


**EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II) USING  
2-(5- BROMO-2- OXOINDOLIN-3-YLIDENE) HYDRAZINE CARBOTHIOAMIDE AS AN  
ANALYTICAL REAGENT**
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**ABSTRACT**

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of Cu(II) by using 2-(5-Bromo -2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide as an analytical reagent. 2-(5-Bromo-2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide has been synthesized and characterized by elemental and spectral analysis. 2-(5-Bromo -2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide extracts Cu (II) quantitatively (99.92%) into n-amyl alcohol from an aqueous solution of pH range 4.0-6.0 and in the presence of 3cm<sup>3</sup> of phosphate buffer (pH 5.0). The n-amyl alcohol extract shows an intense peak at 510 nm ( $\lambda$  max). Beer's law is obeyed over the Cu(II) concentration range of 1.0-8.0  $\mu$ g/cm<sup>3</sup>. The Sandell's sensitivity and molar absorptivity for Cu-2-(5-Bromo -2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide system is 25.0ngcm<sup>-2</sup> and 2538 L mole<sup>-1</sup>cm<sup>-1</sup> respectively. The composition of extracted species is found to be 1:2 [Cu: 2-(5-Bromo -2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide] by Job's Continuous Variation and Mole Ratio Method. Interference by various ions has been studied. The proposed method is rapid, sensitive, reproducible and has been successfully applied for determination of Cu(II) in alloy and pharmaceutical samples.

**KEYWORDS:** Extractive Spectrophotometry, Cu(II), [2-(5-Bromo -2-Oxoindolin-3-ylidene) Hydrazine Carbothioamide or 5-Bromo Isatin thiosemicarbazone [HBITSC], Samples.

**INTRODUCTION**

Copper is one of the essential elements in human body. Lack of copper in the body results in health problems such as anemia (Cu work together with iron for R.B.Cs.), Osteoarthritis and osteoporosis. Abnormality of copper metabolism in the body will cause some hereditary diseases (e.g., Wilson disease). Copper is an essential element only at very low levels and is toxic at higher levels in plants.

Hence, it is necessary to seek highly, accurate and selective analytical methods for quantitative determination of copper at trace levels.

A solvent extraction is becoming important separation technique in chemistry. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donor atoms.<sup>[1-5]</sup> Most of them possess biological and catalytic activity<sup>[6-7]</sup> and are also used as an efficient analytical reagent in trace analysis of some metal cations.<sup>[8-23]</sup> In the present communication, we describe the extractive spectrophotometric determination of Cu (II) with 2-(5- bromo-2- oxoindolin-3-

ylidenehydrazine carbothioamide), i.e.[5- Bromoisatin thiosemicarbazone (HBITSC)]

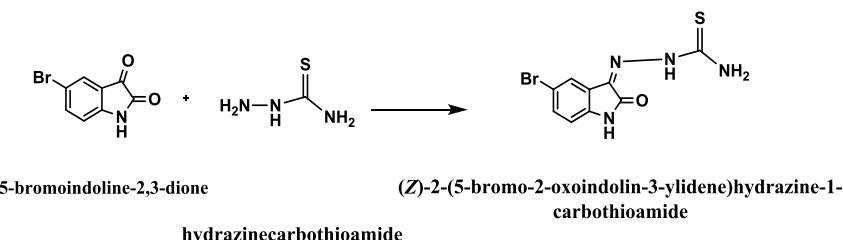
**MATERIAL AND METHODS**

All the used chemicals and solvents were of AR grade and were used without further purification and all the solutions were prepared in doubly distilled water.

ELICO - SL 159 spectrophotometer optically matched quartz or glass cells of 1cm path length were used for absorbance measurement. An ELICO LI-127 pH meter was employed for pH measurements.

**Synthesis of ligand with 2-(5-Bromo -2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide or 5-BromoIsatin thiosemicarbazone].**

Schiff base ligand **HBITSC** was synthesized by refluxing equimolar amount of ethanolic solution of 5-Bromoisatin with thiosemicarbazide for 4 - 5 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (80%, yield) which was collected by filtration. The resulting **HBITSC** was recrystallised using aqueous ethanol as the procedure recommended by Vogel.<sup>[22]</sup> The product was characterized by elemental and spectral analysis.



Its solution was prepared in Dimethylformamide (DMF). A stock solution of Cu (II) was prepared by dissolving copper sulphate in water containing; dilute sulphuric acid and it was standardized by Benzoin  $\alpha$  oximate method.<sup>[22]</sup> Working solutions of Cu (II) were made by suitable dilutions. All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water.

### Extractive Spectrophotometric Determination of Cu (II)

To an aliquot of aqueous solution containing 10-80 $\mu$ g of Cu (II), 3ml of phosphate buffer solution of pH 5.0 and 1ml of 0.5% solution of HBITSC prepared in DMF were added. The volume of solution was made up to 10 ml with distilled water and then equilibrated for 1 min with 10 ml of n-amyl alcohol and the phases were allowed to separate. The n-amyl alcohol extract was collected in a 10 ml measuring flask and made up to mark with n-amyl alcohol. The absorbance of n-amyl alcohol extract was measured at 510 nm against a reagent blank prepared under identical conditions. The Copper content of the sample solution was determined from calibration curve. To study the effect of other ions, the respective foreign ions were added to aqueous phase before the extraction and adjustment of pH.

### Determination of Cu (II) in alloy and Pharmaceuticals samples

#### Procedure for Determination of Cu (II) in (Copper-Aluminum based alloy)

0.1 to 0.2 gm. sample of copper was dissolved in 10 ml of aqua regia. The solution was evaporated to dryness and the residue was dissolved in 10 ml of 1M HCl filter, if required and resulting solution was diluted to 100 ml with water. 1ml aliquot of this solution was analyzed for Cu (II) by the procedure as described earlier.

#### Procedure for Determination of Cu (II) in Pharmaceuticals samples

Boiling with 10 ml of aqua regia dissolved 0.5gm of Pharmaceuticals samples. The solution was evaporated to dryness and the residue was dissolved in 10 ml of 1M HCl filter, if required and resulting solution was diluted to 100 ml with doubly distilled water.

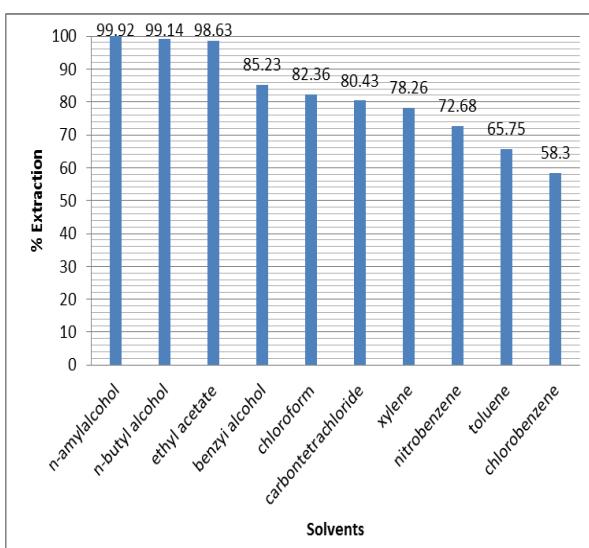
The working solution was prepared by appropriate dilution of stock solution. From an aliquot of this solution 1 ml was analysed for Cu(II) by the procedure as described earlier.

### RESULT AND DISCUSSION

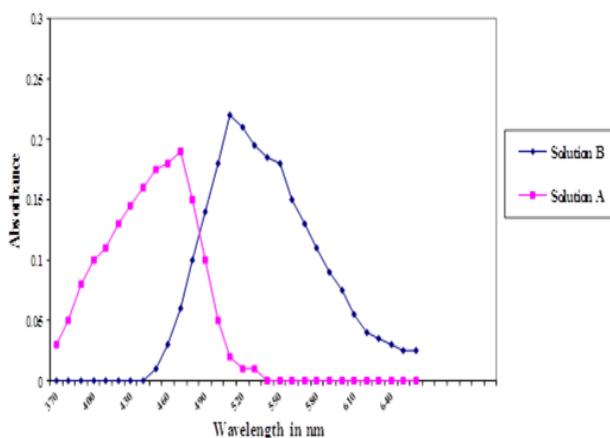
Copper (II) could be extracted quantitatively (99.92%) by HBITSC into n-amyl alcohol from an aqueous solution of pH 4.0 to 6.0. Organic solvents used for extraction of Cu (II) can be arranged on the basis of their extraction coefficient values as n-amyl alcohol > n-butanol > ethyl acetate > benzyl alcohol > chloroform > carbon tetrachloride > xylene > nitrobenzene > toluene > chlorobenzene (Fig.1). n-amyl alcohol was found to be the best extracting solvent; hence, it was selected for extraction throughout the work. The n-amyl alcohol extract of Cu- HBITSC complex showed intense peak at 510 nm. (Fig.2).

The absorbance due to the reagent is negligible at this wavelength, so the absorption measurements were taken at this wavelength. The result shows that the system confirmed to Beer's law at this wavelength over a copper concentration range 1.0 to 8.0 $\mu$ g/cm<sup>3</sup> (Fig.3).

The molar absorptivity of the extracted complex on the basis of Cu (II) content was calculated to be 2538 L mol<sup>-1</sup> cm<sup>-1</sup>. The Sandel's sensitivity was found to be 25.0 ng/cm<sup>2</sup>. It was found that 1 ml of 0.5% DMF solution of HBITSC was sufficient to extract 80 ug of Cu (II). The colour of the n-amyl alcohol extract was found to be stable at least 48 hrs at room temperature.

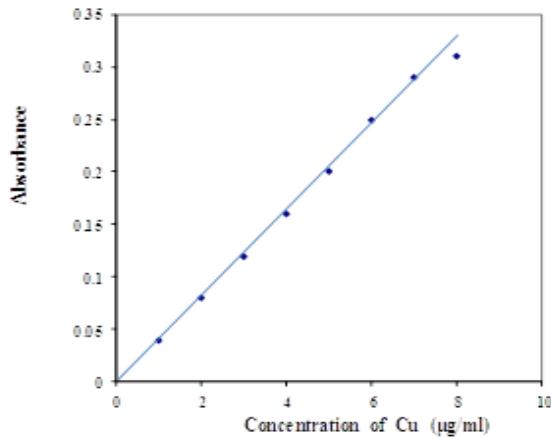


**Fig. 1: Percentage Extraction Coefficient of Cu (II) into Various Organic Solvents.**



**Fig. 2: Solution A: Absorbance spectra of HBITSC**

**Solution B: Absorbance spectra of Cu – HBITSC Complex**



**Fig. 3 Calibration curve for Cu(II).**

**Effect of other ions**

Cu (II) (50 $\mu$ g) was determined in the presence of various ions. The following ions in the amount indicated, did not interfere in the spectrophotometric determination of Cu (II) (50 $\mu$ g):

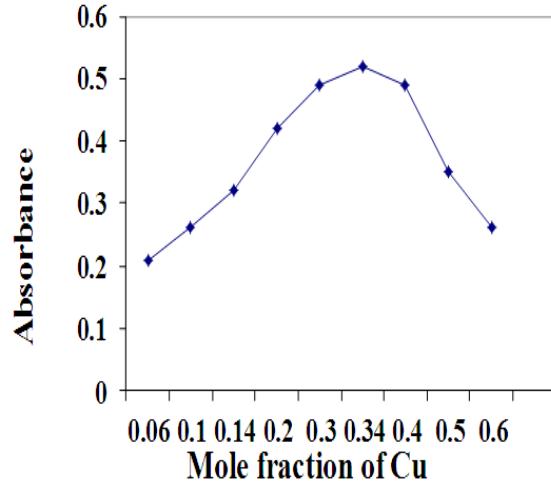
- 10 mg each of Li(I), Ca(II), Mg(II), Al(III), Ba(II), Sr(II), Pb(II), Sn(II), Be(II), W(VI), Mo(VI), U(VI), V(VI).
- 5mg each of Zn(II), Hg(II), Ag(I), As(III), Bi(III), Sb(III).
- 2mg each of Mn(II), Cd(II).
- 1mg each of Cr(III), Ce(IV), Th(IV), Zr(IV).
- 0.5mg each of Fe(II), Fe(III), Ni(II).
- 0.1 mg each of Co(II), Pt(IV), Ru(III), Ir(IV), Os(IV), Pd(II).
- 20 mg each of - chloride, bromide, fluoride, sulphate, persulphate, nitrate, phosphate, acetate, oxalate, citrate, tartarate.

Interference due to iodide, nitrite and thiosulphate, EDTA was removed by boiling solution with concentrated HNO<sub>3</sub> before the adjustment of pH.

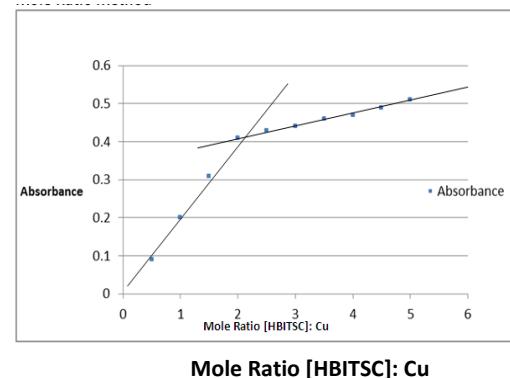
**Composition of the Extracted Complex**

The composition of the extracted complex was found to be 1:2(Cu:HBITSC) by Job's continuous variation and Mole ratio method (Fig-4 and Fig-5).

**Mole Ratio Method**



**Fig. 4 Composition of extractive species Cu:HBITSC by Job's Continuous variation method.**



**Fig. 5: Composition of extractive species Cu:HBITSC by Mole Ratio Method.**

**Precision, Accuracy, Sensitivity and Application of Method**

The precision and accuracy of the method were tested by analyzing the solution containing a known amount of Cu(II) following the recommended procedure. The average of 10 determination of 30  $\mu$ g of Cu (II) in 10 cm<sup>3</sup> solutions was 30.05 $\mu$ g, which is varied between 29.787 $\mu$ g and 30.313 $\mu$ g at 95% confidence limit and standard deviation was 0.368. The proposed method has been applied for the determination of Cu(II) in alloy and pharmaceuticals sample samples.

The results of the analysis of the samples were comparable with those obtained by diethyldithiocarbamate method<sup>[22]</sup> for Cu (II) (Table-1).

**Table – 1: Determination of Cu (II) in samples.**

Samples	Cu(II) found	
	Present method	Diethyldithiocarbamate method
Cu-Al alloy	7.98 %	8.01 %
Revital Capsule	0.49 mg	0.50 mg

\*Average of three determinations.

#### ACKNOWLEDGEMENT

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