Direct and Derivative Spectrophotometric Determination of Copper(II) with 5-Bromosalicylaldehyde Thiosemicarbazone

G. Ramanjaneyulu, P. Raveendra Reddy[*], V. Krishna Reddy and T. Sreenivasulu Reddy

Department of Chemistry, Sri Krishnadevaraya University, Anantapur-500013, A.P., India

Abstract: A rapid and sensitive spectrophotometric method is developed for the determination of Copper (II) in aqueous DMF medium. The metal ion forms a light greenish yellow coloured complex with 5-bromo salicylaldehyde thiosemicarbazone (5-BSAT) in acidic medium. The complex shows absorption maximum at 390nm. Beer's law is obeyed in the range $0.31 – 6.35 \mu gml^{-1}$ of Copper (II). The molar absorptivity (ε) and Sandell's sensitivity are found to be 1.08×10^4 l mole^{-1} cm^{-1} and $0.062 \mu gcm^{-2}$ respectively. A method for the determination of copper by third derivative spectrophotometry is also proposed. The methods have been employed successfully for the determination of copper in grape leaves and aluminum based alloy samples.

INTRODUCTION

Copper is an important trace element in animal metabolism. The major concentration of copper in human body is in liver and bones. Blood contains number of copper proteins and it is necessary for the synthesis of haemoglobin. Though copper is essential for human metabolism, it becomes hazardous when present in excess. An excessive accumulation of copper in liver, kidney and brain leads to kidney failure and various neurological abnormalities causing Wilson's disease.

A number of spectrophotometric methods have been developed in recent years for the determination of copper. Among the various organic reagents employed, thiosemicarbazones occupy a significant place [1-4]. Some of the recently proposed methods using thiosemicarbazones are less sensitive or require the use of solvent extraction [5-8]. The present paper describes very selective, sensitive, direct and derivative spectrophotometric methods for the determination of micro amounts of copper in aqueous DMF medium by complexing with 5-bromosalicylaldehyde thiosemicarbazone (5-BSAT).

MATERIALS AND METHODS

A Shimadzu UV-Visible spectrophotometer model 160-A equipped with 1cm quartz cells was used for spectrophotometric measurements. The pH measurements were made with a Phillips digital pH meter model pp 9046. Suitable settings for derivative mode were as follows: spectral band width 2nm wavelength readability 0.1 nm increment; scan speed, fast (nearly 2400 nm min^{-1}); wavelength accuracy ±0.5nm with automatic wavelength correction.

The reagent 5-bromo salicylaldehyde thiosemicarbazone (III) was prepared by condensing 5-Bromosalicylaldehyde (I) with thiosemicarbazide(II) as reported earlier [9]. The structure of the reagent is as follows:
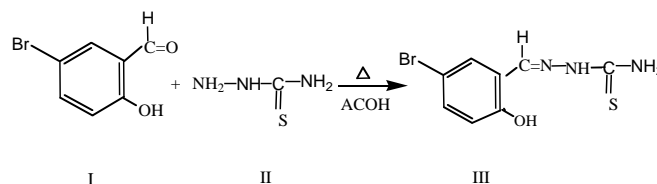
A 0.01m solution in DMF was used in the studies

Cu(II) Solution

Stock solution of Cu(II) was prepared by dissolving 2.4968 g of Cu SO$_4$ 5H$_2$O (AR, BDH) in 1000 ml of distilled water and standardized iodometrically [10]. Working solutions were prepared by diluting the stock solution to an appropriate volume.

Buffer solutions were prepared by employing 1M HCl and 1M CH$_3$COONa (pH 1-3) and 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0). All other chemicals used were of A.R. grade.

Procedures

Direct Spectrophotometry: In each of a set of different 10 ml standard flasks, 5ml buffer solution (pH 4.5), various volumes (0.1-2.0ml of 5X10^{-4} M) of Cu(II) solution, DMF (1.5ml) and 1ml of reagent (5-BSAT) solution (1X10^{-2} M) were taken and made up to the mark with distilled water. The absorbance was measured at 390nm against the reagent blank. The calibration curve was prepared by plotting absorbance against the amount of copper.

Derivative Spectrophotometry: For the above solutions the first, second, third and fourth derivative spectra were recorded at 400-600nm. The derivative amplitudes of the crusts and troughs of various ordered derivative curves were measured at appropriate wavelengths and plotted against the amount of Cu(II) to get the determinable ranges.

The calibration graphs follow the straight line equation A = mc+b, where 'c' is the concentration of the solution, A is the measured absorbance or derivative amplitude and m and b are constants. By substituting the corresponding data into the above equation. Calibration equations were obtained as

*Address correspondence to this author at the Department of Chemistry, Sri Krishnadevaraya University, Anantapur-500013, A.P., India;
E-mail: raveendrareddy_sku@yahoo.com

A = 0.164C+0.01 for the zero order data and A = 0.096C+0.0009; A = 0.156C+0.0013; A = 0.816C+0.0007 and A = 0.360C-0.00007 for first, second, third and fourth derivative data respectively.

RESULTS AND DISCUSSION

The absorption spectra of greenish yellow coloured of [Cu (II)-BSAT] complex solution and the reagent blank were recorded in the wavelength region 360-600 nm and shown in Fig. (**1**). It was observed that the complex showed the maximum absorbance at 390 nm where the reagent blank had negligible absorbance. Hence, the analysis was carried out at 390 nm.

Studies on the effect of variation in pH of the reaction mixture over the absorbance exhibited that a single complex species with a constant and maximum absorbance in the pH range 4.0-5.0 formed in the entire pH range of study. A five fold molar excess of the reagent was necessary for the maximum colour development. The yellowish green colour formation between Cu (II) and the reagent was instantaneous and the colour was stable for more than 24 hours.

Beer's law was obeyed in the concentration range 0.31-6.35 $\mu g\ ml^{-1}$ of Cu(II). The molar absorptivity of the complex at 390nm and at pH 4.5 was $1.08X10^{4}\ L\ mol^{-1}\ cm^{-1}$. The Sandell's sensitivity of the method was found to be 0.062 μgcm^{-2}. The standard deviation of the method for ten determinations of 3.81 $\mu g\ ml^{-1}$ of Cu(II) was ± 0.0021.

The composition of the complex determined using Job's and mole-ratio methods, was found to be 1:1. The stability constant determined by Job's method was $4.30X10^{5}$.

Effect of Foreign Ions

The selectivity of the proposed method was evaluated by studying the effect of diverse ions on the absorbance of the experimental solution. The tolerance levels of the diverse ions were calculated as the amounts caused an error in absorbance by ± 2.0%. The results are presented in Table **1**. It can be seen from the table that large number of foreign ions does not interfere in the present method. However Fe(III) (180-fold) Ni(II) (100-fold), Al(III) (130-fold) were masked with phosphate, citrate and fluoride respectively.

Determination of Cu(II) by Derivative Spectrophotometry

Derivative spectrophometric methods have been developed for the determination of copper in lower amounts than the zero order method. The first and second derivative spectra showed maximum amplitude at 415nm and at 430nm respectively. The third derivative curve exhibited zero amplitude at 430.2nm and maximum amplitude at 445nm. For the fourth derivative spectrum, the zero point and the maximum amplitudes were at 448.2nm and 460nm respectively (Fig. **2**). All the derivative amplitudes were found to be proportional to the concentration of Cu(II). The plots between the derivative amplitude of the respective curve and concentration of Cu(II) were found to be linear in the range 0.15-4.20, 0.20-3.80, 0.15-3.50 and 0.09-3.12 $\mu g\ ml^{-1}$ of Cu(II) for 1st, 2nd, 3rd and 4th derivative curves respectively. The statistical data of linear plots indicate that the third derivative spectrophotometric method is highly sensitive for the determination of Cu(II).
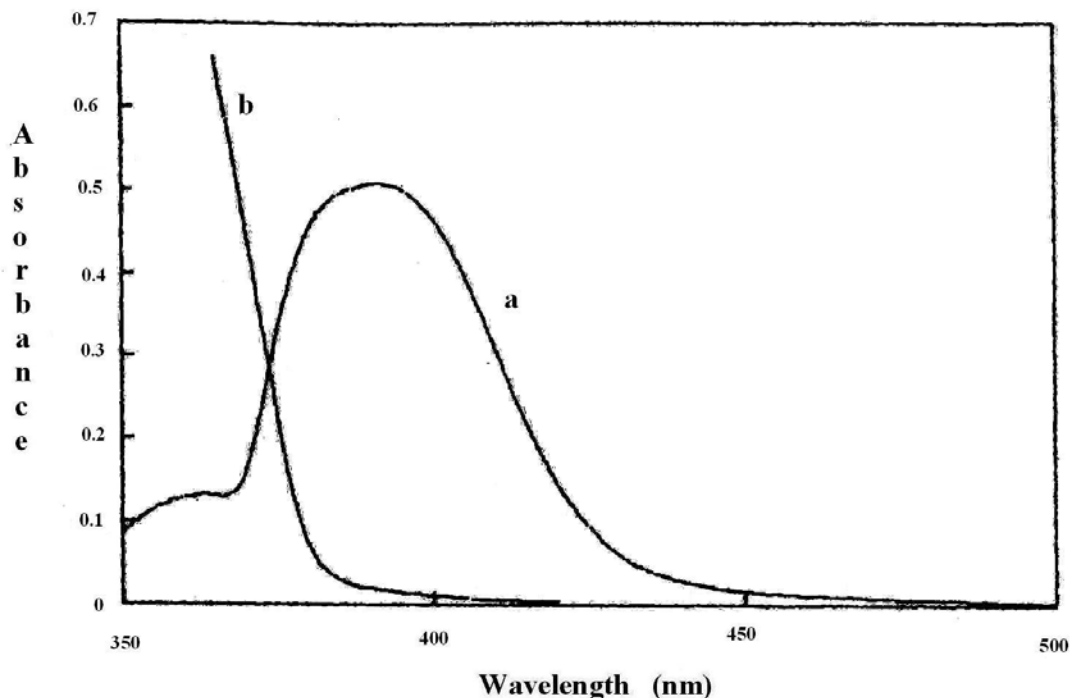

Fig. (1). Derivative spectra of Cu (II) – BSAT system. (**a**) Cu (II) – BSAT system *vs* reagent blank, (**b**) BSAT *vs* Buffer blank [Cu (II)] = 5 X 10^{-5} M: [BSAT] = 1X 10^{-3}M; pH = 4.5.

Table 1.   Tolerance Limit of Foreign Ions in the Determination of Cu(II)

pH = 4.5.
Amount of Cu(II) = 3.15 µg ml^{-1}

Foreign Ion	Tolerance Limit (µg ml^{-1})	Foreign Ion	Tolerence Limit (µg ml^{-1})
Citrate	865	K(I)	900
DMG	630	Ba(II)	686
Iodide	635	Fe(III)	559[a]:279[b]
Ascorbate	522	Th(IV)	464
Sulphate	480	Sr(II)	438
Phospahate	475	Pb(II)	414
Nitrate	460	W(VI)	368
Bromide	400	Ni(II)	293[b]:250[d]
Chloride	355	Mn(II)	275
Carbonate	300	Ti(IV)	240
Tartrate	296	Ca(II)	200
Fluoride	285	Mg(II)	181
Thiosulphate	224	Al(III)	162:405[c]
Oxalate	176	Ce(IV)	70
EDTA	Interferes	Mo(VI)	48
Thiourea	Interferes	Co(II)	29[b]
		Sb(III)	25
		Cd(II)	23
		Cr(III)	10
		Zn(II)	Interferes
		V(V)	Interferes

Masked in presence of [a] Phosphate: [b] Citrate: [c] Fluoride: [d] Precipitated with DMG and filtered.
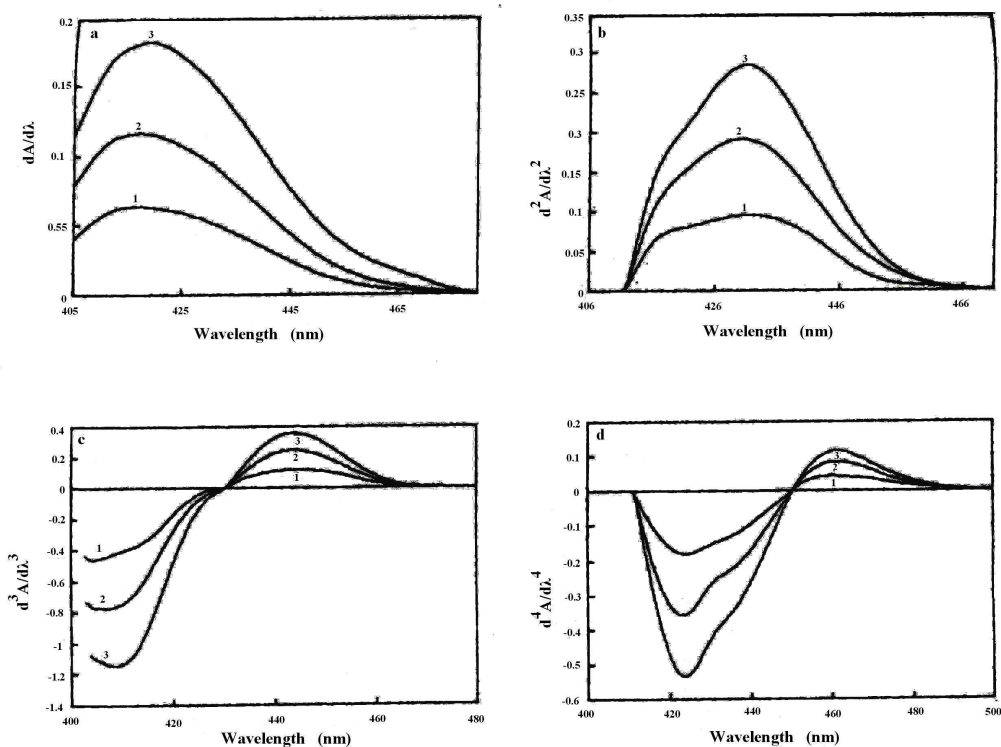

Fig. (2). Derivative spectra of Cu (II) –BSAT system (**a**) First order. (**b**) Second order. (**c**) Third order. (**d**) Fourth order [Cu (II)], µg ml^{-1}: (1) 0.63: (2) 1.27: (3) 1.90.

Table 2.   **Determination of Copper in Grape Leaves (Vitis V in Ifera)**

Sample	APARI Value (µg ml⁻¹)	Amount of Copper (µg ml⁻¹)			
		Present Method (n = 5)			
		Direct Method*	Relative Error (%)	3ʳᵈ Derivative Method*	Relative Error (%)
Grape Leaves	55.40	54.5	-1.6	55.90	+0.9
	83.10	82.0	-1.3	82.65	-0.5

Determination of Copper in Aluminium Based Alloys

Sample	Certified Composition (%)	Amount Taken (µg ml⁻¹)	Amount Found (n = 5)			
			Direct Method*	Relative Error (%)	3ʳᵈ Derivative Method*	Relative Error (%)
BAS-20	Cu.4.10; Niᵃ1.93; Feᵇ0.43; Mn 19; Si 0.29; Mg 1.61; RestAlᶜ	0.62	0.63	+1.61	0.61	-1.61
		1.20	1.26	+1.61	1.25	+0.81
BAS-85	Cu.0.90; Niᵃ0.91; Feᵇ1.15;Mn 0.02; Si 2.04; Mg 0.18; Zn 0.01; RestAlᶜ	0.70	0.68	-2.85	0.71	+1.42
		1.40	1.42	+1.43	1.39	+0.71

* Average of five determinations.
Masked in presence of ᵃ Citrate: ᵇ Phosphate and ᶜ fluoride.

Table 3.   **Comparison with Other Methods**

Reagent	λ_{max} (nm)	ε*	Interference/Remarks	Ref.
p-Anisaldehyde thio semicarbazone	402	0.61	-	[12]
2-Furaldehyde thiosemicarbazone	370	2.86	Extraction	[13]
Quinoline 2-aldehyde thiosemicarbazone	430	1.33	Extraction; Zn, Cd, Fe interfere	[14]
Salicyladehyde thiosemicarbazone	375	0.92	Extraction	[15]
Thiophene-2-aldehyde thiosemicarbazone	372	3.90	Extraction	[16]
Acenaphtaquinnone mono thiosemicarbazone	430	0.58	Ethanol Present	[17]
Acetophenone thiosemicarbazone	418	0.83	Extraction	[18]
Cyclohexanone thiosemicarbazone	405	0.24	Extraction	[19]
1,2-cyclohexanedione dithiosemicarbazone	467	0.57	-------	[20]
1,3 cyclohexanedione bis dithiosemicarbazone mono hydrochloride	390	0.5	-----	[21]
1,4 cyclohexane dione bisthiosemicarbazone	410 / 600	0.25 / 0.41	-------- / Extraction	[22]
2, 4 Dihydroxy acetophenone thiosemicarbazone	390	1.5	Extraction	[23]
2, 2¹- Dihydroxy benzophenone thiosemicarbazone	385	0.86	------	[24]
Glyoxal Dithiosemicarbazone	485	0.67	----	[25]
2-Hydroxy iminocyclohexanone thiosemicarbazone	465	0.55	-----	[26]
5-Bromosalicylaldehyde thiosemicarbazone	390	1.08	-----	Present Method

* Molar absorptivity (10^4 lmol⁻¹ cm⁻¹).

Applications

The proposed direct and third derivative spectrophotometric methods were employed for the determination of Cu(II) in aluminium based alloy samples and in grape leaves. The aluminum based alloy samples were obtained from Bureau of Analysed Samples (BAS) and the grape leaves were procured from the grape gardens in the surroundings of Anantapur town, Andhra Pradesh, India.

The extract of the leaf sample was obtained from Andhra Pradesh Agricultural Research Institute (APARI), Hyderabad. The sample solution was prepared following the procedure described by Piper [11]. The sample solution thus prepared was diluted appropriately with distilled water and analyzed for copper.0.5ml of 0.5M citrate solution was added to mask iron(II).

Solutions of the aluminium based alloy samples were prepared by the following procedure. About 0.4g alloy sample was treated with 15ml of 1:1 HCl. To this, 3ml of HNO_3 were added and boiled until dissolution was complete. 10 ml of water and 40 ml of ammonium hydroxide solution were added and filtered through a whatman no.41 filter paper. The filtrate was collected into 250ml volumetric flask and made upto the mark with distilled water. The sample solutions were appropriately diluted and analyzed for copper. 0.5ml of 0.5M citrate solution was added to mask iron and nickel. The amount of copper present in the samples was calculated from the predetermined calibration plot. The results obtained in these studies are presented in Table **2**.

The results of the present method were compared (Table **3**) with those reported in the literature employing thiosemicarbazones. Most of the reported methods require rigid experimental conditions. The more sensitive methods involve extraction procedure. The derivative method is suitable for the determination of Cu(II) in microgram quantities in vegetable tissues.

CONCLUSION

The proposed direct and derivative spectrophotometric methods are simple, fast, sensitive and reasonably selective for the determination of copper in complex materials. The comparison of the results of the present method with already reported methods (Table **3**) reveals that the present method is more sensitive than many methods except those proposed by Lodhi *et al.* [10], Khanis *et al.* [11] and Leyva *et al.* [13].

REFERENCES

[1]   Singh, R.B.; Garg, B.S.; Singh, R.P. *Talanta*, **1975**, *25*, 619.
[2]   Asuero, A.G.; Cano, J.M. *Analyst*, **1978**, *103*, 140.
[3]   Singh, R.B.; Ishii, H. *Crit. Rev. Anal. Chem.*, **1991**, *22*, 381.
[4]   Reddy, K.J.; Kular, J.R.; Narayana, S.L.; Ramachandraiah, C.; Thriveni, T.; Reddy, A.V. *Environ. Monit. Assess.,* **2007**, *124*, 309.
[5]   Bhatt, G.H.; Patel, I.J; Desai, K.R. *J. Inst. Chem.*, **1993**, *65*, 190.
[6]   Patel, I.J.; Bhatt, G.H.; Desai, K.R. *J. Inst. Chem.*, **1995**, *67*, 120.
[7]   Prasad, N.B.L.; Hussain, R.K. *Indian J. Chem.,* **2004**, *43*(A), 111.
[8]   Vidyasagar, B.S.; Hussain, R.K. *J. Indian Chem. Soc.*, **2006**, *83*(1), 20.
[9]   Sha, P.T.; Daniels, T.C. *Rev. Trav. Chim.*, **1950**, *69*, 1545.
[10]   Vogel, A.I. *A Text book of Quantitative Chemical Analysis*, Longman., group pub. London, UK, **1989**.
[11]   Piper, C.S. *Soil and Plant analysis, Hans Publishers*, Bombay, India, **1966**.
[12]   Thimmaiah, K.N.; Sanke, G.H.; Maqbool, A. *Indian J. Chem.,* **1983**, *22A*, 690.
[13]   Lodhi, M.A.; Mir, I.; Shah, R.A. *Pak. J. Sci. Ind. Res.*, **1977**, *20*, 346.
[14]   Khanis, D.V.; Shinde, V.M. *J. Indian Chem. Soc.*, **1984**, *61*, 275.
[15]   Subbarami, R.N.; Venkata, R.D. *Microchem. J.*, **1985**, *31*, 318.
[16]   Munoz Leyva, J.A.; Cano Pavan, J.M.; Pino, F. *An. Quim.,* **1973**, *69*, 251.
[17]   Singh, S.K.; Sharma, R.K.; Sindhwani, S.K. *Bull. Chem. Soc. Jpn.*, **1986**, *59*(6), 1223.
[18]   Calzolari, L.C.; Coassini, L.L.; Benci, P.; Pavretto, I. *Ann. Chim.*, **1973**, *63*, 363.
[19]   Gensar, G.; Bedito, D.P.; Sanchez, F.G.; Valcarcel, M. *An. Quim.,* **1978**, *74*, 1522.
[20]   Munoz Leyva, J.A.; Cano Pavan, J.M.; Pino, L. *An. Quim.,* **1976**, *72*, 392.
[21]   Hussain, R.K.; Venkata, R.D. *Acta Cienc. Indica.,* **1984**, *10*(4), 207.
[22]   Raman, C.M.; Berzas Nevado, J.J.; Martinez, G.J. *Microchem. J.,* **1982**, *27*, 380.
[23]   Reddy, A.V.; Reddy, Y.K. *Talanta*, **1986**, *33*(7), 617.
[24]   Toribio, F.; Lopez Fernandez, J.M.; Bendito, D.P.; Valcarcel, M. *Microchem. J.*, **1980**, *25*, 338.
[25]   Hoshi, S.; Yotsuyanagi, T.; Aomura, K. *Bunseki Kaguku.*, **1977**, *26*, 592.
[26]   Francisco, S.; Jimenez, S.J.C.; Galeano, D.T.; Lopez-Arza, V. *Ann. Chim. (Rome),* **1986**, *76*(9-10), 387.