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Spectrophotometric Method for determination of Copper (II) using p-Chlorobenzaldehyde -4-(2'-carboxy-5-sulphophenyl)-3-thiosemicarbazone [p-CBCST]

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Abstract

p-Chlorobenzaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone [p-CBCST] is spectrophotometric reagent for copper (II) in DMF. Reaction between metal ion and p- Chlorobenzaldehyde -4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone [p-CBCST] forming a pale yellow colored complex in the pH range 3.0-4.5. The complex shows maximum absorption at 325 nm. The molar absorptivity found to be 5.137×10^3 lit. mol.$^{-1}$ cm.$^{-1}$. The complexes have been characterized on the basis of elemental analysis, UV, IR, NMR spectra. p-CBCST is found to be a selective and strong chelating agent for copper. The 1:2 metal:ligand ratio of complex found from the mole ratio and the slope ratio method and the Job's method of continuous variation. The stability constant of the complex found to be 1.184×10^{12}.

Keywords: p- Chlorobenzaldehyde, thiosemicarbazone, p-CBCST.

Introduction

Thiosemicarbazone compounds give antifungal and antibacterial activity with different transition metal ions. Thiosemicarbazone are known as analytical reagents[1-7]. Thiosemi-carbazones are also found to have biological activity[8]. Thiosemicarbazone[9-12] and its metal complexes are known for its biological application and the great medicinal value including antibacterial, antifungal, antimalarial, antitumor and antiviral activity[12-19]. Patric Raymond P[20] and et al studied the role of binary complex for its physiological activity of substances in storage and transport. Copper and nickel metal react directly with thiosemicarbazide in organic solvents to get corresponding metal complexes and the resultant complexe has been successfully applied in the determination of copper content in brass and bronze powder[21, 22].

In the view of these finding, we report the use of p-chlorobenzaldehyde -4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone[23] (p-CBCST) as a spectrophotometric reagent for copper (II).

Material and Methods

All the reagents used were of AR grade and were used without further purification. Salts were obtained from BDH. The reagent p- Chlorobenzaldehyde -4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone (p-CBCST) [M.P. 198ºC] was prepared by condensation of p-chlorobenzaldehyde with 4-(2'-Carboxy-5'-sulphophenyl)-3-thiosemicarbazide by using the reported procedures[24].

2.17 gm (0.01 mole) 5-sulphoanthranilic acid, 30 ml ethanol and 20 ml ammonium hydroxide were mixed and cooled below 20ºC. 8 ml carbon disulphide was then added with continuous stirring for 15 minutes. It was then allowed to stand for 1 hr. then 4 ml of $ClCH_2COONa$ and 14 ml of 50 % hydrazine hydrate were added and the bulk was reduced to half by heating. It was then allowed to stand overnight. The product was crystallized from DMF and water, yield 75 %, M.P. 169ºC.

The thiosemicarbazone ligand was prepared from the equimolecular quantity of aldehyde and thiosemicarbazide dissolved in 50 mL of ethanol. The mixture was heated at reflux temperature for 2 hr.[25] and allowed to stand for overnight and will get corresponding thiosemicarbazone. The product was crystallized from DMF-water, light yellow color crystals were obtained [M.P. 198ºC]. The reagent p-CBCST is insoluble in common organic solvent but soluble in DMF, DMSO, and NMP. The structure of Cu- p-CBCST is presented below.

p- Chlorobenzaldehyde -4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone [p-CBCST]: Light yellow crystals; m.p. 198ºC; yield 80 %; IR (KBr, cm^{-1}): 1578 (C-N), 1089 (C=S), 1275 (N-N), 1622 (C=O) , NMR (400.1 MHz, $CHCl_3$): δ_H 9.97 (s, -OH or -NH), 2.35 (s, 3H, -H), 7.4-7.8 (m, 7H,Ar-H), 9.45 (s, 1H, -NH); Anal. Calcd for: $C_{15}H_{12}N_3O_5S_2Cl$ (413.5); Found (C, 43.45; H, 2.79; O, 19.44; N, 10.06; S, 15.26; Cl, 8.32 %); requires (C, 43.53; H, 2.90; O, 19.34; N, 10.15; S, 15.47, Cl, 8.58 %).

Synthesis of Cu (II) Complex: A solution of copper sulphate (0.005 mol) of $CuSO_4.5H_2O$ in ethanol (40 mL) was added to a solution of p-CBCST (0.01 mol) in ethanol (40 mL). The

mixture was refluxed on water bath for about two hrs. The precipitated solid was filtered, washed with ethanol and dried under vacuum.

Cu (II) complex of p- Chlorobenzaldehyde -4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone [Cu (p-CBCST)$_2$]: Pale yellow color; yield 82 %; IR (KBr, cm^{-1}): 1436 (C-N), 1089 (C=S), 1275 (N-N), 1606 (C=O), Anal. Calcd for: $C_{30}H_{22}N_6O_{10}S_4Cl_2Cu$ (888.546); Found (C, 40.33; H, 2.45; O, 17.98; N, 9.51; S, 13.97; Cl, 7.93%); requires (C, 40.51; H, 2.47; O, 18.006; N, 9.45; S, 14.40; Cl, 7.99 %).

Results and Discussion

p- Chlorobenzaldehyde -4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone with copper gave pale yellow color in acidic pH. The pH studies showed that the absorbance was maximum in a solution of pH 4.0. The studies relating to the effect of Cu (II) showed linear relationship between metal ion concentration and absorbance in the range 24.88 - 34.21 ppm. Table 2 describes spectrophotometric data of Cu (II) p-CBCST. The stoichiometry of the Cu (II) - p-CBCST complex was determined by two methods namely, Job`s method[26] continuous variation and molar ratio method[27]. The ratio of 1:2 (metal: ligand) complex with p- Chlorobenzaldehyde -4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone formed a stable pale yellow Cu (II) complex. The stability constant of the complex was found to be 1.184×10^{12} as described in table 3.

A Shimadzu UV-visible spectrophotometer (Model UV-160A) equipped with 1-cm matched quartz cells was used for absorbance measurements. A EUTECH Li-127 digital pH meter was used for pH measurements. Melting points of the synthesized compounds were determined in open-glass capillary on Stuart SMP10 melting point apparatus and are uncorrected. The purity of the compounds was checked by thin layer chromatography (TLC). Silica gel plates (Kieselgel 0.25 mm, 60G F254), were used for TLC and the spots were visualized by iodine vapors / ultraviolet light as visualizing agents. IR spectra of the ligand and complex were recorded using KBr pellets on Shimadzu – Japan 8400 FTIR. IR bands[28,29] for the ligand and complex are presented in table 4. NMR spectra were recorded on "Varian 400" using DMSO. Table 5 describes results for Cu (II) p-CBCST having ratio of Metal: Ligand, 1:2.

Analytical Application: Determination of Copper in Brass: Brass alloy sample was brought into solution as described in the standard procedure by using Conc. HNO_3 and Conc. HCl**.** Solutions were analyzed for Cu (II) as described in the general procedure. To an aliquot of alloy solution (1.0 ml) in 50 ml beaker, pH was adjusted to 4.0 and 2.0 ml of 0.001M reagent solution was added and solution was diluted to 10 ml with distilled water.

Absorbance was measured at 325 nm. Brass solution: 0.2347gm brass in 250 ml stock solution. 1 ml aliquot contains 0.09388 mg brass. Absorbance was found to be 0.205 (figure 3), it corresponds to 0.0635 mg of copper in 1 ml diluted solution.

Determination of Copper in German-Silver: German silver alloy sample was brought into solution as described in the standard procedure by using Conc. HNO_3 and Conc. HCl**.** Solutions were analyzed for Cu (II) as described in the general procedure. To an aliquot of alloy solution (1.0 ml) in 50 ml beaker, Ph was adjusted to 4.0 and 2.0 ml of 0.001M DMF solution of reagent was added and diluted to 10 ml with DMF.

Absorbance was measured at 325 nm. German-silver solution: 0.250 gm in 250 ml stock solution. Absorbance was found to be 0.191 nm, (figure 3), it corresponds to 0.04953 mg of copper in 1 ml sample solution.

Thermogravimetric Analysis: TG curve of Cu (II) complex of p-CBCST shows that there is no weight loss up to 200ºC indicating the absence of lattice as well as co-ordinate water molecules in complexes. A gradual increase in temperature above 200ºC has been accompanied by loss in weight up to 300ºC. it indicate part decomposition of ligand moiety (% wt. loss obs./cal.17.00/16.67). The remaining part of the ligangd break at 350-400ºC. A horizontal curve has been observed after 600ºC. The total weight loss up to 550ºC is nearly 82 % and equal to two moles of ligand indicating 1:2 compositions of the complex[30]. This constant weight region corresponds to metal oxides, the final pyrolysis produce.

Antibacterial Activity: Cu (II) ligand complexes have been screened for their inhibitory effects against four organisms viz, *Staphylococcus aureus, Escherichia coli, Bacillus subtilis* and *Pseudomonas aeruginosa.* Table 4 showed the results obtained for zone of inhibition of the growth of bacteria of the tested compounds and under similar condition using Ciprofloxacin as a standard for comparison, control experiment was carried out by Kirby-Bauer method[31]. Cu-complex showed less activity towards the *Staphyloccucus aureus* than other organism[32]. The zones of inhibition have been measured and the activity results regarding the ligands and their complexes have been recorded.

Table-1
Determination of Copper in Various Samples Using the Spectrophotometric Method

Sr No.	Composition	Copper content		Relative Error (%)
		Reported (%)	Found (%)	
1	Brass	63.5	64	-0.78
2	German – silver	50.00	49.53	- 0.94

*Average value of three determinations

Table-2
Spectrophotometric data of Cu (II) – p-CBCST

Characteristics	Results
Molar absorptivity (L $mole^{-1}cm^{-1}$)	5.137×10^3
Stability constant(k)	1.184×10^{12}

Table-3
Stability of Cu (II) p-CBCST at 30ºC

Method Employed	Em	Es	α	$K_s = (1- \alpha)/4c^2\alpha^3$
Mole ratio method	0.483	0.467	0.0331	1.184×10^{12}

Table-4
Antibacterial activity of p-CBCST ligands and its metal chelates

Sample	Antibacterial activity (20 mm)			
	Staphylococcus aureus	***Escheriachia coli***	***Bacillus subtilis***	***Pseudomonas aeruginosa***
p-CBCST	13	12	14	12
Cu (II)-pCBCST	9	14	10	11
Ciprafloxacin	20	20	21	19

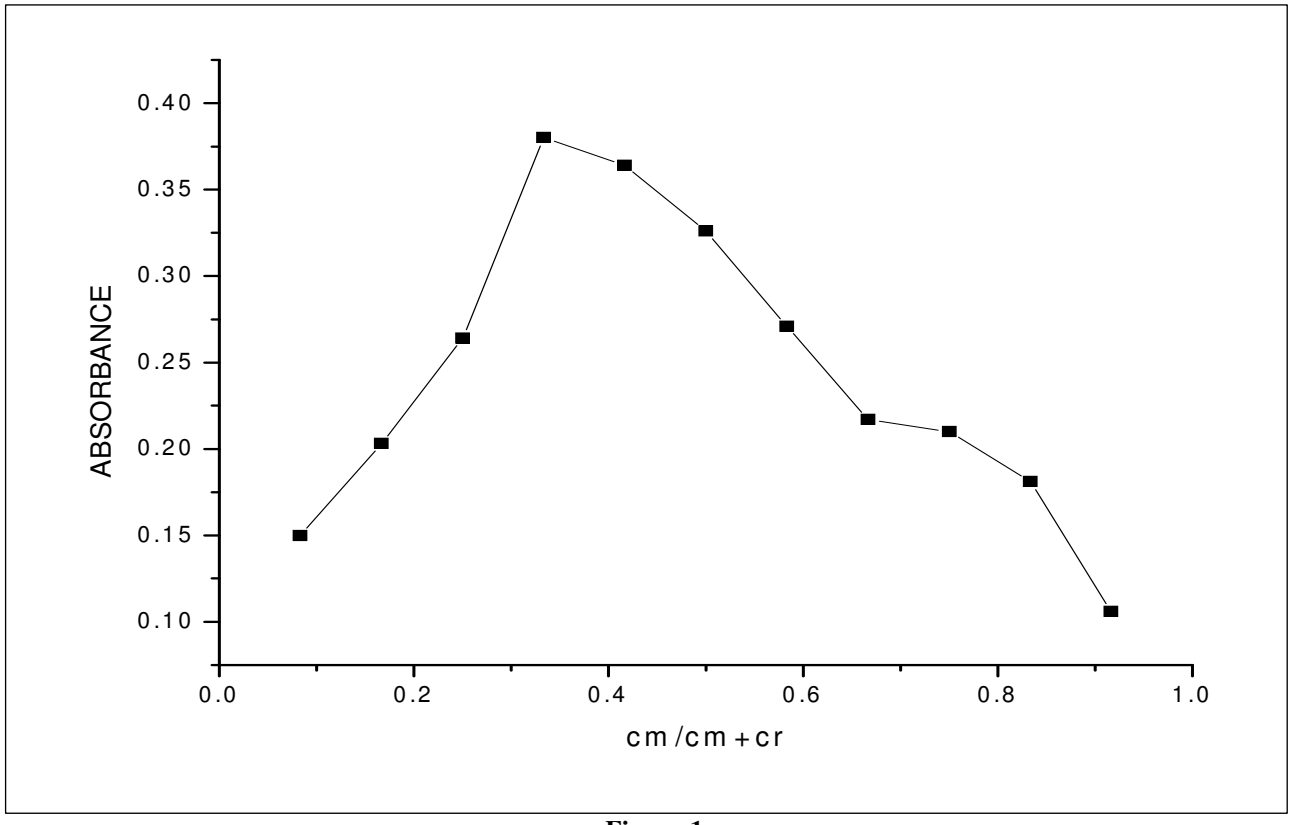

Figure-1
Job's Method

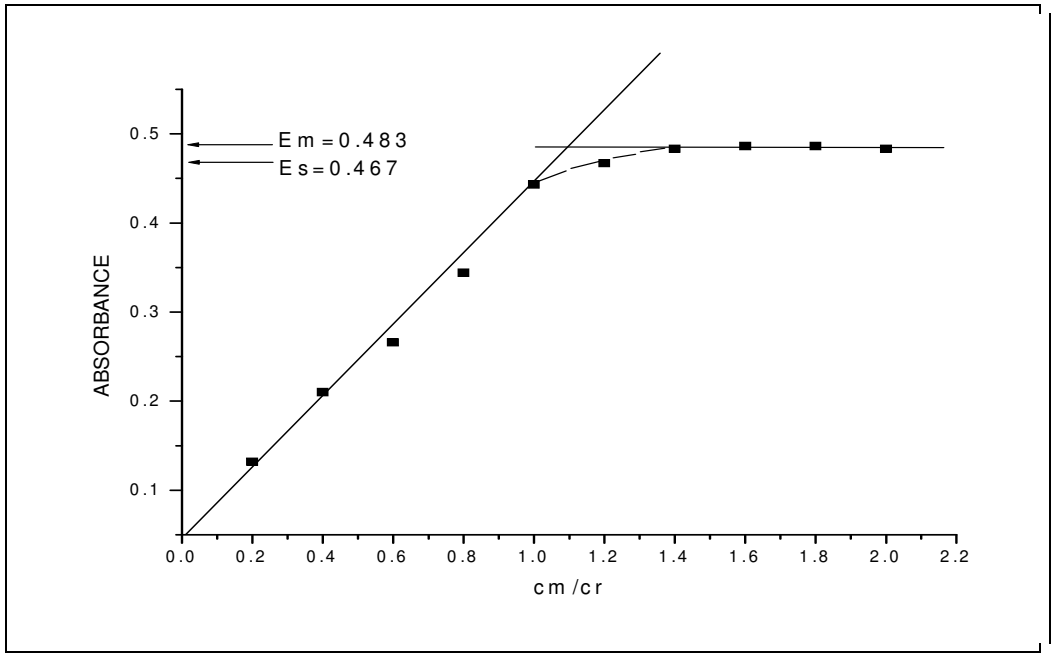

Figure-2
Mole ratio Method

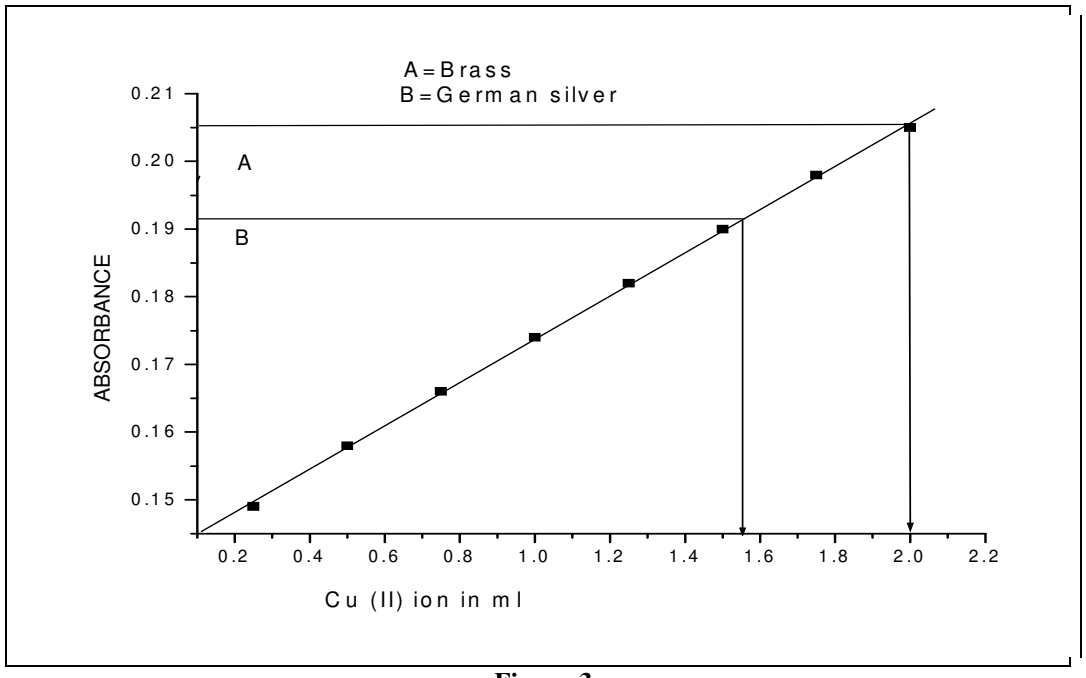

Figure-3
Cu (II) ion in ml×0.03175

Conclusion

The proposed procedure was simple, sensitive and rapid. The stability constant and the molar absorptivity of the proposed method were reported to be 1.184×10^{12} and 5.137×10^{3} lit mole^{-1}cm^{-1}. Cu (II) forms a 1:2 stable pale yellow colored complex with p- Chlorobenzaldehyde -4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone. This complex is used for the determination of copper in microgram quantities. The method has been applied for the analysis of copper in synthesized mixtures and also in alloys. The proposed structure of Cu (II) complexes with p-chlorobenzaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone where M = Cu (II) has been shown in figure-4.

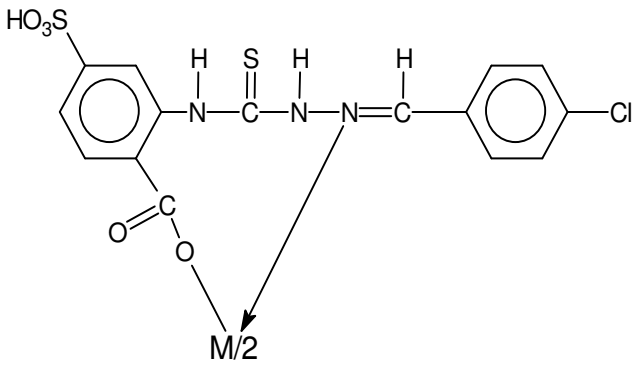

Figure 4

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