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DIRECT AND DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) AND NICKEL(II) IN BEER, WINE AND EDIBLE OILS

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ABSTRACT

Derivative spectrophotometric determination of copper(II) and nickel(II) based on the formation of their complexes with Diacetylmonoxime-4-hydroxybenzoylhydrazone (DM-4-HBH) reagent has been proposed. Direct and derivative method has been developed for the spectrophotometric determination of micro quantity of Cu(II) and Ni(II) in basic medium. The reagent gives yellowish green and light green coloured complex in pH 10.5 and 9.0 respectively. The maximum absorbance measured at λ_{max} 396 nm and λ_{max} 380 nm for copper(II) and nickel(II) complexes. The molar absorpitivity and sandell's sensitivity are 1.8 x 10^4, 2 x 10^4 L.mol^{-1}.cm^{-1} and 0.0035, 0.0029 µg.cm^{-2} respectively. Copper(II) and nickel(II) forms (M:L) 1:1 complex and stability constant of the complexes are 4.2 x 10^6 and 7.5 x 10^5 respectively. The derivative amplitude was measured at λ_{max} 433 nm and 404 nm respectively. The developed method was applied for the determination of Cu(II) in Beer, Wine and Ni(II) in edible oil samples.

KEYWORDS

Diacetylmonoxime-4-hydroxybenzoylhydrazone (DM-4HBH), derivative Spectrophotometry, Copper(II), Nickel(II) determination.

INTRODUCTION

Oximes and hydrazones are two different classes of chromogenic reagents widely used for the derivative spectrophotometric determination of metal ions. The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al[1]. In the light of analytical potentialities of oximes and hydrazones, here in we report the analytical properties of reagents containing both functionalities viz. oximes and hydrazones. Diacetylmonoxime-4-hydroxybenzoylhydrazone (DM-4-HBH) reagent was synthesized and employed for the spectrophotometric determination of copper(II) and nickel(II) in Beer, wine and edible oils. Derivative Spectrophotometry is a very useful technique, in the sense that, it decrease the interference i.e. increase the tolerance limit value of the foreign ions. The great interest towards derivative spectrophotometry is due to the increased resolution of spectral bands, allowing the detection and location of the wavelengths of poorly resolved components of complex spectra and reducing the effect of spectral background interferences. Because of these characteristics, the process of isolation and pre-concentration of active components, usually required in qualitative and quantitative spectrophotometric procedures applied in the analysis of complex systems, is completely avoided. However reagents containing two functional groups are not exploited much in the derivative spectrophotometric methods for the determination of metal ions[2-4].

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In this paper a derivative spectrophotometric method is described for the determination of Cu(II) in Beer, Wine and Ni(II) in edible oil samples.

MATERIAL AND METHODS

Apparatus

A Shimadzu 160A microcomputer based UV-Vis Spectrophotometer equipped with 1.0 cm quartz cells was used for all spectral measurements. The instrumental parameters were optimized and the best results were obtained with a scan speed 145 nm/min., slit width of 1nm and $\Delta\lambda$ = 2nm for the first order derivative mode in the wavelength range 350-650 nm. ELICO LI-120 digital pH meter was used for pH adjustments.

Reagents

All reagents used were of A.R grade unless otherwise stated. All solutions were prepared with distilled water. The standard copper(II) and nickel(II) solutions (1x 10^{-2} M) were prepared by using analytical reagent grade $NiSO_4.7H_2O$ (BDH) and $CuSO_4.5H_2O$ (GR MERCK) respectively. The stock solutions of copper(II) and nickel(II) were prepared separately in distilled water and standardized[5].

Synthesis and characterization of DM-4-HBH

Diacetylmonoxime-4-hydroxybenzoylhydrazone was synthesized by refluxing equimolar amounts of diacetylmonoxime and 4-hydroxybenzoylhydrazide in ethanolic medium for 3 h. The resulting hydrazone was recrystalised from ethanol (yield, 73%; mp 306 °C). IR spectrum of reagent recorded in KBr ν, 3300-3320 (OH&NH), 1647 (C=O), 1608, 1580 (C=N), 972 (N-O). ^{1}H-NMR spectrum of reagent recorded in DMSO (300 MHz) δ11.34 (s,1H,oximeOH), 10.48 (s,1H,phenolic OH), 10.08 (s, 1H, NH), 2.27 (s, 6H, 2xCH_3),6.84 (d,J8.4Hz,2H,ArH), 7.76 (d,J8.4Hz, 2H,ArH). Mass spectrum shows molecular ion peak at m/z 236 equal to its molecular weight. The structural formula of DM-4-HBH is given in Figure 1. 0.01 M reagent solution was prepared by dissolving 0.236 g of DM-4-HBH in 100 ml of DMF.

Structure of Diacetylmonoxime-4-Hydroxybenzoylhydrazone

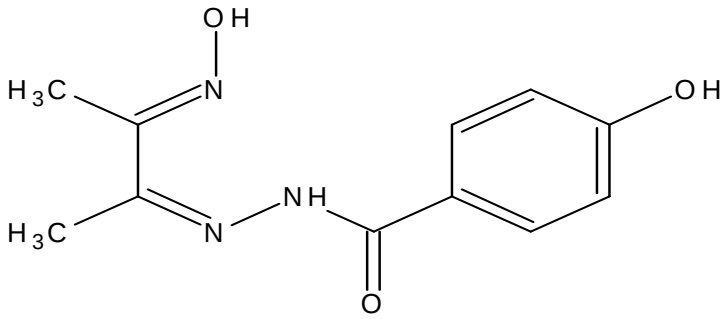

Fig.1

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General procedure (Direct Spectrophotometry)

In each set of 25ml standard flasks, varying amounts of Cu(II) and Ni(II) were taken separately, 10 ml of buffer solution pH 10.5 for Cu(II), pH 9.0 for Ni(II) and I ml of 0.01 M Diacetylmonoxime-4-Hydroxybenzoylhydrazone (DM-4-HBH) reagent were added and the solution was diluted up to the mark with distilled water. The absorbance of the solutions was recorded λ_{max} at 396 nm for copper(II) and 380 nm for nickel(II) against reagent blank. The measured absorbance was used to construct the calibration plot.

First Derivative Spectrophotometry

For the above solution of Cu(II) and Ni(II) complexes with DM-4-HBH first derivative spectrum was recorded with scan speed having degrees of freedom 9 in a wavelength range 350 to 600 nm. Calibration graphs were constructed by plotting the derivative amplitude against the concentrations of Cu(II) and Ni(II). The wavelengths of the spectrum was measured by peak height (h) method at 433 nm for Cu(II) and 404 nm for Ni(II), and a calibration graph was plotted by measuring first derivative amplitudes at the same wavelength of the metals. The amplitude at these wavelengths was proportional to the concentration of Cu(II) and Ni(II) respectively.

RESULTS AND DISCUSSION

Diacetylmonoxime-4-hydroxybenzoyl hydrazone (DM-4-HBH) reagent is easily obtained as any other Schiff base. So far the new DM-4-HBH was not used for the Spectrophotometric determination of Cu(II) and Ni(II). Diacetylmonoxime-4-Hydroxybenzoyl hydrazone (DM-4-HBH) is a blend of two functional group viz. oxime and hydrazone. The reagent solution is stable for 48 h. In basic medium, the ligand presumably co-ordinates the metal ions as di-anion to give a neutral complexes.

Determination of Cu(II) and Ni(II) Using DM-4-HBH

Copper(II) and nickel(II) when reacted with DM-4-HBH gives yellowish green and light green water soluble complexes in basic medium. The colour reactions of these complexes are instantaneous even at room temperature in the pH range 8.5 to 11.0 for Cu(II)–DM-4-HBH and 7.0 –11.0 for Ni(II)–DM-4-HBH. The absorbances of these yellowish green and light green colored species remain constant for more than 2 h. The maximum colour intensity is observed at pH 10.5 and 9.0 for Cu(II) and Ni(II) complexes respectively.

A 5 fold molar excess of reagent is adequate for the development of full colour. Addition of excess of reagent and the order of addition of metal ion, reagent and buffer solution has no adverse effect on the absorbance of the complexes.

The complex formation reactions between Cu(II) and Ni(II) with DM-4-HBH has been studied in detail based on the composition of the complexes as determined by Job's continuous variation method and molar ratio methods. Important analytical parameters of Cu(II) and Ni(II) with DM-4-HBH are summarized in Table 1.

Table 1

Photometric parameters and calibration data for the determination of Cu(II) and Ni(II)

Parameter	Results			
	Cu (II) complex		Ni (II) complex	
	Zero order	First order derivative	Zero order	First order derivative
λ_{Max} (nm)	396	433	380	404

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Detection limit (µg/ml)	0.055	0.043	0.042	0.063
Limit of quantization (µg/ml)	0.163	0.130	0.127	0.189
Regression equation [a]		**y = a+ bx**		
Slope (b)	0.3077	0.1684	0.3591	0.2197
Intercept (a)	0.0422	0.011	0.043	0.0055
Relative standard deviation (%)	0.12	0.42	0.16	1.22
Correlation coefficient	0.99	0.99	0.99	0.99

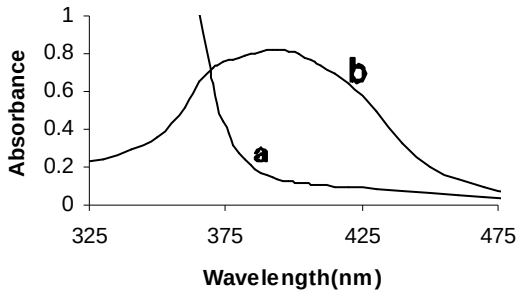
[a] *y = a+ bx*

Where y, absorbance/peak height/through depth; b, slope; a, intercept; x, analyte concentration.

Derivative spectrophotometry is a very useful technique, in the sense that, it decreases the interference i.e. increase the tolerance limit value of the foreign ions and it may be advantageously used for the determination of metal ions having overlapping spectra. The recommended procedure has been employed for the determination of copper(II) and nickel(II).

The Zero and first derivative spectra of Cu(II) and Ni(II) complex of DM-4-HBH are given in Fig. 2. These spectra indicate that the peak amplitude is proportional to the metal ion concentration.

Zero order and first order derivative spectra of Cu(II) and Ni(II) complex of DM-4-HBH



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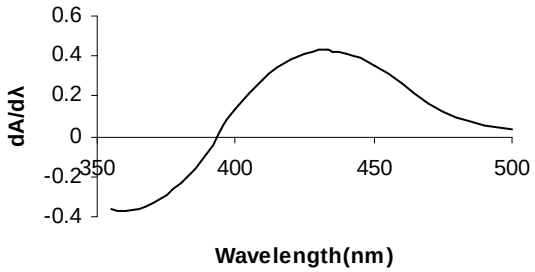

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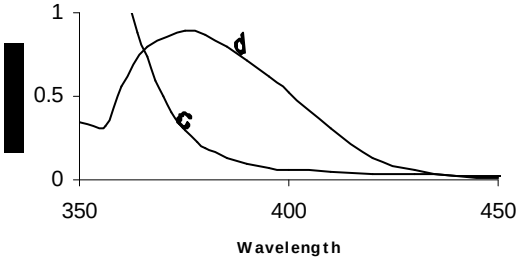

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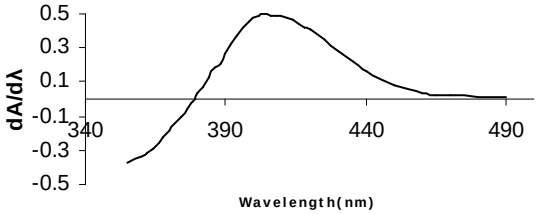

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Fig. 2

i) Zero order Absorption spectra of Cu(II)-DM-4-HBH, (a) Reagent DM-4-HBH Vs Water blank at pH 10.5. (b) Cu(II)-DM-4-HBH Complex reagent Vs Reagent blank at pH 10. ii) First order derivative spectra of Cu(II)-DM-4-HBH reagent Vs Reagent blank at pH 10.5, Cu(II) 4 x 10^{-5} M, DM-4-HBH 4 x 10^{-4} M. iii) Zero order Absorption spectra of Ni(II)-DM-4-HBH, (c) Reagent DM-4-HBH Vs Water blank at pH 9.0. (d) Ni(II)-DM-4-HBH Complex reagent Vs Reagent blank at pH 9.0. iv) First order derivative spectra of Ni(II)-DM-4-HBH Complex reagent Vs Reagent blank at pH 9.0, Ni(II) 4 x 10^{-5} M, DM-4-HBH 4 x 10^{-4} M

Effect of diverse ions

The effect of various diverse ions in the determination of 0.51 µg/ml Cu(II) and 1.17µg/ml Ni(II)were 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 presented in the Table-2.

Table 2

Tolerance limit of foreign ions in the determination of 0.51 µg/ml Cu(II) and 1.17µg/ml Ni(II)

Ion added	Tolerance limit (µg/ml)			
	Cu(II)		Ni(II)	
Direct /derivative	Zero order	First order	Zero order	First order
Iodide	1523	1593	761	771
Tetraborate	1474	1524	246	246
Citrate	1364	1364	379	395
Tartarate	1189	1200	593	593
Phosphate	1140	1140	760	760
Bromide	960	960	639	649
Thiourea	917	935	245	255
Thiosulphate	897	920	1121	1121
Nitrate	744	784	496	496
Thiocyanide	696	696	349	349
Urea	480	487	120	135
Acetate	472	472	236	256
Chloride	425	490	284	294
Fluoride	228	305	152	212
Na^{+}	744	800	496	516
W^{+6}	147	150	59	59
La^{+3}	139	145	45	50
Ba^{+2}	110	120	28	39
Bi^{+3}	100	110	131	141
Sn^{+2}	85	85	47	47
Sr^{+2}	70	90	17	19
Se^{+4}	63	63	16	26
Ce^{+4}	45	45	3.0	7.0
Mo^{+6}	30	35	19	29
Hg^{+2}	16	20	16	25
Al^{+3}	10	15	4.0	4.0

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Li^{+2}	5.0	6.0	1.0	1.0
Pd^{+2}	4.0	50	4.0	4.0
Zr^{+4}	4.0	50	4.0	4.0
Fe^{+3}	3.0†	3.9†	2.0*	2.0*
Ti^{+4}	3.0	3.0	2.0	3.0

†*Masked by phosphate 1140 μg/ml,* **Masked by phosphate 760 μg/ml*

The data suggests that several associated anions and cations such as iodide, phosphate, tartarate, bromide, thiosulphate, nitrate, citrate, W(VI), La(III), Ba(II), Bi(III) and Sn(II) do not interfere when they are present in excess. Further, their tolerance limits for many anions and cations were generally higher in derivative method than those in the zero order determination of Cu(II) and Ni(II).The interference of Fe(III) was decreased by masking with Phosphate.

Applications

i) Determination of Copper in Beer and Wine

A 50 ml of beer or wine sample was taken in separate 250 ml beakers and digested in 5.0 ml of 5.0 M HNO_3 and evaporated to dryness. The residue thus obtained was dissolved and diluted up to the mark in 100-ml volumetric flask with distilled water. The suitable aliquots of sample were analyzed by recommended procedure for the determination of copper(II). The results obtained are presented in Table-3.

Table 3
Determination of copper(II) in Beer and Wine

Sample	Copper(II) (μg/ml)		Error (%)
	Amount taken	Amount found*	
Beer (50ml)	5.32	5.19	+2.4
Wine (50ml)	7.45	7.26	+2.5

**Average of the best three determinations among five determinations*

ii) ***Estimation of Nickel in Edible oils***

Oil sample solutions were prepared by following the procedure given in the literature[6]. A 50 g of the sample was digested in 40 ml of conc. HNO_3, heated on a water bath and shaken vigorously until fine emulsion was formed. The heating was continued with the gradual addition of 40 ml of 6% hydrogen peroxide. The aqueous phase was then transferred in to the beaker with the help of separating funnel. The extraction was repeated thrice with further addition of 20 ml of Conc. HNO_3 and 20 ml of 6% hydrogen peroxide. The extracts were evaporated to dryness. The residue was dissolved in minimum amount of 1.0 M HCl and transferred into a 50-ml volumetric flask and diluted to the mark with distilled water. The suitable aliquots of the above sample were analyzed by recommended procedure for the determination of nickel(II). The results obtained are compared with AAS method and presented in Table 4.

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Table 4
Estimation of nickel(II) in Edible oils

Oil Sample	Amount of nickel(II) (µg/ml) found		Error (%)
	AAS method	Present method*	
Sun flower oil	0.66	0.65	+1.5
Groundnut oil (Hydrogenated)	0.42	0.43	-2.4

**Average of the best three determinations among five determinations*

CONCLUSIONS

The present method using DM-4-HBH as Spectrophotometric reagent for the determination of copper(II) and nickel(II) in aqueous medium is sensitive and simple. These methods were favorably compared with recently reported Spectrophotometric methods[7-10] for Cu(II) and Ni(II) respectively. Most of the Spectrophotometric methods involve the extraction of components. The determination of copper(II) and nickel(II) using DM-4-HBH is not laborious as it does not require the methods of heating or extraction. Further, the reagent is easy to synthesize using available chemicals. Moreover, the present method is simple, rapid, reasonably sensitive and selective for the determination of copper(II) and nickel(II).

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