Spectrophotometric Determination of Copper(II) with Phenanthrenequinone Monosemicarbazone

H.C. Rai*, Patanjali Kashyap, Shiv Ranjan Kumar† and Shalamuddin

Department of Chemistry, L.S. College, Muzaffarpur-842 001, India
E-mail: hcrai_chem@yahoo.co.in

Investigations on the use of phenanthrenequinone monosemi-carbazone as a colorimetric reagent for copper have been made. Optimum conditions for the determination and selectivity of the method have been studied.

Key Words: Spectrophotometric determination, Cu(II), Phenanthrenequinone monosemicarbazone.

INTRODUCTION

Colorimetric methods of analysis are gaining importance these days due to simplicity and speed[1, 2]. In continuation of our studies on use of phenanthrene-quinone monosemicarbazone (PQSC) as spectrophotometric reagent for estimation of platinum metals[3], we have evaluated the property of this compound as spectrophotometric reagent in determination of copper(II).

EXPERIMENTAL

A stock solution of copper(II) was prepared by dissolving BDH, AnalaR sample of cupric sulphate pentahydrate in double distilled water and standardized gravimetrically by thiocyanate method.

Absorption spectra, effect of pH and stability of the complex

A series of solutions containing a fixed amount of copper(II) (1 mL of 1×10^{-3} M) and an excess of the ligand (2 mL of 5×10^{-3} M) were prepared. pH's of the solutions were adjusted by the use of acetate buffers in a total volume of 10 mL or by adding sodium hydroxide for higher pH's. The solutions were extracted in 10 mL of chloroform and the absorbances were measured against reagent blanks prepared under similar conditions. The values plotted in Fig. 1 exhibit maximum absorption at 480 nm. The absorbance (at 480 nm) was found to remain constant in the pH range 7.2–10.0 (Fig. 2). In subsequent studies the pH of solutions was adjusted to 8.0 and absorbances were measured at 480 nm.

†Department of Physics, B.R.A. Bihar University, Muzaffarpur, Bihar.
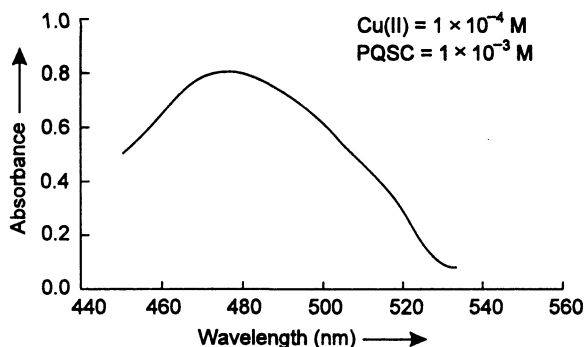
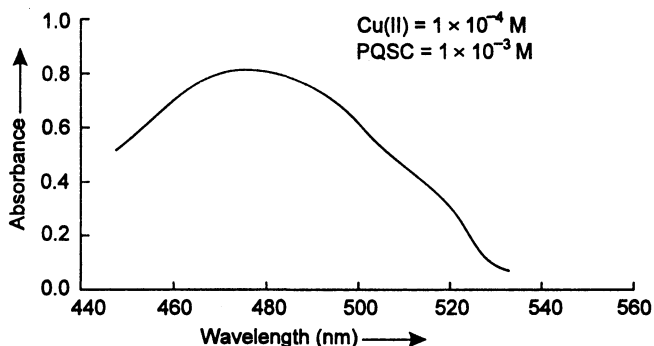Fig. 1.   Absorption spectrum of Cu-PQSC complex at pH 8.0.

Fig. 2.   Effect of pH on Cu-PQSC complex.

The absorbance of the complex was found to remain constant for 24 h after which a slow decrease takes place.

Effect of reagent concentration

A number of solutions containing 1 mL of 1×10^{-3} M copper(II) and varying amounts of the reagent were prepared. The chelates were extracted in 10 mL of chloroform and the absorbances were measured at 480 nm against the corresponding reagent blanks. For full colour development at least five times the molar excess
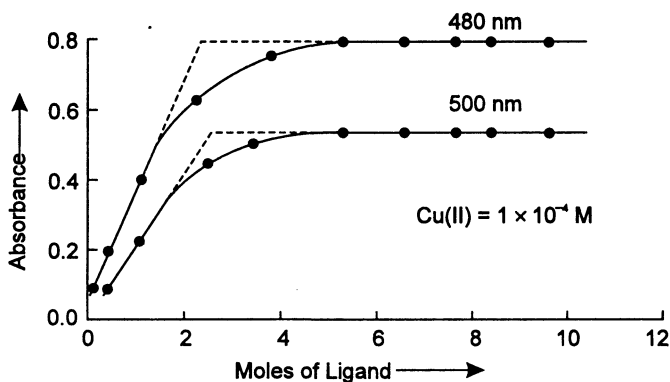

Fig. 3.   Effect of reagent concentration on Cu-PQSC.

of the reagent is required (Fig. 3). However, in subsequent studies 10 times molar excess of the reagent was maintained.

Calibration data

A series of solutions, containing varying amounts of copper(II) and an excess of the reagent were prepard. The pH was adjusted to 8.9 in total volume of 10 mL and the absorbances of chelates extracted in 10 mL of chloroform were measured at 480 nm against the reagent blank. The graph, obtained by plotting absorbed against copper ion concentration, is a straight line, which shows that the system obeys Beer's law (Fig. 4) up to 8.9 ppm of copper. The optimum concentration range, evaluated by Ringbom method, is found to be 1.82 to 6.76 ppm (Fig. 5).
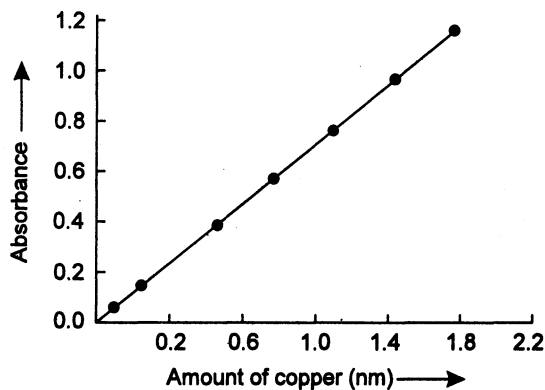
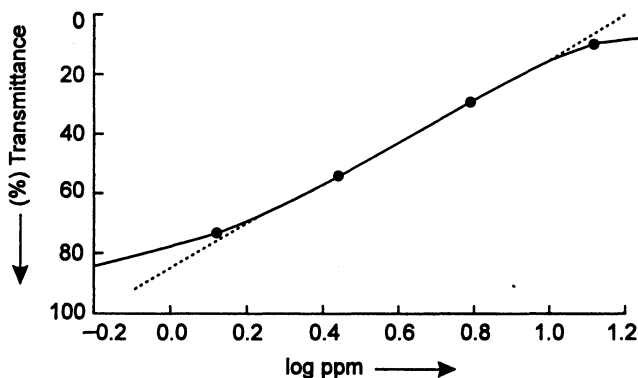Fig. 4.   Beer's law plot for Cu-PQSC complex, 1 mL = 6.35 ppm.

Fig. 5.   Ringbom plot for Cu-PQSC complex.

Physical constants of the complex

The sensitivity of the reaction, as evaluated from Beer's plot, is 0.008 μg of Cu/cm^2 at 480 nm for log $I_0/I = 0.001$. The molar extinction coefficient of the complex is 7.7×10^3. The values of E_m and E_s, obtained from the study of the effect of reagent concentration, are 0.770 and 0.605 respectively. 'a' is found to be 0.2143 and the formation constant of the complex comes out to be 1.99×10^9.

Procedure for the determination of copper(II)

A suitable aliquot of solution containing 18.2–67.6 μg of copper(II) is taken and 10 times molar excess of ethanolic solution of PQSC is added. The pH is adjusted between 7.2–10.0 with sodium acetate and sodium hydroxide in a total volume of 10 mL and 10 mL of the freshly distilled chloroform is added. The contents are shaken for 5 min on a shaking machine and set aside for equilibration. The chloroform layer is pippetted out and centrifuged to remove any droplets of water in the organic layer. The absorbance of extracted chelates is measured at 480 nm against a reagent blank prepared under similar conditions. Knowing the absorbance, the amount of copper is deduced from the calibration curve.

RESULTS AND DISCUSSION

Absorbance deviation

Eight solutions each containing 1×10^{-4} M copper(II) were taken and the complex was extracted in chloroform as given under recommended procedure. The main value of absorbance was found to be 0.770 with standard deviation of 0.0042. The coefficient of variation was 0.545% with relative average deviation of ± 0.403%.

Composition of the complex

The stoichiometry of the complex has been determined by Job's and mole ratio methods.

Job's method

The maximum occurring at 0.23 mole fraction of metal (Fig. 6) indicates that copper and the reagent are present in the ratio of 1 : 2 in the chelate. The same results are obtained by application of the mole ratio method.
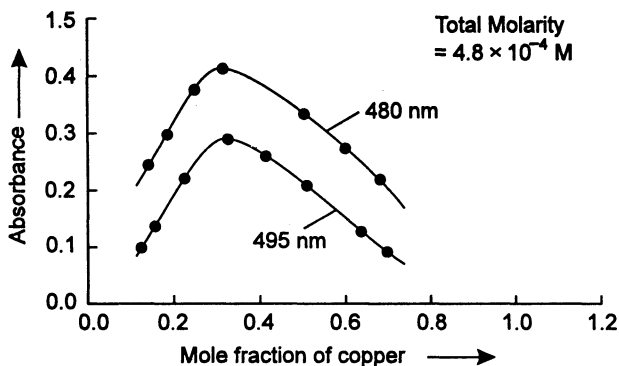

Fig. 6.   Composition of Cu-PQSC Complex by Job's method.

Effect of foreign ions

Effect of diverse ions on the determination of copper(II) has been studied (Table-1). For this purpose, solutions were prepared. The absorbance of chelate

extracted in 10 mL of chloroform were measured at 480 nm against reagent blank and copper content was then deduced from the calibration curve.

TABLE-1

EFFECT OF DIVERSE IONS IN THE DETERMINATION OF COPPER(II)

Amount of copper = 6.35 ppm

Foreign ions	Amount liberated in ppm	Foreign ions	Amount liberated in ppm
Chloride	1000	Zinc	5
Bromide	800	Cadmium	5
Nitrate	1000	Mercury	5
Fluoride	800	Lead(II)[1]	10
Sulphite	500	Iron(III)[2]	50
Nitrite	400	Magnesium(II)	50
Perchlorate	1000	Aluminium(III)	75
Phosphate	200	Silver(I)[3]	50
Citrate	70	Ruthenium(III)	30
Borate	300	Rhodium(III)	25
Oxalate	100	Osmium(VIII)	8
Phthalate	200	Iridium(III)	25
Barium(II)	200	Platinum(IV)	30
Strontium(II)	200	Thorium(IV)[2]	35
Calcium	100	—	—

1. Masked with sulphate.
2. Masked with fluoride.
3. Removed as chloride.

Phenanthrenequinone monosemicarbazone is not so selective as cuprone. However, the tolerance for platinum metals and some other cations is an advantage of the present method. The method is more sensitive than other reagents· and the pH range is fairly wide (7.2–10.0).

ACKNOWLEDGEMENT

REFERENCES

1. E.B. Sandell, Colorimetric Determination of Traces of Metals, Interscience Publishers, Inc., New York (1959).
2. E.D. Snell and C.T. Snell, Colorimetric Methods of Analysis, Van Nostrand, Princeton, Vol. II, p. 352 (1964).
3. I. Chakraborti and H.C. Rai, *Asian J. Chem.*, **15**, 1572, 1665, 1687 (2003).