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Short Communication

ANALYTICAL PROPERTIES OF p-[N,N-BIS(2-CHLORO ETHYL) AMINO] BENZALDEHYDE THIOSEMICARBAZONE: SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) IN ALLOYS, COMPLEXES AND PHARMACEUTICAL SAMPLES

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INTRODUCTION

Thiosemicarbazones have been frequently employed as chromogenic reagents for the spectrophotometric determination of metal ions and their analytical potentialities have been reviewed[1,2]. The survey of literature reveals the use of Acetophenone thiosemicarbazone[3], Cyclohexanone thiosemicarbazone[4], Cyclohexane-1,4-dione bisthiosemicarbazone[5], Phenanthrenequinone monothiosemicarbazone[6], 3,5-Dibromo salicyladehyde-4-phenyl thiosemicarbazone[7], Thiophenaldehyde-4-phenyl-3-thiosemicarbazone[8], Thiophene-2-carbaxaldehyde thiosemicarbazone[9], Quinoline-2-aldehyde thiosemicarbazone[10], β-iononethiosemicarbazone[11], as extractive spectrophotometric reagents for copper. However, these methods have some limitations, such as, low sensitivity[3-6], longer extraction period[7,8], slow color reaction[5,9], use of either masking or synergic extractant[10] and a large number of interferences[3,11]. The proposed method is free from these drawbacks. The method is rapid as the copper-reagent complex is soluble in water-ethanol-DMF mixture and not requiring any extraction for the complex. The method is employed for the estimation of copper in alloys, complexes and pharmaceutical samples.

EXPERIMENTAL

Apparatus and reagents

A Shimadzu (Model – 160A) double beam UV/VIS spectrophotometer with 1.0 cm quartz cell and ELICO pH meter (LI 127) with a combined electrode were used for the measurements of absorbance and pH respectively. All reagents and chemicals used were of analytical or chemically pure grade.

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Stock solution of copper sulfate

A stock solution of copper(II) was prepared by dissolving calculated amount of $CuSO_4.5H_2O$ (AR, CDH, 99%) in doubly distilled water, standardized gravimetrically by salicylaldoxime method[12] and volumetrically by iodometric method[12]. This stock solution was further diluted to get 0.32 μg mL^{-1} with double distilled water.

Synthesis and characterization of CEABT

The starting material p-[N,N-bis(2-Chloroethyl)amino]benzaldehyde was prepared by the reported procedure[13]. The purity of the compound was checked by the elemental analysis and by melting point. The title compound was prepared by the simple condensation reaction of p-[N,N-bis(2-Chloroethyl)amino]benzaldehyde with thiosemicarbazide. Ethanolic solution of 5 mmol (1.23 g) of p-[N,N-bis(2-Chloroethyl)amino]benzaldehyde was taken in a 250 mL round bottom flask. 5 mmol (0.5 g) of thiosemicarbazide (AR, CDH, 99%) in 5 mL of water and 0.5 mL hydrochloric acid (35 %) was added to it. Refluxing of the mixture for 2 hrs, and cooling to 5^oC, results in the separation of a yellow precipitate. The resulting precipitate was collected by filtration and then washed with ethanol followed by ether. The product was twice recrystallised from ethanol to get a pure shiny yellow crystals and is characterized by the elemental analysis. (Yield 80 %). [Found (Calcd), % are C=45.70(45.14), H=5.19(5.02), N = 17.45(17.55), S=9.81(10.03)].

p-[N,N-bis(2-Chloroethyl)amino]benzaldehyde thiosemicarbazone solution (0.008 %)

This solution was prepared by dissolving the requisite amount of CEABT in a known volume of pure acetone.

Solutions of alloy, complexes and pharmaceutical samples

The complexes of Cu were prepared as per the reported procedures. Solutions of the complexes were prepared by evaporating with aqua regia to near dryness and dissolving the residue with distilled water. The solutions of alloys and pharamaceutical samples were prepared as per the reported procedure[14, 15, 16].

General procedure

Different aliquots of solutions, containing 0.96 - 2.56 μg mL^{-1} of Cu(II) were pipetted out into a 25 mL standard flask, 2-3 mL of CEABT [Cu:R,1:2], 1 mL of buffer (pH 8.6), 10 mL dimethyl formamide, 5 mL of ethanol were added and the mixture was diluted up to the mark with double distilled water. After 5 min the absorbance was measured at 392 nm against a reagent blank. The copper content in an unknown sample was determined using a concurrently prepared calibration graph.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectrum of the Cu(II) - CEABT complex was recorded against the reagent blank and that of the reagent against the solvent as blank. The Cu(II) - CEABT complex and the reagent show maximum absorbance at 392 nm and 350 nm, respectively (Fig. 1). The reagent has a negligibly small absorbance at the λ_{max} of the complex. Thus, further absorbance measurements of the complex were made at 392 nm. The physico-chemical and analytical properties of Cu(II) – CEABT complex are presented in the table 1.

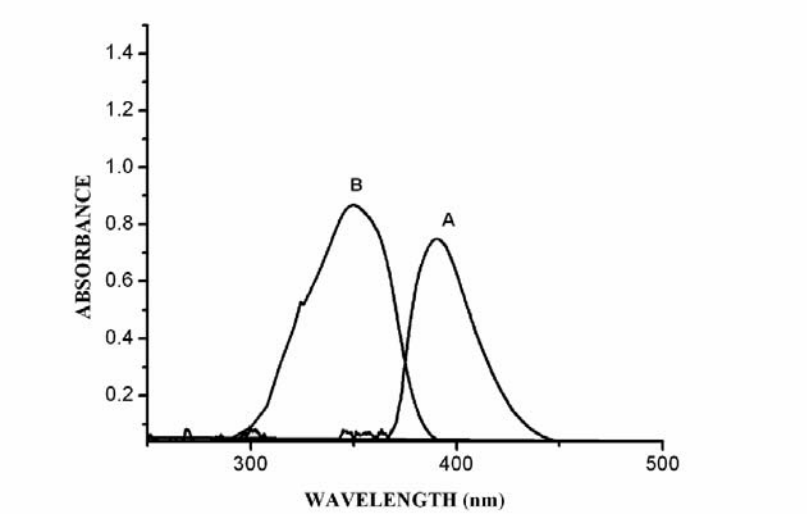

FIGURE 1. – (A) Absorption spectra of Cu(II)-CEABT complex Vs reagent blank. (B) Absorption spectra of CEABT Vs Acetone blank.

TABLE 1. - Physico-chemical and analytical properties of CEABT complex of copper(II)

Characteristic	Cu(II) - CEABT
Absorbance maximum (nm)	392
pH range (optimum)	8 – 9
Buffer	KCl (0.2M) – Boric acid (0.2M) – NaOH (0.2M)
Moles of reagent required for full color development	2
Beer's Law range (μg mL^{-1})	Up to 2.88
Ringbom plot (μg mL^{-1})	0.96 - 2.56
Molar absorptivity (L mol^{-1} cm^{-1})	4.42 x 10^4
Sandell's sensitivity(μgcm^{-2})	0.0014
Composition of the complex (M:L)	1:2
Stability of the color (in hrs)	2
Relative error (%)	± 0.50 %
Coefficient of variation (%)	0.37 %

Effect of foreign ions

The influence of the presence of diverse ions on the absorbance value of Cu(II) - CEABT complex system was studied with 1.28 μg mL^{-1} Cu(II) in the presence of foreign ions. An error of ± 2 % in the absorbance value was considered as the tolerance limit. No interference was observed for the following ions at the amounts in (μg mL^{-1}) shown: Pb(II) (500), Zn(II), Cd(II) and Mn(1000), Co(II) (100), Ni(II) (40), Fe(II)(2), Mg(II) and Hg(II) (1), Ba(II) (50), La(III), Y(III), Ce(III), Zr(III) and Al(III)(400), Ru(III)(5), Rh(40), Cr(III) and Tl(III)(2), Se(IV)(50), Sn(IV)(50), U(VI)(400), fluoride (2000), chloride

(4000), bromide and acetate (200), sulfate (200), borate (150), phosphate (75), nitrate (100), thiocyanate (20), thiosulphate (80), citrate, tartarate (15). However, the presence of Pd(II) and Pt(IV) and iodide cause severe interference. The interference of Pd(II) and Pt(IV) is attributed to the formation of their respective colored complexes and hence cause higher absorbance. The presence of iodide decreases the intensity of color. Tolerance of Fe(II) up to 20 μg mL^{-1}can be achieved by adding 200 μg of NaF (2-3 mL).

Analytical applications

The proposed spectrophototmetric method employed for the determination of copper(II) in alloys, complexes and pharmaceutical samples. The results are presented in Table 2 - 4. It is evident from these results that, the proposed method can be conveniently employed for the determination copper in alloy, complexes and pharamaceutical samples with a fair degree of accuracy.

TABLE 2. - Determination of Cu(II) in alloys (n=5)

Alloy	Copper present (%)	Copper found (%)	Relative error (%)
Brass	62.59	62.50	-0.14
Bronze	89.79	89.68	-0.12
Copper Foil	99.01	99.00	-0.01
Gun Metal	87.85	87.75	-0.11

TABLE 3. - Determination of copper(II) in complexes (n=5)

Complex	Copper(II) calculated (%)	Copper(II) found (%)	Relative error (%)
[a]$Cu(C_7H_6O_2N)_2$	18.93	18.86	-0.36
[b]$Cu(C_9H_5N_4S)$	32.98	32.90	-0.24
[c]$Cu(C_5H_9N_4S)$	28.78	28.73	-0.17
$[Cu(en)_2(H_2O)_2]I_2$	15.36	15.30	-0.39
$[Cu(NH_3)_4]SO_4.H_2O$	34.90	34.85	-0.14

Copper complexes of [a]Salicylaldoxime; [b]4-amino-5-mercapto-3-methyl-1,2,4-triazole; [c]4-amino-5-mercapto-3-methyl-1,2,4-triazole.

TABLE 4. - Determination of Cu(II) in pharmaceutical samples (n=5)

Sample	Amount of Cu(II) present		Standard deviation	Coefficient of variation (%)
	Certi. Value (mg/tablet)	Present method (mg/tablet)		
A-Z (Alchem)	2.5	2.481	0.004	0.16
AO-7 (Nicholas India)	2	1.988	0.002	0.10
Supradyn (Nicholas India)	0.863	0.860	0.001	0.14

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