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Identification of zinc (II) with 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrozone by adopting direct and derivative spectrophotometry

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Abstract: Highly sensitive and selective direct spectrophotometric method is proposed for the determination of zinc in various real samples. 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone reacts with Zn (II) forming an yellow coloured soluble complex in aqueous dimethyl formamide which has a λmax at 430 nm in the pH range 2-6. The system obeyed the Beer's law is obeyed in the range of 0.317-3.175 µ g/ml of Zn (II).The molar absorptivity and Sandell's sensitivity are 1.58 ± 0.002×10^{4} 1 mol^{-1} cm^{-1} and 0.0040 µg/ml of Zn(II) is 0.008. The correlation coefficient (γ) of the calibration equation of the experimental data is 0.9994. Studies on effect of diverse ions showed almost all the anions, except Thiosulphate, Oxalate, EDTA and Ascorbate and a majority of the cations do not interfere. The interference from Mo (VI), Zr (IV), Th (IV) and Ti (IV) was eliminated using suitable masking agents. The direct method was applied for the determination of zinc in sheep liver and buffalo milk.

Keywords: Zn(II), direct spectrophotometric determination,2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone.

1. INTRODUCTION

Being a constituent of enzymes, which catalyse oxidation reactions in a variety of metabolic pathways, several zinc containing proteins has been identified in biological processes. Zinc ion is directly

responsible for maintenance of the myelin within the nervous system. At high concentration it is toxic for example, in human system, it causes Wilson's disease and in plants it reduces the chlorophyll content.Though the number of hydrazones are employed, for the spectrophotometric determination of zinc (II), p-hydroxybenzoic hydrazones for the spectrophotometric determination of zinc (II) are less.. 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrozone is used for the determination of zinc(II). Derivative spectrophotometry is a very useful approach for determination of the concentration of simple components in mixtures with overlapping spectra as it eliminates much of the interference. 2-HNHBH reacts with zinc (II) in aqueous DMF forming a highly sensitive and stable yellow coloured complex. This has been systematically studied both by direct and first derivative spectophotometrically and the results are presented in this paper.

2. MATERIALS AND METHODS

2.1. The absorbance and pH measurements were made on a Perkin Elmer (LAMDA 25) UV-Visible Spectrophotometer (Model UV-160A) controlled by a computer fitted with a 1cm path length quartz cells and an ELICO digital pH meter of (Model LI 613) respectively. Suitable settings for first order derivative are as follows: spectra , band width 5 nm: wavelength readability 0.1 nm increment, scan speed fast (nearly 2200 nm min^{-1}); wave length accuracy±0.5 cm with automatic wavelength correction and with 9 degrees of freedom.

2.2.2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrozone: This reagent was prepared by condensing 2-hydroxy-1-naphthaldehyde and p-hydroxy benzoic hydrazide in methanol using a general procedure. A freshly prepared solution in dimethylformamide is used in the studies.

2.3 .Zinc solution (0.01M):A stock solution of zinc (II) (0.01M) was prepared by dissolving 0.249 g of zinc sulphate (A. R. Glaxo) in 100 ml volumetric flask with distilled water and solution of lower concentrations were prepared by successive dilution of the stock solution.

2.4 Direct spectrophotometry: In each set of different 10 ml standard flasks, 5 ml of buffer solution (pH 2.0), 3 ml of DMF and 0.5 ml of 2-HNHBH (1×10^{-3} M) were taken. Various amounts of zinc (II) were added to these flasks and made up to the mark with DMF. The absorbance was measured at 430 nm against the reagent blank[2-5]. The calibration curve was prepared by plotting the absorbance against the amount of zinc.

2.5. First order derivative spectrophotometry: For theabove solutions, first order derivative spectra were recorded with degrees of freedom 9 in the wavelength range from 350-500 nm. The derivative peak height was measured by peak-zero method at 442 nm. The calibration equations were calculated as A_{430}=0. 32857C-0.00457 for zero order and $A_{442=}$0. 00767C+0.000188 for the first order derivative data by fitting experimental data[7-8]. The amount of zinc present in the sheep liver and buffalo milk was determined by the zero order, first order derivative method and compared with the certified values.

3 RESULTS AND DISCUSSION

3.1. The absorption spectra of the reagent and the complex were recorded in wavelength region 350-500 nm at pH 2.0(fig.1). The complex shows absorbance maximum at 430 nm where reagent has a negligible absorbance. Hence analytical studies were made at 430 nm against reagent blank[9]. The study of the effect of pH on the colour intensity of the reaction mixture showed that maximum colour was

obtained at the pH 2.0. Thus analytical studies were carried out at pH 2.0. A 10 fold molar excess of 2-HNHBH was found necessary for maximum colour development. The yellow colour of Cu^{II}-2-HNHBH complex was stable for more than 24 hours. The beer's law is obeyed in the range of 0.317-3.175 µ g/ml of Zn (II). The molar absorptivity and Sandell's sensitivity are $1.58 \pm 0.002 \times 10^4$ 1 mol^{-1} cm^{-1} and 0.0040 µg/ml of Zn(II) is 0.008. The correlation coefficient (γ) of the calibration equation of the experimental data is 0.9994.

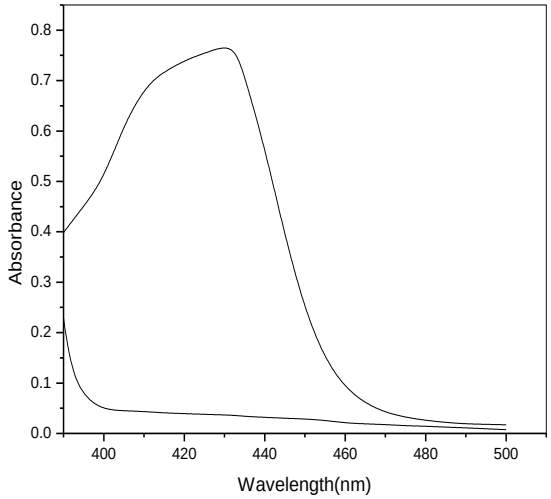

Fig.1: Absorption spectra of a) 2-HNHBH Vs buffer blank b) [Zn(II)] – 2-HNHBH Vs reagent blank

[Zn(II)] = 5×10^{-4} M: [2-HNHBH] = 5.0×10^{-3} M pH = 2.0

3.2. Effect of foreign ions: The effect of various cations and anions on the determination of Zn(II) under optimal conditions developed was studied to find out the tolerance limits of these ions in the present method. The results are presented in **Table 1**. Large amounts of commonly associated cations and anions do not interfere in the present method. 10 fold excess of each of Th(IV), Ti(IV), Mo(VI),Zr(IV) and Fe(III) is masked by fluoride. The composition of the complex was determined using Job's method as 1:1 and confirmed by mole-ration method. The stability constant of the complex was calculated from Job's method and was obtained as 7.26×10^6.

3.3. Determination of zinc(II) by first order derivative spectrophotometry: In the zero-order spectrophotometric determination of zinc with 2-HNHBH, the commonly associated metal ions such as Ti^{IV}, Zr^{IV}, Mo^{VI} and Th^{IV} interferes and were masked by using masking agents. The first derivative spectrophotometric method allows selective determination of Cu^{II} in presence of these interfering ions without using masking agents. The first derivative spectra of Cu^{II} -2-HNHBH complex with different concentrations of zinc are as shown in **Fig 2.** The peak zero method was followed for peak height measurements and preparation of calibration plot. The maximum peak amplitude was observed at 442 nm where many foreign ions do not interfere. Hence Cu^{II} is determined by measuring the peak zero amplitude at 442 nm. The correlation coefficient of the experimental data is 0.999. The standard deviation of the method for the determinations of µg/ml of Zn(II) is 0.006.

The effect of various cations and anions on the derivative amplitude was studied. It was noticed that all the ions that do not interfere in the zero order determination of Zn(II) **(Table 1)** did not interfere in the first derivative method also. Further, their limits were in general higher than those of the zero order determination.

Table 1: Tolerance limits of foreign ionsAmount of Zn(II) = 3.27 µg/ml ; pH = 2.0

Ion	Tolerance limit µg/ml	Ion	Tolerance limit µg/ml
Tartarate	2210	Mg(II)	2000
Citrate	1800	Hg (II)	196
Fluoride	1200	Al (III)	200
Iodide	940	W (VI)	116
Sulphate	910	Cd (II)	100
Bromide	720	Mn (II)	50
Phosphate	680	Zn (II)	48
Nitrate	600	Ce (IV)	40
Carbonate	590	Co (II)	40
Thiocyanate	410	Pb (II)	40
Chloride	350	Se (IV)	30
Thiourea	100	Te (IV)	26
Thiosulphate	Interferes	Tl (III)	18
Oxalate	Interferes	Ni(II)	12
Ascorbate	Interferes	Cr (VI)	8
EDTA	Interferes	Fe (III)	4 ; 60*
		V (V)	7
		Zr (IV)	Interferes
		Mo (VI)	Interferes
		Ti (IV)	Interferes
		Th(IV)	Interferes

***Masked with fluoride or tartarate**

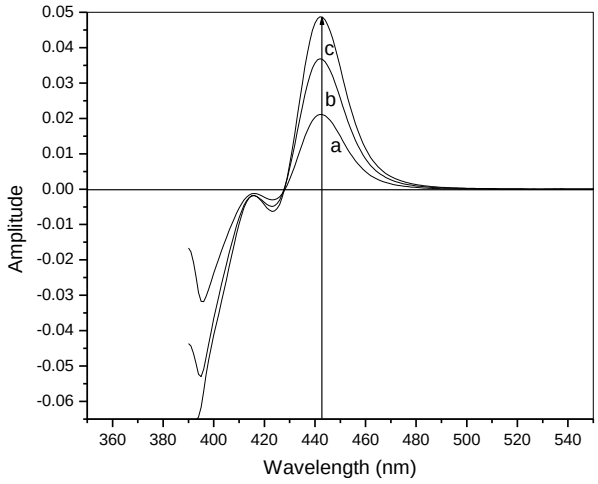

Fig. 2: First derivative spectra of Zn(II)-2-HNHBH Vs reagent blank

Zn(II) =a) 2.54 µg/ml; b) 5.08 µg/ml; c) 6.35 µg/ml; pH = 2.0

4. APPLICATIONS

The present method was employed for the determination of Sheep liver. The amount of zinc present in alloy sample was determined by the following procedure. A known aliquot of the sample solution is taken in a 10 ml of volumetric flask containing 5 ml of buffer solution of pH 2.0, 0.5 ml of 0.5 M citrate solution (to mask Fe and Ti), 2.5 ml of DMF and 1 ml of $(1.0\times10^{-2}$ M) reagent solution. The contents of the flask are diluted to 10 ml. The contents, if necessary, are filtered and the absorbance of the filtrate is measured at 430 nm against the reagent blank and the amount of zinc is calculated from the predetermined calibration plot. The derivative amplitude of the solution is measured at 442 nm.

5. CONCLUSIONS

The first derivative spectrophotometric method was found to be more sensitive and selective than the zero order method for the determination of zinc (II).

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