| SCN^- | 14 |
| $\text{P}_2\text{O}_7^{4-}$ | 10 |
| $\text{Ag}^+, \text{Fe}^{3+}$ | 8 |
| $\text{Pd}^{2+}, \text{Oxalate}$ | 2 |

a: Concentrations above the stated values were not tested.

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