

## A comparative Study of Simultaneous Determination of Nickel (II) and Copper (II) using 4-Hydroxy-3,5-Dimethoxy Benzaldehyde-4-hydroxybenzoylhydrazone and Cinnamaldehyde-4-hydroxybenzoylhydrazone by First Order Derivative Spectrophotometric Technique

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### ABSTRACT

4-Hydroxy-3,5-dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone (HDMBHBH) and Cinnamaldehyde-4-hydroxybenzoylhydrazone (CMHBH) are used as chromogenic reagents for Simultaneous spectrophotometric determination of Nickel (II) and Copper (II) ions. The reagents (HDMBHBH & CMHBH) gives intense yellow colour water soluble complexes with Nickel (II) and Copper (II) in presence of micellar medium (Triton-X-100 (5%) at pH 9.0. The maximum absorbance of Nickel (II) and Copper (II) was observed at  $\lambda_{\max}$  408 nm, 383 nm and  $\lambda_{\max}$  400 and 375 nm for HDMBHBH and CMHBH respectively. Beer's law was obeyed in the range 0.058-0.586, 0.063-0.635  $\mu\text{g ml}^{-1}$  and the optimum concentration range from ringbom plot was 0.117-0.528, 0.127-0.571  $\mu\text{g/ml}$  for Ni (II)&Cu (II)-HDMBHBH and 0.146-1.467, 0.158-1.588  $\mu\text{g ml}^{-1}$  and 0.293-1.320, 0.317-1.429 for Ni(II)&Cu (II)-CMHBH. The molar absorptivity and sandell's sensitivity of Nickel (II) and Copper (II) complexes are found to be  $3.22 \times 10^4$ ,  $3.41 \times 10^4 \text{ L.mol}^{-1}\text{.cm}^{-1}$  and 0.0018, 0.0018  $\mu\text{g/cm}^2$  and  $2.17 \times 10^4$ ,  $2.77 \times 10^4 \text{ L.mol}^{-1}\text{.cm}^{-1}$  and 0.0027, 0.0022  $\mu\text{g/cm}^2$  for HDMBHBH and CMHBH respectively. The reagents (HDMBHBH & CMHBH) forms 1:1 [M:L] complexes with Nickel (II) and Copper (II) with stability constants  $5 \times 10^6$ ,  $14.12 \times 10^6$  and  $8.17 \times 10^5$  and  $10.10 \times 10^6$  for HDMBHBH & CMHBH respectively. The standard deviation for ten determination of Ni (II) &Cu (II) are found to be 0.003, 0.006 for HDMBHBH and 0.002, 0.004 for CMHBH. The Relative standard deviation for Ni (II) &Cu (II) are found to be 2.17, 2.05% HDMBHBH and 2.33, 2.27% for CMHBH. The First order derivative spectrophotometric technique has been developed for the simultaneous determination of Nickel (II) and Copper (II) at  $\lambda_{\max}$  450 and 405 nm and  $\lambda_{\max}$  460 and 410 nm for HDMBHBH & CMHBH in synthetic mixtures, alloy samples and edible oils.

**Keywords:** Copper (II), Nickel (II), 4-Hydroxy-3, 5-dimethoxy benzaldehyde-4-hydroxybenzoylhydrazone.

### INTRODUCTION

Hydrazones are important organic analytical reagents for the spectrophotometric determination of metal ions in microgram quantities. They react with metal ions forming colour complexes and act as chelating agents. The potential applications of hydrazone derivatives for the spectrophotometric determination of metal ions have been reviewed by Singh et.al<sup>1</sup>.

The great interest towards derivative spectrophotometry was due to the increased resolution of spectral bands, that means it is resolving two overlapping spectra and eliminating matrix interferences in the assay of two component mixtures using zero-crossing technique.<sup>2-3</sup> In the absence of zero-crossing point, two simultaneous equations can be solved to determine the components in such a mixture.<sup>4-5</sup> Hydrazone

reagents are widely used in our laboratories for the derivative spectrophotometric determination of metal ions<sup>5-8</sup>. Derivative spectrophotometric analysis of two-component mixtures was also carried out without need to solve simultaneous equations<sup>6-8</sup>. In the light of good analytical characteristics of hydrazones, here in we report the simultaneous first order derivative spectrophotometric determination of Nickel (II) and Copper (II) using 4-Hydroxy-3, 5-dimethoxy benzaldehyde 4-hydroxybenzoylhydrazone (HDMBHBH) and Cinnamaldehyde-4-hydroxybenzoylhydrazone (CMHBH). The proposed simultaneous method involves the use of peak-to-base line measurement technique.

## EXPERIMENTAL

### MATERIALS & METHODS

#### Apparatus

Shimadzu 16A microcomputer based U.V-Visible spectrophotometer equipped with 1.0 cm quartz cells used for all absorbance studies and amplitude measurements in derivative spectrophotometry. An ELICO LI-120 digital pH meter was used in pH adjustments.

#### Recommended procedure for Simultaneous determination of Nickel (II) and Copper (II)

For simultaneous determination of Nickel (II) and Copper (II), a solution containing both Nickel (II) and Copper (II) in the optimum concentration range 0.117-0.528  $\mu\text{g/mL}$ , 0.127-0.571 and 0.293-1.320  $\mu\text{g/mL}$ , and 0.317-1.429 are used. The absorption spectra indicates that Nickel (II) and Copper (II) complexes shows maximum amplitude in derivative spectrophotometric technique at  $\lambda_{\text{max}}$  450, 405 nm and  $\lambda_{\text{max}}$  460, 410 nm for HDMBHBH and CMHBH respectively. Calibration curves are prepared between amplitude and amount of metal ion at their respective wavelength. The amount of metal ion [Ni (II) or Cu (II)] was calculated from calibration graphs.

At  $\lambda_{\text{max}}$  415 and 420 nm Ni (II) complexes have a zero crossing point for HDMBHBH and CMHBH respectively, which was independent of the metal ion concentration and at this wavelength Copper (II), has appreciable amplitude shown in Fig.2&3. Hence, simultaneous first order derivative spectrophotometric determination of Ni (II) and Cu (II) has been carried out by measuring peak-base line technique at  $\lambda_{\text{max}}$  450, 405 and 460, 410 nm for HDMBHBH and CMHBH respectively without employing the simultaneous equations. Calibration plots are constructed at  $\lambda_{\text{max}}$  450 and 405 nm and  $\lambda_{\text{max}}$  460 and 410 nm for HDMBHBH and CMHBH respectively by plotting the derivative amplitudes against the corresponding amounts of Ni (II) and Cu (II)

respectively. The plots thus obtained are linear obeying the relationship.

Ni (II) & Cu (II)-HDMBHBH

Ni (II)  $A_{450 \text{ nm}} = 0.45459C - 0.02242$

Cu (II)  $A_{405 \text{ nm}} = 0.42385C - 0.02152$

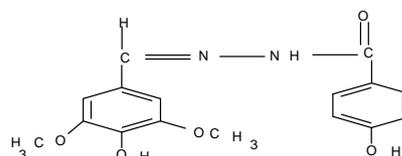
Ni (II) & Cu (II)-CMHBH

Ni (II)  $A_{460 \text{ nm}} = 0.23522C - 0.02563$

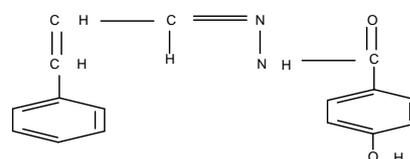
Cu (II)  $A_{410 \text{ nm}} = 0.29136C - 0.04629$

## RESULTS AND DISCUSSION

4-Hydroxy-3,5-dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazoe (CMHBH) are novel type of reagents. These reagents are easily synthesized as any other Schiff base. Aldehyde-4-hydroxybenzoylhydrazone reagents are not exploited much for spectrophotometric determination of metal ions. Moreover, the derivative methods using this class of reagents are scare.



Structure of HDMBHBH



Structure of CMHBH

## INTERFERENCE

The effect of foreign ions was studied to know the selectivity of the derivative methods. The amount of foreign ions, which brings about change in amplitude by  $\pm 2\%$ , was taken as the tolerance. The data obtained in derivative method was also incorporated. In order to assess the analytical potential of the proposed methods, the effects of some diverse ions which often accompany Nickel (II) & Copper (II) are examined by carrying out the determination of 0.293, 0.317  $\mu\text{g/mL}$  for HDMBHBH and 0.733, 0.794  $\mu\text{g/mL}$  for CMHBH respectively. It is noticed that all the ions that do not interfere in the zero-order determination of metal ions also do not interfere in the first derivative analysis. The tolerance limit values, for many anions and cations are higher in the first order derivative methods than those in the zero-order determination of metal ions. The interference

of associated metal ion such as Fe (III) was decreased by adding the masking agent fluoride.

### CONCLUSIONS

The present method, using SA as spectrophotometric reagent for the simultaneous determination of Ni (II) and Cu (II) in presence of Triton X-100 is simple, rapid, reasonably sensitive and selective. The present method is not laborious and there is no need of heating the components or pre-extraction. Some factors such as initial cost of instrument, technical know-how, consumable and costly maintenance of technique restrict the wider applicability of these techniques, particularly in laboratories with limited budget in developing countries and for fieldwork are to be taken as the consideration for the determination of Copper and Nickel at microgram quantities, a number of hydrazone derivatives and several analytical techniques such as AAS, ICP-AES, ICP, X-Ray fluorescence spectroscopy and UV-visible spectrophotometry are employed. Among them

spectrophotometric methods are preferred because they are cheaper and easy to handle. In general the technique of solvent extraction was widely used in the spectrophotometric determination of metal ions. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. Large amounts bromide; iodide, tartarate and nitrate do not interfere in the present method. This method was also free from the interference of strontium, arsenic, tungsten, lanthanum and other rare earth metals. Triton X-100 enhances the stability of the metal complexes. Further, the simultaneous determination of Ni (II) and Cu (II) carried out without the need of employing the simultaneous equation.

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### Applications

**Table 4: Determination of Ni (II) and Cu (II) in Alloy samples**

Alloy sample	Certified (%)		HDMBHBH				CMHBH			
			Amount found (%)		Error (%)		Amount found (%)		Error (%)	
	Ni (II)	Cu (II)	Ni (II)	Cu (II)	Ni (II)	Cu (II)	Ni (II)	Cu (II)	Ni (II)	Cu (II)
Monel 400	31.00	63.00	30.77	62.56	+0.74	+0.69	30.85	62.67	+0.48	+0.52
Cu-Ni; BAS 180/2	68.12	30.35	67.89	30.24	+0.33	+0.36	67.98	30.18	+0.20	+0.56
Al alloy	4.10	1.93	4.04	1.89	+1.46	+2.07	4.02	3.98	+1.95	+2.92

**Table 3: Simultaneous determination of Ni (II) and Cu (II) in Synthetic mixtures**

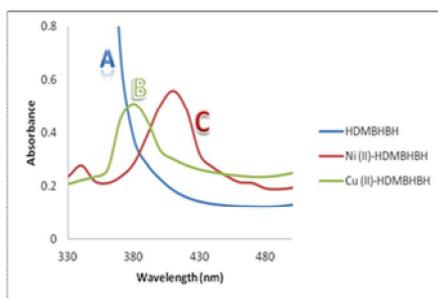
Amount taken ( $\mu\text{g/mL}$ )		HDMBHBH				CMHBH			
		Amount found ( $\mu\text{g/mL}$ )		Error (%)		Amount found ( $\mu\text{g/mL}$ )		Error (%)	
Ni (II)	Cu (II)	Ni (II)	Cu (II)	Ni (II)	Cu (II)	Ni (II)	Cu (II)	Ni (II)	Cu (II)
0.5869	0.6355	0.5763	0.6348	+ 1.80	+0.11	0.5792	0.6336	+1.31	+0.29
0.7043	0.6355	0.7034	0.6343	+0.12	+0.18	0.7028	0.6334	+0.21	+0.17
0.9391	0.6355	0.9364	0.6355	+ 0.28	0.00	0.9382	0.6352	+0.09	+0.04
1.1739	0.6355	1.1774	0.6609	- 0.29	- 3.84	1.1728	0.6339	+0.09	+0.25
0.7043	0.7626	0.7010	0.7622	+ 0.36	0.050	0.7034	0.7618	+0.12	+0.10
0.7043	0.8896	0.6809	0.8887	+3.32	+0.10	0.6889	0.8899	+0.12	-0.03
0.7043	1.0167	0.6874	0.9994	+ 2.39	+ 1.70	0.6878	0.9984	+2.76	+1.79
0.7043	1.1438	0.6809	1.1384	+ 3.32	+ 0.47	0.6869	1.1394	+2.47	+0.38
0.7043	1.2709	0.6869	1.2502	+ 2.47	+ 1.68	0.6899	1.2542	+2.04	+1.31

**Table 5: Determination of Ni (II) and Cu (II) in Edible oils**

Oil sample	AAS method		HDMBHBH				CMHBH			
	Ni (II)	Cu (II)	Present method <sup>a</sup>		Recovery (%)		Present method <sup>a</sup>		Recovery (%)	
			Ni (II)	Cu (II)	Ni (II)	Cu (II)	Ni (II)	Cu (II)	Ni (II)	Cu (II)
Groundnut oil	0.07	4.46	0.067	4.44	95.71	99.55	0.065	4.39	92.85	98.43
Sunflower oil	0.08	0.68	0.078	0.65	97.50	95.50	0.075	0.63	93.75	92.64
Vegetable oil (hydrogenated)	0.13	0.04	0.128	0.038	98.46	95.50	0.122	0.035	93.84	90.0

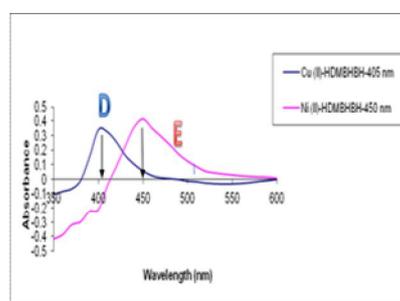
<sup>a</sup> Average of best three among five determinations.

<sup>a</sup> standard addition method (1.0  $\mu\text{g/mL}$  each of Ni (II) and Cu (II) added to the sample).



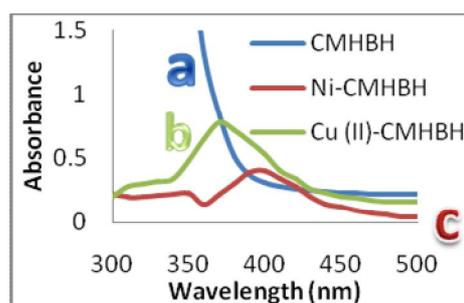
**Fig. 1: Zero order Absorption Spectra Simultaneous D<sub>1</sub> Spectra**

(a) HDMBHBH Vs water blank,  
 (b) Ni (II)-HDMBHBH Vs Reagent blank  
 (c) Cu (II)-HDMBHBH Vs Reagent blank.  
 Ni (II) & Cu (II) =  $1 \times 10^{-5}$ ,  
 pH = 9.0



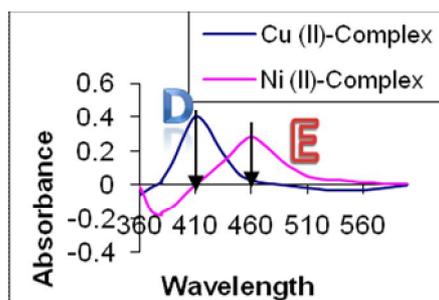
**Fig. 2: Simultaneous D<sub>1</sub> Spectra**

(D) Cu (II)-HDMBHBH  
 (E) Ni (II)-HDMBHBH  
 [ HDMBHBH ] =  $2 \times 10^{-3}$  M,  
 Triton X-100 (5%) = 0.5 mL



**Fig. 3: Zero order Absorption Spectra**

(a) CMHBH Vs water blank  
 (b) Ni (II)-CMHBH Vs Reagent blank  
 (c) Cu (II)-CMHBH Vs Reagent blank  
 Ni (II) & Cu (II) =  $2.5 \times 10^{-5}$ ,  
 pH = 9.0



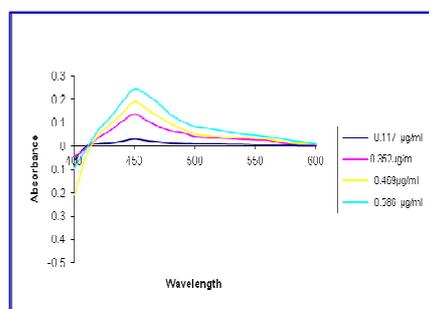
**Fig.4: Simultaneous D<sub>1</sub> Spectra**

(D) Cu (II)-CMHBH

(E) Ni (II)-CMHBH

[CMHBH] =  $5 \times 10^{-3}$  M

Triton X-100 (5%) = 1.0 mL



**Fig. 5: Typical D<sub>1</sub> spectra of**

Ni (II)-HDMBHBH

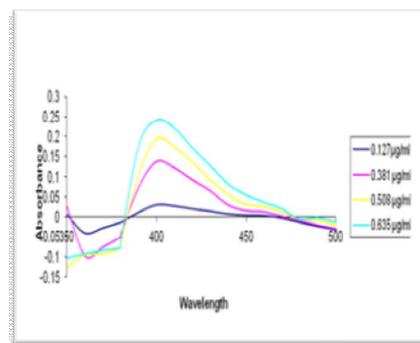
[Ni (II)] =  $1 \times 10^{-6}$

[HDMBHBH] =  $2 \times 10^{-3}$

pH = 9.0

Triton-X-100 (5%) = 0.5 mL

$\lambda_{\max}$  = 450 nm



**Fig.6: Typical D<sub>1</sub> spectra of**

Cu (II)-HDMBHBH

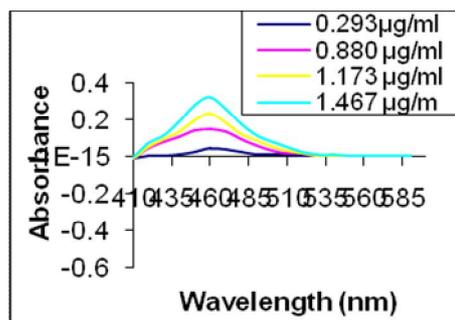
[Cu (II)] =  $1 \times 10^{-6}$

[HDMBHBH] =  $2 \times 10^{-3}$

pH = 9.0

Triton-X-100 (5%) = 0.5 mL

$\lambda_{\max}$  = 405 nm



**Fig. 7: Typical D<sub>1</sub> spectra of**

Ni (II)-CMHBH

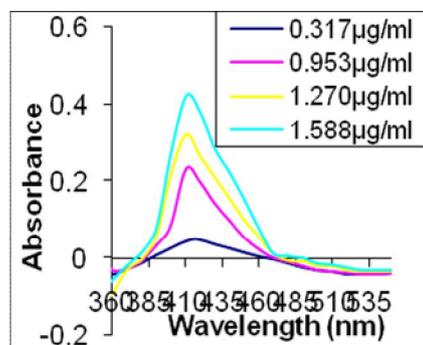
[Ni (II)] =  $2.5 \times 10^{-6}$

[CMHBH] =  $5 \times 10^{-3}$

pH = 9.0

Triton-X-100 (5%) = 1.0 mL

$\lambda_{\max}$  = 460 nm



**Fig. 8: Typical D<sub>1</sub> spectra of**

Cu (II)-CMHBH

[Cu (II)] =  $2.5 \times 10^{-6}$

[CMHBH] =  $5 \times 10^{-3}$

pH = 9.0

Triton-X-100 (5%) = 1.0 mL

$\lambda_{\max}$  = 410 nm

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