



## SENSING OF TRACE COPPER ION BY A SOLID PHASE EXTRACTION–SPECTROPHOTOMETRY USING A POLY(VINYL CHLORIDE) MEMBRANE CONTAINING BATHOCUPROINE

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**Summary**—A new sensitive and selective spectrophotometric method for the determination of trace copper using a poly(vinyl chloride) membrane containing 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine) and *o*-nitrophenyl-octylether as the solid phase extraction medium. Copper(I) in an aqueous sample solution is trapped on the membrane with an anion species, picrate ion, to form copper(I)–bathocuproine–picrate complexes, and the copper complexes, *i.e.* copper(I), were concentrated in the membrane. The absorbance of the orange membrane was measured at 480 nm using a spectrophotometer, and the concentration of the copper was then calculated using a calibration graph, which expressed the relationship between the copper(I) concentration and the membrane absorbance after coloring for 10 min. The detectable concentration of copper in a sample solution was in the range of  $1.5 \times 10^{-7}$ – $4.3 \times 10^{-5} M$ . The reproducibility of the absorbances of membranes was  $0.193 \pm 9.44 \times 10^{-3}$  with a 4.9% relative standard deviation on five repeated measurements for the sample containing  $1.2 \times 10^{-5} M$  of copper(II) under the same experimental conditions.

The measurement of the concentration of various metal ions which are presented in aqueous samples such as industrial or life waste waters has been widely performed by liquid–liquid extraction–spectrophotometry. The determination of sample at low concentration levels by conventional liquid–liquid extraction–spectrophotometry often suffers from the lack of sensitivity and selectivity. Further, the running cost using large amounts of chelate compounds and organic solvents is expensive in routine analysis, and the treatment of the used solvent is required.

The solid phase-spectrophotometry, which directly measures the medium by spectrophotometry using a solid phase medium such as a poly(vinyl chloride) (PVC) membrane instead of an organic solvent in the liquid–liquid extraction, was recently reported.<sup>1–6</sup> A method using a solid phase as the extraction medium possesses many advantages over liquid–liquid extraction in spectrophotometry.

(1) Trace metal ions at ppb level can be determined because the targeted ion is enriched in small membrane.

(2) Selective detection of the metal ion will be possible by using a solid phase containing a ligand having a high reactivity to the targeted metal ion.

(3) It is free from difficult phase separation, which is caused by mutual solubility between water and organic solvent layers.

(4) The solid phase extraction methods are free of interference from particulate matter suspended in aqueous samples because particles are not adsorbed onto the solid phase medium.

(5) The extraction method is an economical method since it uses only a small amount of ligand and extraction solvent.

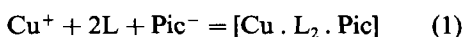
(6) The concentration of metal ion can be visibly estimated from the color intensity of the membrane if the metal complex formed in the membrane possesses absorption in the visible wavelength region.

For the application of solid phase extraction–spectrophotometry using a PVC membrane as an extraction medium, the determining methods of anionic surfactant,<sup>3,4</sup> aluminium(III)<sup>5</sup> and iron(III)<sup>6</sup> were reported. The detection of the targeted component by spectrophotometry in

these studies is based on the color change of the PVC membrane, which was due to adsorption of the colored analyte species (ion pair) on the membrane surface. None of the membranes, however, possess a high selectivity to the analyte ion. The author has investigated a selective and sensitive sensing method of a metal ion, specifically copper ion, using a PVC membrane containing a chelate agent, 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine), which possesses, a high reactivity and selectivity to the copper ion.<sup>7,8</sup> In this study, the effect of counter ion species vs the coloring rate of the membrane was discussed, and as a result, it was found that the coloring rate of the membrane increased by the addition of picrate ion as a pairing ion.<sup>9</sup> As a consequence, a rapid determination of copper was accomplished by means of shorter coloring time (10 min) of the membrane.

#### Principle: coloring mechanism of membrane

The assumed coloring model of the PVC membrane is shown in Fig. 1. The copper(I) in aqueous solution produces coordinate bonds with the nitrogen atoms of bathocuproine (L) at the PVC membrane surface to form a positive-charged complex ion  $[\text{Cu} \cdot \text{L}_2]^+$  with a molar ratio of 1:2 which, in turn, forms an ion pair with a picrate ion ( $\text{Pic}^-$ ); *i.e.* a neutral complex  $[\text{Cu} \cdot \text{L}_2 \cdot \text{Pic}]$ . The molar ratio of copper(I), bathocuproine and picrate ion for the formation of the copper(I) complex formation is 1:2:1, and the complex formation is expressed by



The color of the PVC membrane changes from colorless to orange because the color of the copper(I) complex is orange, and the color intensity of the membrane depends on the concentration of the copper(I)–bathocuproine–picrate complex, *i.e.* copper(I). Accordingly,

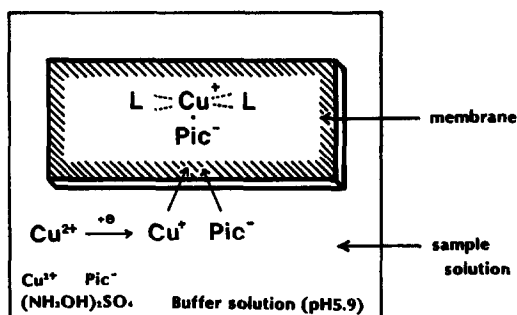


Fig. 1. Extraction profile of copper(I) into the PVC membrane containing bathocuproine.

from the color intensity of the membrane, copper(I) in a sample solution can be determined with a calibration graph using a spectrometer.

## EXPERIMENTAL

### Reagents and instruments

Bathocuproine and *o*-nitrophenyloctylether (NPOE) were of analytical reagent grade from Dojindo Laboratory Co. Copper(II) nitrate trihydrates, PVC (which consists of the degree of polymerization of 1100), sodium picrate, acetic acid, sodium acetate and other reagents were obtained from Wako Pure Reagents Industrial Co.

The membrane absorbance was measured using a UV–VIS spectrophotometer (Shimadzu Model UV-150-02) with a minimum absorbance of 0.0001, and the concentrations of the prepared copper(II) solutions were confirmed using an atomic absorption spectrometer (Shimadzu Model AA-680) with a commercial copper(II) standard solution of 1000 ppm (Wako Pure Reagents Industrial Co.).

### Preparation of PVC membranes

Samples of 0.01750 (0.7), 0.8561 (34.3), and 1.6224 g (65.0 wt%) of bathocuproine, PVC, and NPOE, as a plasticizer, were placed in a 100 ml beaker, respectively, and 25 ml of tetrahydrofuran (THF) was then added to the mixture. After stirring until the membrane feed had completely dissolved, the solution was cast in a flat Petri dish with a diameter of 147 mm and stored until the THF had evaporated. The membrane obtained had a light yellow color and was flexible. The membrane was cut into 30 × 5 mm pieces (0.15 mm thickness). The volumes of the membranes, which were used in the experiments, were  $2.3 \times 10^{-2} \pm 5.6 \times 10^{-4} \text{ cm}^3$ .

### Measurements

A 5 ml aliquot of aqueous sample solution containing copper was placed in a 30 ml glass sample tube with a PTFE stirring rod (20 × 7 mm diameter), and then 0.5 ml of  $6.5 \times 10^{-2} \text{ M}$  hydroxylammonium sulphate,  $1 \times 10^{-4} \text{ M}$  sodium picrate and acetic acid–sodium acetate buffer solution (pH 5.9) were each added. A sheet of PVC membrane was put into the solution and stirred (150 rpm) for 10 min at 60°C. The membrane removed from the solution was rinsed with a small amount of deionized water, and wiped to remove any water droplets. The membrane was then put on a quartz plate and

the absorbance of the colored membrane was measured at 480 nm using the spectrophotometer. The same procedure was also carried out with 5 ml of deionized water instead of the copper solution as a blank test. To obtain an accurate absorbance of the membrane for the copper sample, the absorbance value of the membrane for the blank test was subtracted from that for the sample containing copper. The copper concentration was calculated from a calibration graph.

## RESULTS AND DISCUSSION

### Absorption spectra

The UV-VIS absorption spectra for a PVC membrane containing the copper(I)-bathocuproine-picrate complex, a PVC membrane without the complex and an aqueous solution of picrate ion are shown in Fig. 2. The maximum absorption wavelength of the colored membrane was 480 nm. On the other hand, no absorption in the same wavelength region for the reagent blank was observed.

### Effect of temperature

Figure 3 shows the relationship between the temperature and the membrane absorbance at different coloring times with a copper concentration of  $1.0 \times 10^{-3} M$ . The membrane absorbance increased with temperature and time, so a higher temperature is possible to determine trace copper. At  $60^\circ C$ , the membrane absorbance became constant when the copper solution containing a membrane was stirred for more than 40 min. When the temperature was increased to more than  $70^\circ C$ , however, the absorbance of the membrane increased continu-

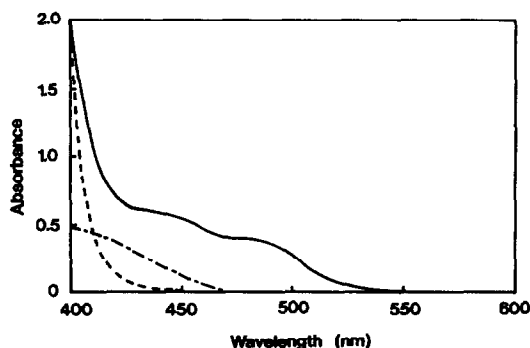


Fig. 2. Absorption spectra of colored PVC membrane (solid line) containing  $1 \times 10^{-4} M$  copper(I)-bathocuproine complex, colorless PVC membrane (dotted line) without complex, and aqueous solution containing  $1 \times 10^{-3} M$  picrate ion (alternative long and short dash line).

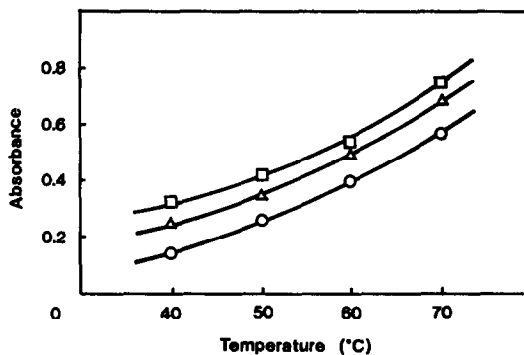


Fig. 3. Relationship between the temperature and the membrane absorbance. Coloring time: (○) 10 min; (△) 20 min; (□) 30 min.

ously with time. It is considered that the contraction of the membrane based on the elution of the extracting solvent, NPOE, from the PVC membrane medium with time was the cause. In this study, a temperature of  $60^\circ C$  was adopted.

### Effect of anion species

The effect of anion species that form ion pairs with the copper(I)-bathocuproine complex ion,  $[Cu \cdot L_2]^+$ , was discussed. The concentrations of the copper(I) and the picrate ion used in experiments were  $1.0 \times 10^{-5}$  and  $1 \times 10^{-4} M$ , respectively, while those of perchlorate, bromide and chloride ions was  $1 \times 10^{-2} M$ . The results are shown in Fig. 4. The color intensity of the membrane was low when using a hydrophilic ion such as chloride and bromide ions as a pairing ion. On the other hand, the use of picrate ion gave a high coloring rate in spite of 1/100th the concentration vs the other anion species, so that about 1.6 times of the membrane absorbance was obtained as compared with chloride ion after coloring for 10 min. It is recognized that the solubility of the copper(I)-bathocuproine-anion complex to the extracting

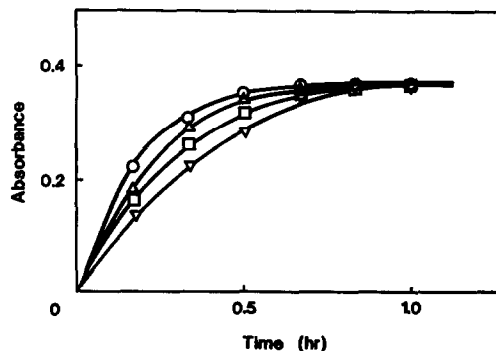


Fig. 4. Effect of pairing ion on the coloring of the membrane. Pairing ions: (○) picrate ion ( $1 \times 10^{-4} M$ ); (△)  $ClO_4^-$  ( $1 \times 10^{-2} M$ ); (□)  $Br^-$  ( $1 \times 10^{-2} M$ ); (▽)  $Cl^-$  ( $1 \times 10^{-2} M$ ).

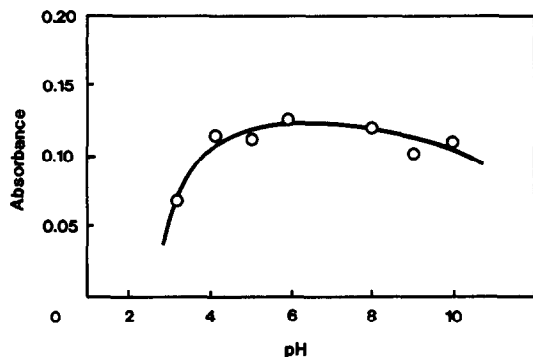


Fig. 5. Relationship between the pH and the membrane absorbance.

solvent, NPOE, in the membrane increased by using a hydrophobic ion as a pairing ion.

#### Effect of pH

The changes in the membrane absorbance by stirring for 10 min with a  $1.0 \times 10^{-5}M$  copper solution versus the pH of the sample solution is shown in Fig. 5. The membrane absorbance depended on pH of the solution, which was nearly constant in the range of pH 4.1 to 8.0. When the pH was less than 4.0 or higher than 8.0, however, the membrane absorbance decreased. Further, the transparency of the membrane was lost at a higher alkali intensity ( $> pH 10$ ), so that the absorbance of the membrane could not be measured with accuracy. In this study, a buffer solution of pH 5.9 was adopted.

#### Coloring rate of PVC membrane and calibration graph

The effect of the copper(I) concentration vs the coloring rate of the membrane,  $\Delta A/\Delta T$ , was investigated, which is shown in Fig. 6. Since the coloring rate of the membrane was proportional to the copper concentration, it is clear that the

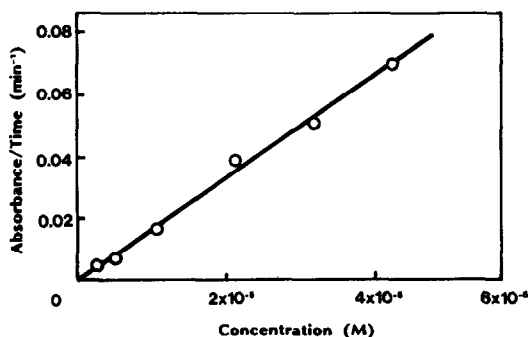


Fig. 6. Relationship between the copper(I) concentration and the coloring rate of membrane.

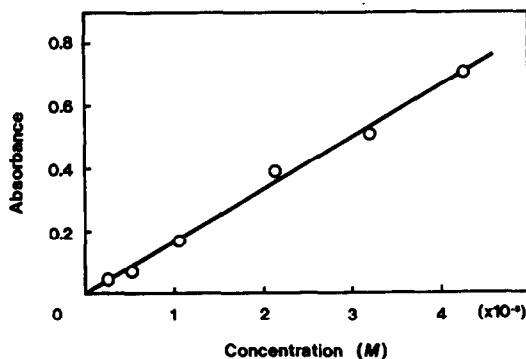


Fig. 7. Relationship between the copper(I) concentration and the membrane absorbance.

copper complex is quantitatively formed in the membrane. This relation can be expressed by

$$\Delta A/\Delta T = 1.66 \times 10^3 \cdot [\text{Cu}^+] \quad (2)$$

where the  $\Delta A/\Delta T$  is the change of membrane absorbance,  $A$ , per time,  $T$ , *i.e.* the coloring rate ( $\text{min}^{-1}$ ), and  $[\text{Cu}^+]$  is the copper(I) concentration (M). In the range of the given concentration, it is surmised that the diffusion rate of copper(I) to the membrane surface from the solution was rate determining.

The relationship between the copper(I) concentration and the membrane absorbance after stirring for 10 min, *viz.* the calibration graph, is shown in Fig. 7. A linear relation between the above two parameters was obtained with a correlation coefficient of 0.9972, and the linear equation was as follows.

$$A = 1.66 \times 10^4 \cdot [\text{Cu}^+] \quad (3)$$

The limit of the detectable concentration for copper to be measured with the proposed membrane method, which is expressed as the concentration equivalent to twice the standard deviation of the blank value of the membrane absorbance was  $1.5 \times 10^{-7}M$ . Then, assuming that 1 mol of copper(I) reacted with 2 mol of bathocuproine, the expected upper limit for the concentration of copper was calculated to be  $4.3 \times 10^{-5}M$  from the content ( $4.3 \times 10^{-7}$  mol) of the bathocuproine contained in a sheet of membrane when a 5 ml sample solution was analyzed. Approximately 220-fold concentration rate of the copper to the membrane ( $2.3 \times 10^{-2} \text{ cm}^3$ ) from the solution ( $5 \text{ cm}^3$ ) will be actually obtained, assuming all copper included in a sample solution was trapped in the membrane sheet.

The reproducibility of the absorbance values of the membrane was  $0.193 \pm 9.44 \times 10^{-3}$  at 4.9% relative standard deviation on five

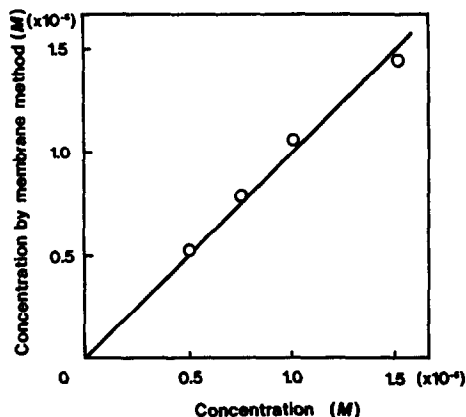


Fig. 8. Correlation between the copper(I) concentration measured by the proposed sensing method using a membrane and the standard concentration.

repeated measurements for a  $1.2 \times 10^{-5} M$  copper sample under the same experimental conditions.

#### *Correlation of the determined values of copper concentration*

The coloring test of the membranes was carried out with same tap water samples to which was added a known amount of copper(II) nitrate. The copper(II) concentrations prepared were  $5.0 \times 10^{-6}$ ,  $7.5 \times 10^{-6}$ ,  $1.0 \times 10^{-5}$  and  $1.5 \times 10^{-5} M$ . In addition, no copper from the tap water oneself was detected.

In Fig. 8, the correlation between the concentration of the prepared copper(II) solution and the concentration determined by spectrophotometry using a membrane as proposed here was shown. It was judged that both concentrations almost agreed, since the slope of the line and the correlation coefficient were 0.923 and 0.9960, respectively.

With regard to interference ions during the determination of copper, any cadmium(II), cobalt(II) and zinc(II) coexisting in the cop-

per(I) sample solutions did not have any significant effects because those complexes are colorless. When iron(II) coexisted at an equimolar concentration with copper(I) in a sample, however, a *ca* 10% increase in the determined value of the copper concentration occurred. Accordingly, when the iron(II) with a high concentration coexists in a copper sample, it would be necessary to first add bathophenanthroline sulphonic salt or citric acid as a masking agent into the sample solution.

In conclusion, by using a new type solid phase extraction-spectrophotometry having a PVC membrane containing bathocuproine as the extracting medium, trace copper in a range of  $1.5 \times 10^{-7}$  to  $4.3 \times 10^{-5} M$ , *i.e.* 9.5 ppb to 2.7 ppm can be determined. The colored membrane was kept for a few months without any color change. It is expected that the proposed sensing method will be widely applied in such fields as measurement of trace copper contained in a variety of aqueous samples, industrial wastewater, river water, etc.

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