Use of 3-Hydroxy-3-*m*-Tolyl-1-*o*-Chlorophenyltriazene in the Spectrophotometric Determination of Copper(II)

KAVITA SHARMA, USHA MAROO, PRADEEP MAROO, R.S. CHAUHAN,
A.K. GOSWAMI and D.N. PUROHIT*
Department of Chemistry
Mohan Lal Sukhadia University, Udaipur-313 001, India

The title reagent has been used for spectrophotometric determination of Cu(II). The composition of yellow coloured complex has been found to be 1 : 2 (Cu : R) with absorption maximum at 390 nm in the pH range 6.6–7.2. Absorbance measurements were made at 400 nm. Beer's law was followed in the studied concentration range 2.0×10^{-5} M to 1.0×10^{-4} M. The value of molar absorptivity, Sandell's sensitivity, stability constant (log β) and free energy of formation were found to be 4107 L/mole cm, 15.47 ng/cm², 10.10 and −13.77 kcal/mole respectively. Interference of twentyfive diverse ions has been examined.

Attempts have been made to develop hydroxytriazenes as spectrophotometric reagents for determination of copper[1–7]. In continuation, the present paper deals with the spectrophotometric determination of copper(II) with 3-hydroxy-3-*m*-tolyl-1-*o*-chlorophenyltriazene.

Systronics UV-visible spectrophotometer-108 has been used for absorbance measurements. For pH measurements Systronics pH-meter-324 was used.

The reagent was prepared as per the reported method[8]. The reagent solution of desired concentration was prepared by dissolving requisite quantity of 3-hydroxy-3-*m*-tolyl-1-*o*-cllorophenyltriazene in ethanol.

The stock solution of copper(II) 1.0×10^{-2} M was prepared by dissolving requisite quantity of AR grade copper sulphate pentahydrate in double distilled water and standardised with standard 1.0×10^{-2} M EDTA using murexide[9] as an indicator. Weaker solutions were prepared by its appropriate dilution with double distilled water.

Copper(II) formed yellow ethanol soluble complex under optimum condition of copper to reagent ratio (1 : 6) and at pH between 6.6–7.2. The yellow complex showed λ_{max} at 390 nm. However, working wavelength was chosen at 400 nm such that the difference between absorbance of the complex and the reagent was maximum. However, still the reagent blank had to be used.

To determine the molar composition of copper(II) complex three methods, namely Job's method[10], mole ratio method[11, 12] and slope ratio method[13] have been used. All the three methods gave the complex composition as 1 : 2 (Cu : R). Beer's law was obeyed in the studied concentration range 2.0×10^{-5} M to

1.0×10^{-4} M. The molar absorptivity and Sandell's sensitivity of the complex were found to be 4107 L/mole cm and 15.47 ng/cm^2 respectively. The standard deviation (σ), under optimum condition of complex formation, was found as 0.007 ppm by measuring the absorbance of ten solutions containing 3.17 ppm of copper.

The conditional stability constant of copper(II) complex was found using Harvey and Manning's[14] mole ratio curve as $\log \beta = 10.10$ and Purohit's method[15] using Job's curve as $\log \beta = 10.30$. Both the methods gave almost identical value of $\log \beta$. Using the value of $\log \beta$ (10.10), the value of free enerty of formation of the complex at 27°C was calculated from the formula $\Delta G = -2.303RT \log \beta$. By substituting the values of R (1.987), T (300) and $\log \beta$ (10.10), the value of ΔG was obtained as -13.77 kcal/mole.

Interference studies revealed that 3.17 ppm of copper can be determined in presence of equimolar amount of nineteen cations and anions, namely: Na(I), K(I), NH_4^+, Mg(II), Ca(II), Sr(II), Cd(II), Hg(II), F^-, Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, SO_3^{2-} and oxalate, whereas equimolar amount of Ni(II), Co(II), Zn(II), Sn(II), Ba(II) and Th(IV) were found to interfere.

REFERENCES

1. Arun M. Golwalkar, Jose Nemesio Rodriguez and D.N. Purohit, *Boll. Soc. Chim. (Peru)*, **50**, 179 (1984).

2. _____, *Acta Ciencia Indica*, **13**, 231 (1987).

3. Ritu Singh, R.S. Chauhan and D.N. Purohit, *J. Indian Chem. Soc.*, **67**, 4 (1990).

4. _____, *Nat. Acad. Sci. Letters*, **14**, 203 (1991).

5. Chayan Mehta, Rekha Bhatt, M.P. Tyagi and D.N. Purohit, *Oriental J. Chem.*, **9**, 258 (1993).

6. _____, *J. Indian Chem. Soc.*, **70**, 845 (1993).

7. _____, *Acta Ciencia Indica*, **19**, 103 (1993).

8. Ochieng Ombaka, Ph.D. Thesis, M.L. Sukhadia University, Udaipur (1995).

9. G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, 5th Edn., ELBS, p. 319 (1994).

10. P. Job, *Ann. Chim.*, **9**, 113 (1928).

11. J.H. Yoe and A.L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

12. Yu.A. Zolotov, Extraction of Chelating Compounds, Ann Arbor, London, p. 136 (1970).

13. A.E. Harvey and D.L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).

14. _____, *J. Am. Chem. Soc.*, **74**, 4744 (1952).

15. D.N. Purohit, A.K. Goswami, R.S. Chauhan and S. Ressalan, *Asian J. Chem.*, **11**, 123 (1999).