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Direct and Derivative Spectrophotometric Determination of Copper (II) using 3, 5-Dimethoxy-4-hydroxy Benzaldehyde Isonicotinoyl Hydrazone (DMHBIH)*

K. Aruna Bai, G. V. S. Valli Nath,
K. B. Chandrasekhar and N. Devanna
Department of Chemistry
Jawaharlal Nehru Technological University Anantapur
Anantapur - 515002, (A. P) India.
E-mail: chandrasekhar_kb@yahoo.co.in

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Abstract: Derivative spectrophotometric determination of Copper (II) with 3, 5 – Dimethoxy – 4 – hydroxyl benzaldehyde isonicotinoyl-hydrazone (DMHBIH) reagent has been proposed. Direct and derivative method has been developed for the spectrophotometric determination of micro amounts of Copper (II) in basic buffer solution(pH 9.0). The reagent DMHBIH gives bright yellow coloured water soluble complex [(Cu(II)- DMHBIH] in basic buffer solution. The maximum absorbance was observed in the pH range 8.0-9.5. The molar absorptivity and sandell's sensitivity of Copper (II) complex with DMHBIH at λ_{max} 440 nm was found to be 3.37×10^4 $L.mol^{-1}cm^{-1}$ and 0.00296 $\mu g/cm^2$. Beer's law validity range varies from 0.317 to 3.17 µg /ml. Copper (II) forms 1:1 complex with DMHBIH and stability constant of Copper (II) complex was $21.3X10^6$. The first order derivative amplitude was measured by the peak height method at λ_{max} 494 nm. The second order derivative amplitude was measured by the peak height method at λ_{max} 510 nm. The developed spectrophotometric method was applied for the determination of Copper (II) in Beer, wine, vegetables and milk samples.
Keywords: Copper (II), derivative spectrophotometry, 3, 5 – Dimethoxy – 4 - hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH).

1. Introduction

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et. al.[1] Hydrazones are important class of known analytical reagents[2-8]. These reagents are formed by the condensation of hydrazides and a carbonyl compound. Hydrazones are also found to have biological activity. These compounds contain an azomethine nitrogen atom

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and this is responsible for their reactivity with number of transition metal ions which form coloured complexes. In continuation of our ongoing work on the analytical applications of hydrazones, we report herein spectrophotometric determination of copper (II) using 3, 5-Dimethoxy – 4 – hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH). Spectrophotometric methods for the determination of metal ions with 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) are not exploited much.

2. Experimental

Spectrophotometric measurements were made in a Schimadzu 160A microcomputer based UV-Visible spectrophotometer equipped with 1 cm quartz cells, an ELICO LI-120 digital pH meter for pH adjustments and Sartorius electronic balance was used for weighing.

All reagents used were of AR grade unless otherwise stated. All solutions were prepared with doubly distilled water. The standard Copper (II) solution (0.1M) was prepared by dissolving 6.2375 g of Copper sulphate ($CuSo_4.5H_20$), AR MERCK in distilled water in a 250 ml standard flask.

The reagent 3, 5 – Dimethoxy – 4 - hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) was prepared by simple condensation of 1 mole of 3, 5-Dimethoxy-4-hydroxybenzaldehyde with 1 mole of isonicotinoylhydrazone (Fig.1). The reagent solution (0.01M) was prepared by dissolving 0.3022 g of DMHBIH in 100 ml of dimethyl formamide. The reagent solution is stable for 48 hrs. Buffer solutions were prepared by using 0.1M HCl, 0.1M NaOH, 0.1M disodium hydrogen phosphate and 0.1M potassium dihydrogen phosphate.

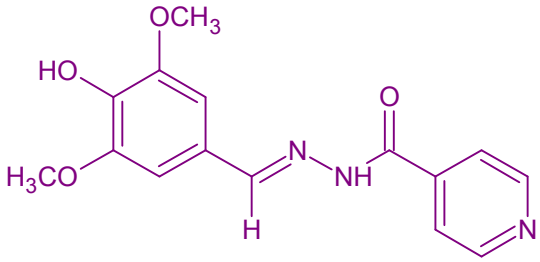

Fig.1. Structure of 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone(DMHBIH)

Reaction with metal ions:

The reactions of some important metal ions were tested at different pH values. The samples were prepared in 10 ml standard volumetric flasks by adding 3 ml of buffer (pH 1.0-11), 0.5 ml of metal ion ($1x10^{-3}$M) and 0.5 ml

of $1x10^{-2}$M DMHBIH solutions. The solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 200-800 nm range against reagent blank. The results are summarized in Table-1.

Table-1
Analytical Characteristics of 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone

Metal ion	p^H	λ_{max} (nm)	Molar absorptivity(ε) ($Lmol^{-1}cm^{-1}$) x 10^4
Ru(III)	4.25	390	1.7
Fe(III)	4.0	386	1.875
Cu(II)	9.0	440	3.37*

Recommended procedure:

Determination of copper (II) (zero order) : An aliquot of the solution containing 0.317 to 3.17 µg/mL of copper (II), 3 ml of buffer solution pH 9.0 and 0.5 ml of $1x10^{-2}$M DMHBIH reagent were taken in a 10ml standard volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 440 nm in a 1.0 cm cell against corresponding reagent blank prepared in the same way but without copper (II) metal solution. The measured absorbance was used to compute the amount of copper (II) from the calibration plot. Wavelength values are plotted against absorbance and presented in fig-2.

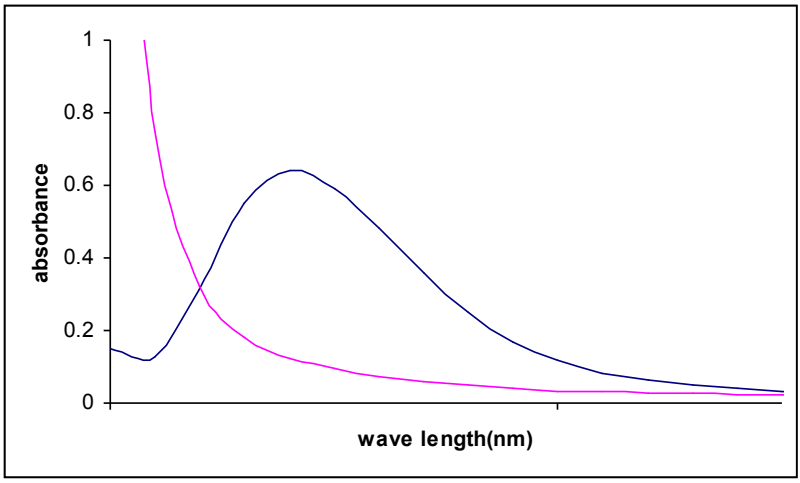

Fig-2. Zero order spectrum of Copper (II)-DMHBIH System

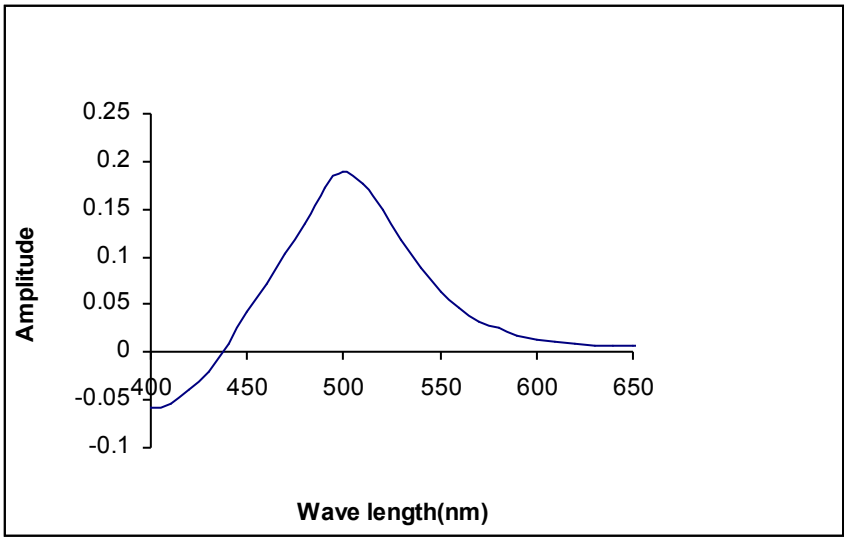

Fig-3. First order spectrum of Copper (II)-DMHBIH System

3. Results and Discussion

3, 5 - Dimethoxy - 4 - hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) reagent is a blend of a carbonyl compound and a hydrazine. The reagent solution is stable for 48 hrs. in alkaline medium. The ligand presumably coordinates the metal ions to give a neutral water soluble complex.

Determination of Copper (II) using DMHBIH:

Copper (II) reacts with DMHBIH in alkaline medium to give bright yellow coloured water-soluble complex. The colour reaction between copper (II) and DMHBIH are instantaneous even at room temperature in the pH range 8.0-9.5. The absorbance of the bright yellow coloured species remains constant for more than 2hrs. The maximum colour intensity is observed at pH 9.0.

A 10-fold molar excess of reagent is adequate for full colour development. The order of addition of buffer solution, metal ion and reagent has no adverse effect on the absorbance. The complex formation reaction between copper (II) and DMHBIH has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Important physico-chemical and analytical characteristics of copper (II) and DMHBIH are summarized in Table-2.

Table-2
Physico-Chemical and Analytical Characteristics of Copper (II)-DMHBIH Complex

Characteristics	Results
Colour	Bright yellow
λ_{max} (nm)	440
p^H range (optimum)	8.0-9.5
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity (L.mol $^{-1}$cm^{-1}) (ε)	$3.37x10^4$
Sandell's sensitivity (μg/cm^2)	0.00296
Beer's law validity range (μg/ml)	0.317-3.17
Optimum concentration range (μg/ml)	0.381-3.144
Composition of complex (M:L) obtained in Job's and mole ratio methods	1:1
Stability constant of the complex	$21.3x10^6$
Standard deviation in the determination of μg/ml of Cu(II) for ten determinations	0.001
Relative standard deviation (%)	0.1

4. Effect of Diverse Ions

Table-3
Tolerance of Foreign ions in the determination of 1.5875 μg/ml Copper (II)

Ion added	Tolerance limit (μg/ml)			Ion added	Tolerance limit (μg/ml)		
	Zero order	D1	D2		Zero order	D1	D2
Bromide	3596	3596	3596	U^{6+}	119	238	238
Iodide	2538	3173	3173	Bi^{3+}	105	209	209
Urea	1500	1500	1500	Co^{2+}	88	118	118
Chloride	1243	1243	1243	Mn^{2+}	82	110	110
Tetraborate	970	970	970	Ca^{2+}	80	100	100
Phosphate	950	950	950	Sn^{2+}	59	59	59
Sulphate	940	1410	1410	Cd^{2+}	56	112	112
Oxalate	880	1760	1760	Zr^{4+}	46	91	91
Thiocyanide	872	872	872	Zn^{2+}	65	98	98
Nitrate	310	620	620	Ni^{2+}	29	59	59
Acetate	295	295	295	Sb^{3+}	12	18	18
Thiourea	230	230	230	Ag^{1+}	11	16	16
Fluoride	190	190	190	Mo^{6+}	10	14	14
Tartarate	148	148	148	As^{3+}	7.5	11	11
Ascorbic acid	88	176	176	Pd^{2+}	5.3	11	11
Hg^{2+}	301	301	401	V^{5+}	5.1	5.1	5.1
Ba^{2+}	275	343	343	Ru^{3+}	5.05	10	10
Pb^{2+}	207	207	207	Fe^{3+}	2.8, 3.8*	2.8,3.8†	2.8,3.8‡
W^{6+}	184	276	276	Al^{3+}	2.7	4.0	4.0
Sr^{2+}	131	131	131	Cr^{3+}	2.6	5.2	5.2

*Masked with 180 μg/ml Fluoride. † Masked with 180 μg/ml Fluoride. ‡ Masked with 180 μg/ml Fluoride

The effect of various diverse ions in the determination of Copper (II) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ±2 % in the absorbance or amplitude. The results are given in Table-3.

The data suggests that several associated anions and cations do not interfere when they are present in large excess such as phosphate, bromide, sulphate, iodide, urea, U(VI), Ba(II), Mn(II), Ca(II). The interference of associated metal ion Fe(III) is decreased with masking agent Fluoride.

5. Applications

The proposed method was applied for determination of Copper (II) in Beer, wine, vegetables and milk samples.

Determination of Copper (II) in Beer and Wine:

50 mL of beer or wine sample was taken in separate 250 mL beakers and digested in 5 mL of 5M HNO_3 and evaporated to dryness. The residue thus obtained was dissolved and diluted up to the mark in a 100 mL volumetric flask with distilled water. Suitable aliquots of sample were analyzed for the determination of Copper (II) by the recommended procedure from a pre-determined calibration plot, the results obtained are presented in Table-4.

Table-4

Estimation of Copper (II) (μg/ml) in Beer and Wine Samples

Sample	Copper (II) μg/ml				Error %		
	Amount present	Amount found*					
		Zero	D_1	D_2	Zero	D_1	D_2
Beer	5.32	5.30	5.31	5.31	-0.375	-0.190	-0.190
Wine	7.45	7.42	7.43	7.43	-0.403	-0.268	-0.268

*average of the best three determinations among five determinations.

Determination of Copper (II) in food samples:

Food samples like vegetables and milk samples were analyzed for the determination of Copper (II) present using the proposed method. The content of Copper (II) present in the solution was determined by using the recommended procedure from a pre-determined calibration plot, the results obtained were confirmed by direct AAS(atomic absorption spectrophotometer). The results obtained are presented in Table-5.

Table-5
Determination of Copper (II) (μg/g) in food Samples

Sample	Amount of Cu(II) μg/g				Error %		
	AAS Method	Present method*					
		Zero	D1	D2	Zero	D1	D2
Amaranthus Gangeticus (thotakura)	15.45	15.12	15.30	15.30	-2.14	-0.97	-0.97
Brassica nigra (Mustard)	16.14	16.09	16.11	16.11	-0.31	-0.18	-0.18
Cow milk	5.0	4.93	4.96	4.96	-1.40	-0.80	-0.80
Dairy milk	4.25	4.20	4.22	4.22	-1.17	-0.71	-0.71

*average of the best three determinations among five determinations.

6. Conclusion

The present method using DMHBIH as spectrophotometric reagent for the determination of Copper (II) in aqueous medium is sensitive and simple. This method was favourably compared with previously reported spectrophotometric methods and presented in Table-6. Most of the spectrophotometric methods involve both extraction and heating of the reaction mixture or only extraction. However heating at a specific temperature for a long time is laborious and time consuming. The determination of Copper (II) using DMHBIH is not laborious and there is no need for heating the components or extraction. Further, the reagent is easy to synthesize using available chemicals. Moreover, the present method is simple, rapid, reasonably sensitive for the determination of Copper (II).

Table-6
Comparison with other Reagents

Reagent	λ_{max} (nm)	PH range	Molar absorptivity (L/mol/cm)	Beer's law validity range (μg/ml)	Stability constant of the complex	Reference
Quinoline-2-aldehyde-2-quinolylhydrazone(QAQH)	536 540	-- --	$4.7x10^4$ $5.8x10^4$	-- --	-- --	9-11
Quinoline-2-aldehyde-2-pyridylhydrazone(QAPH)	512	9.0 Borate	$5.8x10^4$	--	--	12-13
Bicyclohexanoneoxalyl dihydrazone	600	7.0-9.0	$1.6x10^4$	--	--	14-16
DMHBIH*	440	8.0-9.5	$3.37X10^4$	0.317-3.17	$21.3X10^6$	Present work

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