



## 1-(2'Chloro-4'-Sulphophenyl-3-Methyl-4-azo-(2"-Carboxy-5"-Sulphonic acid)-5-Pyrazolone [CSMACSP] as a Spectrophotometric Reagent: Studies on Cu(II) Chelate

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### ABSTRACT

Numerous heterocyclic azo dyes have been reported for the spectrophotometric determination of Cu(II). Here, we report a new heterocyclic azo dye 1-(2'Chloro-4'-sulphophenyl-3-methyl-4-azo-(2"-carboxy-5"-sulphonic acid)-5-pyrazolone [CSMACSP] for the spectrophotometric determination of Cu(II). The method is simple, rapid and sensitive. Light green colour 1:1 (M:L) complex formed between Cu(II) and CSMACSP in the pH range 2.0 - 5.0. The absorption spectrum shows a shoulder at 490 nm. The molar absorptivity and Sandell's sensitivity is found to be  $0.683 \times 10^3 \text{ lit. mol}^{-1} \text{ cm}^{-1}$  and  $0.093 \mu\text{g/cm}^2$ , respectively. A number of foreign ions are tested for their interference. Elemental analysis and IR spectra of the reagent and its complex were reported. The reagent was successfully applied for the determination of Cu(II) content in brass alloy.

**Key words:** Heterocyclic azo dyes, spectrophotometric determination.

### INTRODUCTION

Various heterocyclic azo dyes<sup>1</sup>, having chelating property, find application in analytical chemistry to a great extent. Out of these 2-pyridylazo compounds<sup>2</sup> are most widely used. 1-(2-Pyridylazo)-2-naphthol<sup>3</sup>, 4-(2-pyridylazo)-2-resorcinol<sup>4</sup>, 4-(2-thiazolylazo)-2-resorcinol<sup>5</sup>, 1-(4-sulphophenyl)-3-methyl-4-azo(2"-carboxy-5"-sulphonic acid)-5-pyrazolone<sup>6</sup> and many other azo dyes have been used for the spectrophotometric

determination of transition metal ions. Here, we report the use of 1-(2'Chloro-4'-sulphophenyl-3-methyl-4-azo-(2"-carboxy-5"-sulphonic acid)-5-pyrazolone [CSMACSP] as an analytical reagent for the spectrophotometric determination of Cu(II).

### MATERIAL AND METHODS

#### Instruments

Spectrophotometric measurements were done on Bausch and Lomb Spectrophotometer and

Shimadzu UV-160 A, UV-visible Spectrophotometer. All pH measurements were made with an Elico pH meter LI-10T.

### Synthesis of Reagent [CSMACSP]

Sodium salt of 1-(2'-Chloro-4'-sulphophenyl-3-methyl-4-azo-(2"-carboxy-5"-sulphonic acid)-5-pyrazolone [CSMACSP] was prepared by 1-(2'-Chloro-4'-sulphophenyl-3-methyl-5-pyrazolone with diazotized 5-sulpho-anthranilic acid. CSMACSP was crystallized for the mixture of dimethyl formamide while insoluble in ethanol, methanol, acetone and chloroform. A 0.05 M solution of the reagent was prepared by dissolving requisite quality of the CMSACSP in doubly distilled water.

### Preparation of Cu(II) solution

A stock solution (0.05 M) of Cu(II) was prepared by dissolving requisite quantity of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (A.R.) in doubly distilled water with little hydrochloric acid and diluting it to 250 ml. The stock solution was used after standardization<sup>7</sup> with EDTA. Experimental solution of required concentrations were prepared by appropriate dilution of the above stock solution.

### Spectrophotometric determination of copper Selection of wavelength and effect of pH

To take absorption spectra, 5.0 ml of (0.001 M) metal solution and 1.0 ml of (0.03 M) reagent solution were taken and pH of the solution was adjusted within the range where maximum colour develops. The solution was made upto the mark with doubly distilled water and the absorbance was measured between 380 nm to 750 nm against reagent blank. The absorption spectra showed a shoulder at 490 nm and hence all the measurements were carried at this wavelength. It was observed that the adsorption increased upto pH 4.0 and then decreased with increase in pH. Hence, all the subsequent measurements pH 4.0 was maintained. It was found that colour development is quite rapid and the absorbance of complex remains unchanged for 24 hours. The order of addition of reagents (metal ions, reagents and buffer solution) had no effect on the absorbance of the complex.

### Verification of Beer's law

To 2.0 ml (0.05 M) solution of the reagent CSMACSP in 25 ml flask, varying amount of the

Cu(II) ion solution (0.002 M) were added; and pH of the solution was adjusted to 4.0 by using sodium acetate-acetic acid buffer solution. Then the content was diluted upto mark with doubly distilled water. Absorbance of the coloured complex was measured at 490 nm against reagent blank. The Cu(II) - CSMACSP complex obeys the Beer law upto 15.25 ppm of Cu(II). The molar absorptivity ( $\epsilon$ ) and Sandell's sensitivity of the Cu(II)-CSMACSP complex were found to be  $0.683 \times 10^3 \text{ lit. mol}^{-1} \cdot \text{cm}^{-1}$  and  $0.093 \mu\text{g/cm}^2$  at 490 nm, respectively. The reagent can be used for spectrophotometric determination of Cu(II).

### Effect of diverse ions

Interference due to associated ions was examined in determination of 15.25 ppm of Cu(II) at pH 4.0 using CSMACSP reagent. A 20-fold excess of Zn(II), Cd(II), Sr(II), Ba(II), Mg(II) and Zr(IV) do not interfere. Chloride, bromide, nitrate, sulphate, citrate do not interfere even when they are 150-fold excess.

### Stoichiometry of complex

The Job's method of continuous variation<sup>8</sup> and Yoe and Jones mole ratio method<sup>9</sup>, suggest the composition of complex to be 1:1 (metal : ligand) ratio. The average stability constant found from two methods is  $5.542 \times 10^9$ . The standard free energy change for the complex formation reaction was calculated using the relationship  $\Delta G^\circ = -RT \ln K_s$  and it is found to be  $-7.96 \text{ k.cal./mol.}$  at  $30^\circ\text{C}$ .

### Isolation of Cu(II)-CSMACSP complexes

Copper (II) complex with reagent are soluble in aqueous media but it was isolated in the solid form by using reagent solution in dimethyl formamide (DMF) and the separated complex was recrystallized from DMF and acetone medium.

### Elemental analysis

The elemental analysis of the reagent and Cu(II) chelate was done on Carlo-Erba Elemental Analyser. The results are given in table 1.

### IR spectra

On comparing the IR absorption spectra of ligand and complex, it is seen that the band due to -OH group in pyrazolone nucleus unaffected at  $3400\text{-}3500 \text{ cm}^{-1}$  in ligand and  $3350\text{-}3500 \text{ cm}^{-1}$  in

complex which indicates that this -OH is not participating the forming a bond with metal. Metal forms a bond by replacing H of carboxyl group. This is seen by a slight downward shift of  $>C=O$  stretching frequency from  $1645\text{cm}^{-1}$  ligand to  $1620\text{cm}^{-1}$  in complex. The band due to  $-N=N-$  which is found at  $1580\text{cm}^{-1}$  in ligand shifts slightly to lower frequency in complex at  $1540\text{cm}^{-1}$ . This indicates the coordination of metal through N of azo group. As H of O-H in carboxyl group is replaced by metal, the band due to O-H bending found at  $1120\text{cm}^{-1}$  in ligand is found to disappear in complex.

#### Analytical Application of the Reagent Determination of copper in brass alloy using CSMACSP

Preanalysed sample of brass 0.6651 gm was dissolved in nitric acid (1:1) by heating for 30 minutes. The solution was evaporated to a volume

**Table 1: Elemental analysis of reagent and Cu(II)-CSMACSP**

Compound	%C % found (% cal.)	%N % found (% cal.)
CSMACSP	36.47% (36.39%)	10.04% (9.99%)
Cu(II)-CSMACSP	32.62% (32.74%)	10.14% (10.20%)

of 5 ml but not dryness and the bulk of nitric acid was removed. The resulting solution was diluted in 100 ml with doubly distilled water in volumetric flask. 2.0 ml of above solution was taken in 50 ml volumetric flask and diluted in to mark with doubly distilled water 1.5 ml of the diluted solution was taken and 0.5 ml of 0.05 M CSMACSP solution was added and pH 4.0 was adjusted to using suitable buffer solution. The contents were diluted to 25 ml with doubly distilled water. Absorbance of the solution was measured at 490 nm against reagent blank.

#### Results

1. Weight of brass sample =0.6651gm
2. Absorbance of solution (average of three determination) =0.119
3. From the graph mg of copper in 1.5 ml diluted solution =0.2795mg
4. Amount of Cu(II) in sample taken =0.4658 mg
5. Percentage of copper found in brass sample =70.03 %
6. Percentage of copper reported in brass sample =70.48%
7. Percentage error =-0.45%

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#### REFERENCES

1. R.C. Anderson and G. Nickless, *Analyst*, London, **92**: 207 (1967).
2. S. Shibata, *Gelates in Analytical Chemistry*, IV, edited by H.A. Flaschka and A.J. Barnard Jr. (Marcel-Dekker, Inc, New York) (1972).
3. G. Goldstein, D.L. Manning and O. Menis, *Anal. Chem.* **31**: 192 (1959).
4. F.H. Pollard, P. Hanson and W.J. Geary, *Anal. Chim. Acta.* **20**: 26 (1959).
5. A. Kawase, *Japan Analyst*, **12**: 810 (1963).
6. J.G. Desai, K.K. Desai and K.R. Desai, *J. Inst. Chem.* **62**(3): 108 (1990).
7. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longmans Green and Co., W.I. 3<sup>rd</sup> Ed., pp441 (1961).
8. P. Job, *Ann. Chem.*, **9**: 113 (1928).
9. J.H. Yoe and A.L. Jones, *Ind. Engg. Chem. Anal. Ed.*, **16**: 111 (1944).