ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

A Sensitive and Selective Chromogenic Organic Reagent 2, 4-dimethoxy benzaldehyde-4-hydraoxy benzoyl hydrazone (DMBHBH) Using for Direct and Derivative Spectrophotometric Determination of Zinc (II).

C Viswanatha[1]*, Radhakrishna[2], and N Devanna[3].

[1]Department of Chemistry, Arba Minch University, Ethiopia.
[2]Department of Chemistry, MLA College for Women, Bangalore, Karnataka, India.
[3]Department of Chemistry JNTUA, College of Engineering, Kalikiri-517234, Andhra Pradesh, India.

ABSTRACT

2,4-dimethoxy benzaldehyde 4-hydraoxy benzoyl hydrazone (DMBHBH) is used as a novel chromogenic organic reagent for the determination of Zinc (II) with specterophotometry. The novel chromogenic organic reagent 2,4-dimethoxy benzaldehyde-4-hydraoxy benzoyl hydrazone (DMBHBH) forms yellow coloured complexe with Zinc (II). The colour complexe shows maximum absorption at λ_{max} 466 nm.The beer's law validity range is 0.1634 to 1.9614 (µg/ml) and optimum concentration range is 0.3269 to 1.7979 (µg/ml). The molar absorptivity and sandal's sensitivity 4.27 x10^4 L.mol^{-1}.cm^{-1} and 0.0015 µg/cm^2 respectively. The Zinc (II) forms M:L (I:I) colour complexe with DMBHBH and stability constant of the complex was found to be. 5.76 x 10^6. This developed method was applied for the determination of Zinc (II) in pharmaceutical samples and obtained with good results compared with certified reference results.

Keywords: novel chromogenic organic reagent, derivative spectrophotometry, Zn (II) and pharmaceutical samples.

Corresponding author

ISSN: 0975-8585

INTRODUCTION

Zinc is an essential element for all animals including human beings. The main sources of Zinc can be found in many foods in certain amounts such as meat and liver, seafood (especially oysters) cereals and rice, cheeses and nuts. The recommended daily dosage of Zinc for women is 12 mg and for men 15 mg. Women's dose increases to 19 mg for the pregnant or when they are breastfeeding. The symptoms of zinc deficiency lead to skin problems, slow healing of wounds, reduction in the senses of taste and smell, increased susceptibility to infections, decrease of fertility, retardation of children's growth, mental lethargy, loss of appetite and loss of hair. Very high levels of Zinc can damage the pancreas and disturb the protein metabolism. Extensive exposure to zinc chloride can cause respiratory disorders.

Zinc has been used pharmaceutically in creams, ointments, eye drops, mouth washes and others to defeat various types of infection. Zinc compounds have biological active because they precipitate and denature the bacterial proteins. For this reason, it has been used in dermatology as an antiseptic and disinfectant agent in ophthalmic solutions, mouthwashes and mineral-vitamin preparations.

A number of chromogenic organic reagents were reported for the spectrophotometric determination of the Zinc ion. For the determination of Zinc at micro levels there several frequently adopted methods using analytical techniques such as AAS, ICP-AES, X-Ray fluorescence spectroscopy, voltametry, polorography, specteophotometry and other techniques among them, specterphotometric methods are preferred because they are. Low cost instrument and high sensitivity [1-19].

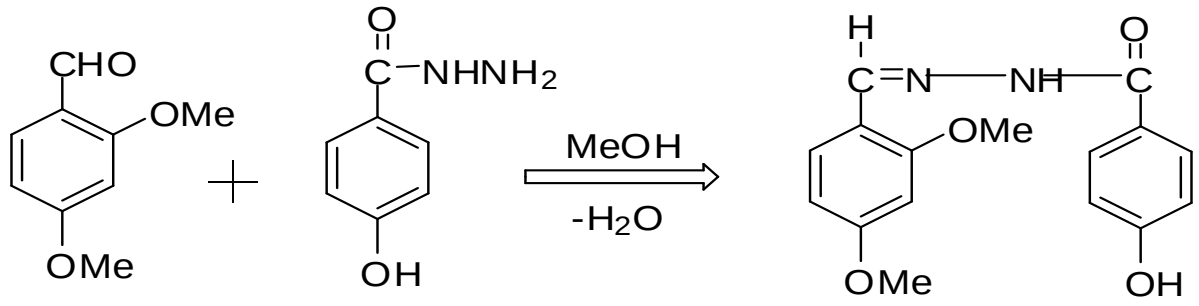
EXPERIMENTAL

Spectrophotometric measurements were made in a shimadzu 160 a microcomputer based UV–Visible spectrophotometer equipped with 1.0 cm quartz cells, an ELICO LI- 120 digital pH meter. All reagents used were of analytical reagent (AR) grade unless otherwise stated. All solutions were prepared with distilled water

REAGENT

Synthesis of 2,4-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (DMBHBH)

2,4-dimethoxy benzaldehyde (1.6617 g, 0.01 mole) dissolved in hot methanol, hot methanolic solution of 4-hydroxybenzhydrazide (1.5215 g, 0.01 mole) were taken in a 250-ml round bottom flask. The contents in flask were refluxed for 3 hours using a water condenser. On cooling the reaction mixture, greenish yellow coloured product was separated out. It was collected by filtration and washed several times with hot water and cold methanol. This compound was recrystallised and dried in vacuum. Yield 80%, m.p. 235^0 C.Fig No 1



Analytical properties of DMBHBH

The reactions of some important metal ions were tested at different pH values The characteristics of the most important metal complexes are summarized in Table:1 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) DMBHBH solutions. The solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 300-800 nm range against reagent blank.

ISSN: 0975-8585

Table 1: Characteristics of DMBHBH complexes in solution

Metal ion	λ_{max} (nm)	pH	Molar absorptivity ($l.mol^{-1}.cm^{-1}$)	Stability constant
Cu(II)	384	10.0	$3.8x10^{4}$	$1.1502x10^{6}$
Mo(VI)	413	3.5-4.5	$3.04x10^{4}$	$1.307x10^{6}$
Pd(II)	389	3.0-5.0	$2.07x10^{4}$	$1.669x10^{6}$
Zn(II)	466	2.0-4.0	$4.27x10^{4}$	$5.76x10^{6}$

Recommended Procedure

Determination of Zinc (II) (zero order)

An aliquot of the solution containing 0.1634 to 1.9614 µg/ml of Zinc (II), 3 ml of buffer solution pH 2.0 to 4.0 and 0.5 ml of ($1x10^{-2}$M) DMBHBH 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 466 nm in a 1.0 cm cell again corresponding reagent blank prepared in the same way but without Zinc (II) metal solution. The absorption spectra of DMBHBH and its Zn (II) complex under the optimum conditions are shown in fig no: 2.The Zn (II)-DMBHBH complex shows the maximum absorbance at 466 nm, where as the reagent blank does not absorb appreciably.

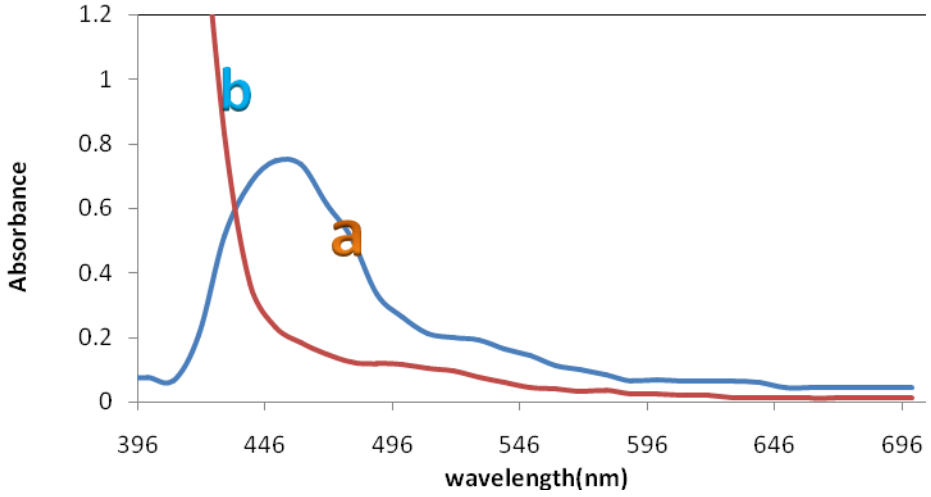


Figure 2: Absorption spectra

(a). [Zn (II)-DMBHBH] complex Vs. reagent blank
(b). DMBHBH Vs. buffer blank.

RESULTS AND DISCUSSION

2,4-dimethoxy benzaldehyde-4–hydroxy benzoyl hydrazone (DMBHBH) reagent is a blend of a carbonyl compound and a hydrazide. The reagent solution is stable for more then 24 hrs. in presence of buffer medium. The ligand presumably coordinates the metal ions to give a neutral water soluble complex.

Determination of Zinc (II) using DMBHBH

Zinc (II) reacts with DMBHBH in acidic medium to give yellow coloured water-soluble complex. The colour reaction between Zinc (II) and DMBHBH are instantaneous even at room temperature in the pH range 2.0 to 4.0 and Triton X-100 (5%) solution The absorbance of the yellow coloured species remains constant for three hours. The maximum colour intensity is observed at pH 3.0. 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 Zinc (II) and DMBHBH has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Important physic-chemical and analytical characteristics of Zinc (II) and DMBHBH are summarized in Table-2.

Table 2: Physico-chemical and analytical characteristics of [Zn (II) – DMBHBH] complex.

Characteristics	Results
Colour	Yellow
λ_{max} (nm)	466
pH range (optimum)	2.0 to 4.0
Mole of reagent required per mole of metal ion for full colour development	10 - folds
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	$4.27x\ 10^4$
Sandal's sensitivity ($\mu g.cm^{-2}$)	0.0015
Beer's law validity range (µg/ml)	0.1634-1.9614
Optimum concentration range (µg/ml)	0.3269-1.7979
Composition of complex (M:L) obtained in Job's and mole ratio method	1: 1
Stability constant of the complex (Jobs method)	$5.76x\ 10^6$
Relative standard deviation (%)	0.01
Regression coefficient	0.996

The first order derivative spectral graph was shown in fig no-3. This shows that the derivative amplitudes measured at 532 nm. First order was found to be proportional to the amount of Zinc (II) respectively.

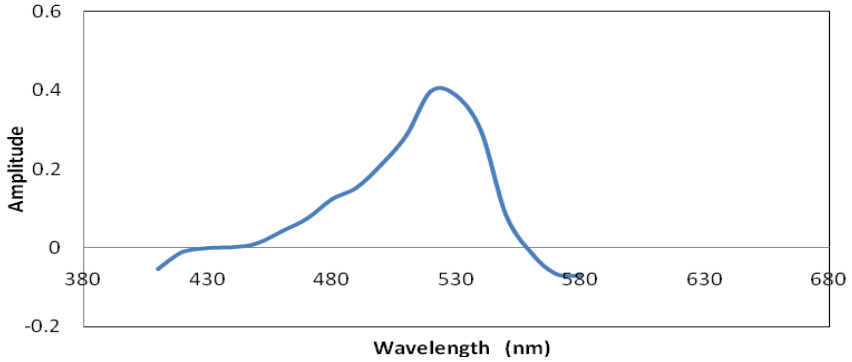


Figure 3: First derivative spectra of [Zn (II)-DMBHBH] Vs reagent

Effect of Foreign Ions

Derivative spectrophotometry is a very useful technique in the sense that it decreases the interference, i.e., increases the tolerance limit value of foreign ions of metal ions having overlapping spectra. The recommended procedures have been employed for the spectrophotometric determination of Zinc (II).The effect of various diverse ions in the determination of Zinc (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.

ISSN: 0975-8585

Table 3: Tolerance limit of foreign ions in the determination Of 0.8127 µg/ml of Zinc (II).

Ion added	Tolerance limit (µg/ml)	Ion added	Tolerance limit (µg/ml)
Bromide	2941	Pb(II)	153
Tetra borate	1061	Sn(II)	71
Iodide	2866	Co(II)	56
Chloride	1219	Ca(II)	67
Nitrate	541	Ni(II)	36
Thiocyanide	658	Ag(I)	18
Oxalate	947	Zr(IV)	56
Sulphate	879	Cd(II)	31
Acetate	633	U(VI)	46
Thiourea	143	Pd(II)	3.67
Phosphate	413	Mo(VI)	5.11
Ascorbic acid	192	As(III)	8.13
Tartarate	185	Sb(III)	7.09
Fluoride	102	Ru(III)	4.33
Ba(II)	256	Al(III)	23
Mn(II)	134	Fe(III) *	1.89*
W(VI)	236	Cr(VI)	4.1
Sr(II)	175	V(V)	3.16

* Masked with 93 µg/ml of fluoride

Applications

Analysis of pharmaceutical sample

The pharmaceutical samples were prepared by destroying organic matter by an established procedure[19] based on the use of perchloric acid. The insulin was treated with 10% m/v chloro acetic acid for the precipitation of proteins. The other samples were previously diluted with doubly distilled water.

The Zinc (II) in this solution was determined by the recommended derivative procedure from a predetermined calibration plot. Results are presented in Table-4.

Table 4: Determination of Zinc (II) in pharmaceutical samples

Sample	Amount of Zn (II)* found (µg/ml)		Error (%)
	AAS method	Present method	
Zingisol (JCPA health products Pvt. Ltd.)	3.99	4.01	0.50
Insulin Zinc Suspension (Knoll Pharma Ltd.)	1.01	1.04	2.97
Biocosules Z (Omni Protech Drugs Ltd.)	3.01	3.03	0.66

*average of best three determinations among five determinations

CONCLUSION

2, 4 - dimethoxy benzaldehyde- 4 – hydroxy benzoyl hydrazone (DMBHBH) has been proven a sensitive and selective chromogenic organic reagent for the determination of Zinc (II). Molar absorptivity of the colour complexe was 4.27×10^4 $L.mole^{-1}.cm^{-1}$. The proposed method was especially sensitive and selective with respect to metals, which commonly seriously interfere with the determination of Zinc performed by literature methods. The proposed method can be successfully applied to the determination of Zinc(II) in pharmaceutical samples. This method was favorably compared with previously reported spectrophotometric[1-20] methods.

ISSN: 0975-8585

ACKNOWLEDGEMENT

The authors are thankful to the Jawaharlal Nehru Technological University, Anantapur, Anthapuramu, A.P, India, for providing research facilities to carryout my present work.

REFERENCES

[1] Krishna Reddy B, Rajesh Kumar J, Subramanyam Sarma L, Andverada Reddy A. Anal Lett 2002;35(8):1415-1427.
[2] Sten Ahriand, Richard G Herman. Anal Chem 1975;47(14):2422-2426.
[3] Maria Das Gracas Andrade Korn, Adriana Costa Ferreira, Leonardo Sena Gomes Teixeira. J Braz Chem Sec 1999;10(1):46-50.
[4] Banjit Barman, Sudarsan Barua. Arch App Sci 2009;1(1):74-83.
[5] Nagarjuna Reddy D, Nagabushna Reddy K. Int J Anal Bioanal Chem 2011;1(3):77-81
[6] Nagarjuna Reddy D, Vasudevareedy K, Hussain Reddy K. Der Pharma Chemica 2011;3(2):496-504
[7] Dipak J Garole, Garole VJ. Int J ChemTech Res 2012;4(1):377-378
[8] Ivanise Gauber, et al. Spectroscopy Lett 2002;35(3):455-465.
[9] Janardhan Reddy K, Rajesh Kumar J, Ramachandraiah C, Thrivani T, Varada Reddy A. Food Chem 2007;101:585-591.
[10] Fakruddin Aliahmed, Lingappa Y. Int J Curr Pharm Res 2011;3:24-26.
[11] Akl MA. Anal Sci 2001;17(4):561-564.
[12] Tazul Islam M, Jamaluddin Ahmed M. Pak J Anal Environ Chem 2013;14(1):1-15.
[13] Georgieva N, Dospatliev L, Yaneva Z. Trakia J Sci 2010;8(2):511-516.
[14] Lengoc, Le van Tan, Nguyen Xuan Chien. Eur Chem Bull 2013;2(6):311-314.
[15] Sivaramaiah S, Raveendra Reddy P. J Anal Chem 2005;60(9):933-937.
[16] Sapana Garg, Devender Sing, Sonia Verma, Pratap Sing Kadyan. J Chem Bio Phy Sci 2012;2(3):1746-1752
[17] Varinder Kaur, ET AL. India J Chem Sec A 2007;46:1432-1436
[18] Nagarjunareddy D, Vasudevareddy K, Hussain Reddy K. J Chem Pharm Res 2011;3(3):205-213.
[19] Kirankumar TN and Revanasiddappa HD. J Indian Chem. Soc 2005;2:161.