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Direct and Derivative Spectrophotometric determination of Copper (ii) in presence of Micellar medium in Grape leaves, Biological materials and Alloy samples using 2,4-Dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone (DMBHBH)

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Abstract: A rapid, simple, sensitive and selective spectrophotometric method has been developed for the determination of Copper (II) using newly synthesized Chromogenic reagent 2,4-Dimethoxy-4-hydroxybenzaldehydebenzoylhydrazone (DMBHBH) in presence of cationic surfactant,CTAB (5%) (micellar medium). Copper (II) forms a orange coluored water-soluble complex with 2,4-Dimethoxy-4-hydroxybenzaldehydebenzoylhydrazone (DMBHBH) in the pH range 8.0-12.0. The complex shows maximum absorbance at λ_{max} 384 nm and in the pH range 9.0-10.0. At λ_{max} 384 nm, the complex shows maximum absorbance while the reagent blank shows negligible absorbance. Hence, analytical studies are carried out at λ_{max} 384 nm and at pH 10.0 (Phosphate buffer) against reagent blank. Beer's law is obeyed in the range 0.1588-1.9063 μg/mL and the optimum concentration range obtained from ringbom plot is 0.3177-1.5886 μg/mL of Copper (II)· The molar absorptivity and Sandell's sensitivity for the coloured solution are found to be 3.8×10^{4} L $mol^{-1}cm^{-1}$ and 0.00585 $\mu g.cm^{-2}$ respectively. The interference effect of various diverse ions has been studied. The complex shows 1:1 [Cu (II): DMBHBH] stoichiometry with stability constant 1.150260×10^{5} obtained from job's method. The standard deviation of the method in the determination of 0.3177 μg ml^{-1} of Copper (II) is 0.003 and the Relative standard deviation is 3.50 %. First and second order derivative spectroscopic method is developed at λ_{max} 440 nm and 455 nm respectively for the determination of Copper (II), which is more sensitive than the zero order method. The developed method has been used for the determination of Copper (II) in Grape leaves, Biological materials and in alloy samples. The results are in good agreement with the certified values.

Keywords: Copper (II), Spectrophotometry, Grape leaves, Biological materials, alloy samples, DMBHBH.

INTRODUCTION

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al[1]. Hydrazones are important class of known analytical reagents. Due to analytical potentialities of hydrazones herein we report the synthesis, characterization and analytical properties of the reagent 2,4-Dimethoxybenzaldehyde-4-hydroxybenzoyl hydrzone (DMBHBH). In the light of the above herein we report the direct and derivative spectrophotometric method for determination of Copper (II) in Grape leaves, biological materials and in alloy samples. Derivative spectrophotometry is a very useful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences. In this paper a first and second order derivative spectrophotometric method is described for the determination of Copper (II) using DMBHBH in Grape leaves, biological materials and in alloy samples.

Copper is available in nature in the Free State in the form of sulphides, chlorides and carbonates. Copper is utilized in electrical industries, electronic industries and industrially useful alloys. It is widely used in printed circuit boards, generators, transformers, computer heat sinks, coins. Because of its biostatic property it is used as roofing material for houses. Copper knobs are used in hospitals to reduce the transfer of disease.

Copper is essential for all plants and animals. It is an essential constituent of about thirty enzymes and glycoproteins and is required for the synthesis of hemoglobin and for some biological processes. It also promotes iron absorption from the gastrointestinal system, is involved in the transport of iron from tissues in to plasma, helps to maintain myelin in the nervous system, and is important in the formation of bone and brain tissues. A deficiency of copper causes diseases such as anemia. Though Copper is an essential element it becomes hazardous when present in excess. Excess of copper causes jaundice and Wilson disease. Excess of copper in water is not only harmful to human beings, but also interferes with the self purification of bulk water and exerts an adverse effect on the microbiological treatment of waste water. Too much Copper in water has also been found to damage marine life.

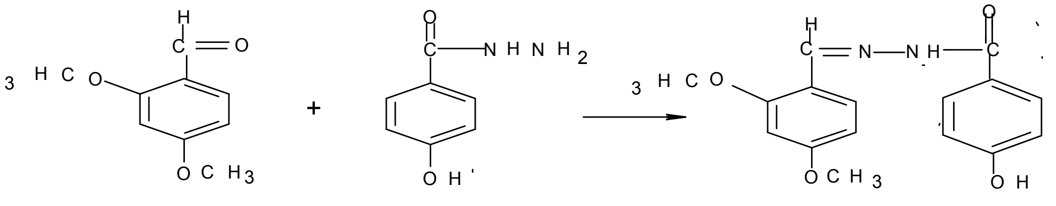
EXPERIMENTAL PART

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy was 0.5 nm with automatic wavelength correction and the recorder was a computer controlled thermal graphic printer with a cathode ray tube and one degree of freedom in the wavelength range 300 – 800 nm.

Reagents

Preparation of 2,4-Dimethoxybenzaldehyde-4-ydroxybenzoylhydrazone

The reagent DMBHBH is prepared by the Sah and Daniels[2] procedure. 1.6617 gm of 2,4-Dimethoxybenzaldehyde (I) and 1.5215 gm of 4-hydroxy benzhydrazide (II) were dissolved in sufficient volume of methanol and the mixture is refluxed for 4 hours. The contents are allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{16}0_4N_2$). The resultant product is recrystallised twice from hot methanol. Pure light greenish crystals of 2,4-dimethoxybenzaldehyde-4-hydroxy benzoylhydrazone (DMBHBH) (III) (m.p. 234-236^{oC}.) were obtained. IR and NMR spectral studies characterized the compound. The mass spectrum shows that molecular ion peak at m/z 300 (M+ 1). The structure of DMBHBH was confirmed based upon IR, NMR and mass spectral data.



I (2,4-Dimethoxybenzaldehyde) II (4-Hydroxy benzhydrazide) III (DMBHBH)

Fig:1 Structure of 2,4-Dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone

For the spectrophotometric determination of Copper (II) an aliquot of the solution containing 0.1588-1.9063 µg/mL of Copper (II), 3.0 mL of buffer solution pH 10.0, 0.5 mL of 5% CTAB and 0.5 mL of 5×10^{-3} M DMBHBH reagent solution were taken in a 10-mL volumetric flask and the solution was diluted up to the mark with doubly distilled Water. The absorbance was read at λ_{max} 384 nm in a 1.0 cm cell against reagent blank prepared in the same way. The measured absorbance was used to compute the amount of Copper (II) from the predetermined calibration curve. The first-order derivative spectra were recorded with scan speed fast having a degree of freedom 9, in the wavelength range from 350-700 nm. The derivative peak height was measured by peak-zero method at λ_{max} 440 nm. The peak height was plotted against the amount of Copper (II) to obtain the calibration curve. The second order derivative spectrum of Copper (II)-DMBHBH system was recorded with reference to the reagent blank in a wavelength range 350–700 nm. In the second order derivative spectrum peak height (h) λ_{max} 455 nm was measured from the zero line of spectrum. Calibration plots were constructed by plotting the derivative amplitude against the amounts of Copper (II).

RESULTS AND DISCUSSION

The reagent 2,4-Dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone (DMBHBH) was easily synthesized as any other Schiff base reagent. The new chromogenic reagent DMBHBH was used for the spectrophotometric method for determination of the Cu (II). The absorption spectra of DMBHBH and its Copper (II) complex under the optimum conditions are shown in Figure2.The Copper (II)-DMBHBH complex shows the maximum absorbance at 384 nm, where the reagent blank does not absorb appreciably.

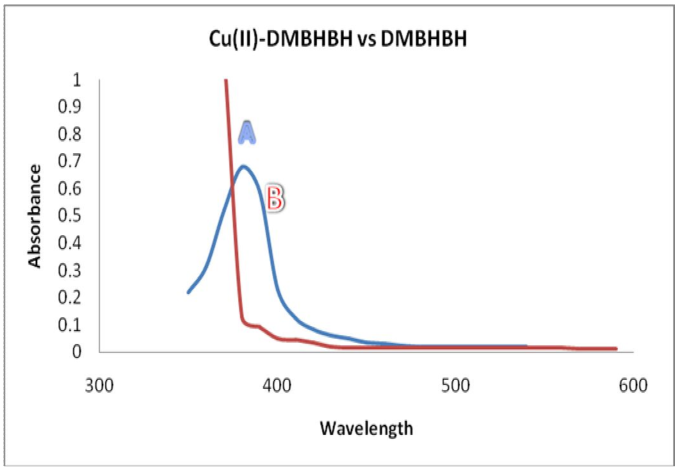


Fig: 2. Zero order Absorption spectra

Reagent (DMBHBH) vs water blank, (B).[Cu (II)-DMBHBH] Complex, Cu (II) 0.5 mL of 5×10^{-4} M, DMBHBH 0.5 mL of 5×10^{-3} M, CTAB (5%) 0.5 ml, pH 10.0 buffer 3.0 mL in a total volume of 10 mL.

Copper (II) reacts with DMBHBH in basic buffer to give orange coloured water-soluble Complex. The colour reaction between Copper (II) and DMBHBH was instantaneous even at room temperature in pH range 9.0-11.0, the maximum colour intensity was observed at pH 10.0 in presence of cationic surfactant CTAB (5%). A slow decrease in absorbance was observed for the coloured complex after 10 min. Adding cationic surfactant CTAB (5%) increased the stability of the complex. The absorbance of Copper (II)-DMBHBH remains constant for more than 24 hours in presence of micellar medium. The effect of various surfactants such as Triton X-100 (5%), sodium dodecyl benzene sulphonate (SDBS) and Cetyl trimethyl ammonium bromide (CTAB) on the absorption profiles of the system has been investigated and presented in Table 2. In presence of CTAB (5%) the complex is more stable and exhibited maximum absorbance, hence CTAB (5%) has been selected for further studies.

Table: 1. Influence of different surfactants on the Copper (II)-DMBHBH complex

Surfactant	Type	Absorbance at 384 nm
None		0.428
Triton X-100 (5%)	Neutral	0.653
CTAB (5%)	Cationic	0.889
SDBS (5%)	Anionic	0.515

Condition: Copper (II) 0.5 mL of 5×10^{-4} M; DMBHBH 0.5 mL of 5×10^{-3} M; CTAB (5%) 0.5 mL, buffer 3.0 mL of pH 10.0 in a total volume of 10 mL.

When varying amounts of 5 % CTAB solution from 0.5 mL to 4.0 mL, the constant absorbance was obtained from 0.5 mL. The absorbance remains constant up to 4.0mL of CTAB(5%).Hence 0.5 mL of 5% CTAB was sufficient in all analytical studies. CTAB (5%) serves to stabilize and sensitize the metal complex. Similarly, when varying the volume of reagent DMBHBH (5×10^{-3} M) from 0.5 mL to 4.0 mL, the constant absorbance was obtained from 0.5 mL. Therefore 10-fold molar excess of reagent is adequate for full colour development. The excess of reagent has no adverse effect on the absorbance of the complex. The order of addition of buffer solution, metal ion, CTAB (5%) and reagent has no adverse effect on the absorbance of Copper (II)-DMBHBH complex. Beer's law was obeyed in the range 0.1588-1.9063 µg/mL. The optimum concentration range of Copper (II)-DMBHBH complex was 0.3177-1.5886 µg/mL. The molar absorpitivity and Sandell's sensitivity of Copper (II)-DMBHBH complex was obtained from the Beer's law. The linear regression analysis of absorbance at λ_{max} of the complex against metal ion (µg/mL) shows a good linear fit. The various important analytical characteristics of Copper (II) and DMBHBH complex are summarized in Table 2.

The stoichiometry of the complex was found to be 1: 1 (metal: ligand) investigated by job's continuous variation method and molar ratio method, with a stability constant 1.1502 x10^5.The effect of various diverse ions in the determination of of 0.794 µg/mL 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 4. The data obtained in the derivative method is also incorporated. The data suggest that several associated anions and cations do not interfere when they are present in large excess, such as iodide, nitrate, thiocyanide, and bromide, Strontium (I), Selenium (II) barium (III), Strontium (V) and Tungsten (VI). The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as iron (III) and copper (II) is decreased by adding masking agent phosphate.

Table:2.Physico-chemical and analytical characteristics of Cu(II)-DMBHBH complex

Characteristics	Results
λmax	384 nm
pH range	9.0-11.0
Optimum pH range	9.0-10.0
Mole of reagent required per mole of metal ion for full colour development	10 (folds)
Molar absorptivity (L.mol^{-1}cm^{-1})	3.8 x 10^4
Sandal's sensitivity (µg/cm^2)	0.00585
Beer's law validity range (µg/ml)	0.1588-1.9063
Optimum concentration range (µg/ml)	0.3177-1.5886
Composition of complex (M: L) obtained in Job's and molar ratio method	1:1
Stability constant of the complex	1.1502 x10^5
Standard deviation in the determination of 0.317µg/ml of Copper (II) for ten determinations.	0.003
Relative standard deviation (%)	3.5
Regression coefficient	0.999

a $y = a \pm bx$ Where y, absorbance / peakhight / trough depth; a, slope; x, analyte concentration; c, intercept. The first order and second order derivative spectral graphs shown in Figure.3 and 4 respectively. This shows that, the derivative amplitudes measured at λ_{max} 440 nm for first order and 455 nm for second order were found to be proportional to the amount of Copper (II).

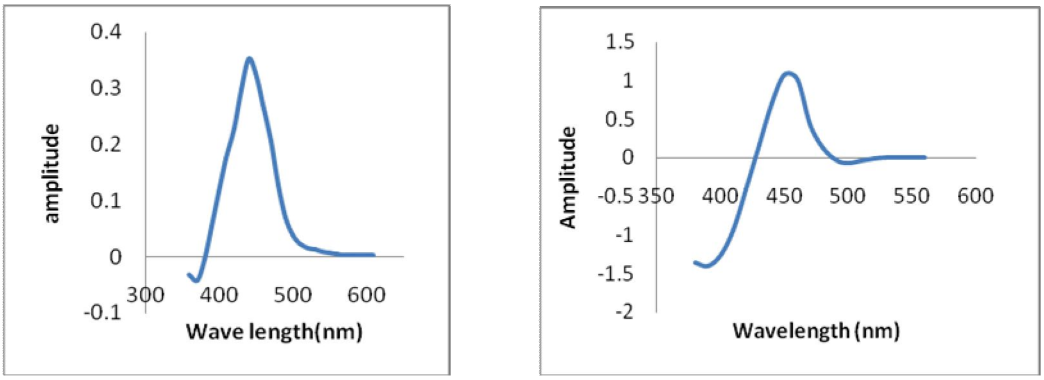


Fig: 3. First derivative spectrum **Second derivative spectrum**

[Cu(II)] = 5 x 10^{-5} M
[DMBHBH] = 5 x 10^{-3} M
pH = 10.0
CTAB (5%) = 0.5 ml

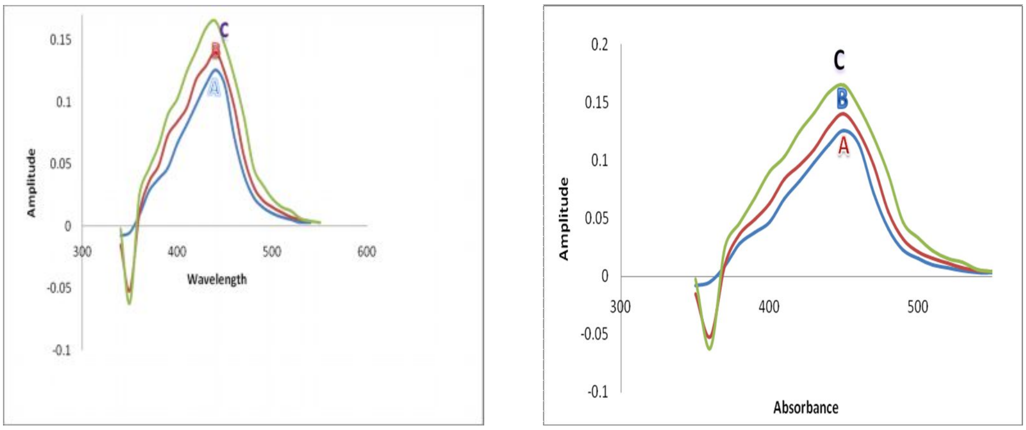


Fig: 4. First order derivative spectrum **Second order derivative spectrum**

Cu (II) (0.5-5.0 mL) of 5×10^{-5} M; DMBHBH 0.5 mL of 5×10^{-3} M; CTAB (5%) 0.5 mL, buffer 3.0 mL of pH 10.0 in a total volume of 10 mL

(A) 0.635µg/ml (B) 0.953 µg/ml (C) 1.27 µg/ml

APPLICATIONS

(a) Determination of Copper (II) in Grape Leaves

The extract of the leaf sample was obtained from Andhra Pradesh Agricultural Research Institute (APARI) Hyderabad.The sample solution was prepared following the proceduredescribed 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 tomask iron(II). The suitable aliquots of sample were analyzed and the results obtained are presented in Table-5.

Table: 3.Tolerance limit of foreign ions in the determination of 0.794 µg/ml of Copper (II)

Ion Added	Tolerance Limit(µg/ml) (Zero order) λmax 384 nm	Tolerance Limit(µg/ml) (D1) λmax 440 nm	Tolerance Limit(µg/ml) (D2)λmax 455 nm
Iodide	1635	1910	1910
Urea	424	540	590
Thiocyanide	581	697	697
Bromide	719	860	860
Thiourea	685	761	761
Nitrate	620	744	744
Tetra borate	1474	1524	1524
Acetate	590	697	697
Phosphate	664	664	664
Chloride	355	426	426
Tartarate	1000	1125	1250
Citrate	1892	2081	2081
Fluoride	284	322	341
Thiosulphate	897	920	970
Na^{+}	460	575	585
Sn^{+2}	59.35	94.96	118.71
Al^{+3}	8.09	13.49	16.18
Ba^{+2}	137.33	164.79	205.99
Mo^{+6}	47.97	55.56	67.15
La^{+3}	166.68	208	208
Sr^{+2}	43.81	52.57	70.09
Se^{+4}	39.48	55.27	63.16
Bi^{+3}	104	146.28	188.08
Ti^{+4}	3.0	3.0	3.0
Li^{+2}	5.0	6.0	6.0
Ce^{+4}	42.03	56.04	70.06
Fe^{+3} *	1.67	2.72	3.35
Zr^{+4}	9.12	18.24	18.24
Pd^{+2}	3.19	5.32	5.32

*Masked by phosphate 712 µg/ml.

Table: 4. Determination of Copper (II) in Grape Leaves

Amount of Copper (µg ml^{-1})					
Sample	Certified value µg/ml	Present Method			
		Direct Method*	Relative Error (%)	Derivative Method*	Relative Error (%)
Grape leaves	55.40	54.8	-1.08	55.7	+0.54
	83.10	83.38	+0.33	82.85	-0.3

*Average of best three determinations among five determinations

(b) Determination of Cu(II) in alloy sample:

Alloy material (0.25 g) was dissolved in concentrated HCl (15 ml) by warming. A little concentrated nitric acid (1 ml) was added and slowly evaporated to dryness. The residue was dissolved in 10 ml of 1M HCl and the resulting solution was concentrated to ca. 5 ml, diluted to ca. 50 ml with distilled water, filtered and made up to 100 ml. Suitable aliquots of the sample were analyzes for the determination of copper (II) by following the recommended procedure.

A suitable aliquot of the sample solution was taken in a 10 ml standard flask containing 3 ml of buffer of pH 10.0 and 0.5 ml of (5x10^{-3} M) DMBHBH solution. The contents were diluted to 10 ml with distilled water and its absorbance was measured at λmax 384 nm against the reagent blank. The absorbance values were referred to the pre-determined calibration plot to compute the amount of Copper (II) present. The results are presented in table.

Table: 5. Determination of Copper (II) in Alloy samples

Alloy Sample	Amount of Copper (II) %		
	Certified Value	Present Method*	Error %
BCS 179/3a(High tension brass)	58.50	58.54	+0.07
BCS 180/2b	68.12	68.09	-0.04
Tin base white metalc	4.58	4.55	-0.65

*Average of five determinations.

(c) Extraction of Copper(II) from biological materials

50 grams of the biological materials was heated in 500 ml conical flasks with 40 ml of concentrated Nitric acid on a steam bath and shaken vigorously until a fine emulsion was formed. The heating was continued with the gradual addition of 6% H_2O_2 (40 ml). The aqueous phase was transferred to the beaker. The extraction was repeated twice with further addition of 20ml concentrated HNO_3 and 20 ml of 6% H_2O_2. The combined extract was evaporated to dryness. The residue was dissolved in a minimum amount of dilute HCl and transferred into a 50 ml standard flask quantitatively. The contents were diluted to the mark with distilled water.

Table: 6. Determination of Copper (II) in biological matter

Biological Sample	Amount of Copper µg/g		
	AAS method	Present method*	Error (%)
Ground nut oil	1.098	1.089	-0.81
Mustard oil	2.251	2.247	-0.17

*Average of five determinations.

Table-7.Comparison of spectrophotometric methods for the determination of Copper (II)

Name of the Chromogenic Reagent	λmax (nm)	pH	Molar absorptivity (L.mol^{-1} cm^{-})x10^{3}	Beer's law Range	Reference
8-Methoxy-2-chloroquinoline-3-carbaldehyde thiosemicarbazone	410	5.0	2.67 x 10^{3}	Up to 3 ppm	4
2,4-Dihydroxybenzaldehyde isonicotinoylhydrazone	430	2.0	1.65 x 10^{4}	0.063-2.55 µg/ml	6
2-Acetyl-4-phenyl-3-thiosemicarbazone	385	3-6	2.92 x 10^{3}	0.10-0.51 µg/ml	7
N-(2,5-Dimethylphenyl)-p-toluimidoyl phenyl hydrazine	370,	9.25	1.2 x 10^{4}	Upto 20 mg/ml	9
Cetyltrimethyl ammoniumbromide in presence of iodide	650	0.5-3.5	1.064x10^{4}	Upto 10 ppm	10
2-Hydroxy-4-n-butoxyacetophenone oxime	370	8.5	1.77 x 10^{4}	0-8 mg/ml	12
2-(2-(4-Methylbenzo thiozolyl)azo-5-dimethylamino benzoic acid (4-Me-BTAMB)	650	2.0-5.0	3.1 x 10^{4}	0.04-2 µg/ml	14
2,4-Dimethoxybenzaldehyde 4-hydroxybennzoylhydrazone (DMBHBH)	384	10.0	3.8 x 10^{4}	0.158-1.906 µg/ml	Present method

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