Direct and derivative spectrophotometric determination of zirconium(IV) with 2-hydroxynaphthaldehyde-p-hydroxybenzoic hydrozone

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ABSTRACT

A simple and sensitive spectrophotometric method is developed for the determination of Zirconium in aqueous medium. The metal ion forms an yellow colored water soluble complex with 2-hydroxynaphthaldehyde-p-hydroxybenzoic hydrozone (2-HNHBH) in the pH 1-10. However, the complex is found to be soluble in DMF. The complex shows an absorbance maximum at 415 nm in the pH range 1-5. Beer's law is obeyed in the range 0.456-4.56 µ g/ml at pH 1.0. The molar absorptivity and the Sandell's sensitivity of the method are $0.986\pm 0.002\times10^4$ 1 mol^{-1} cm^{-1} and 0.0092 µg/cm^2 respectively. The composition of the complex is 1:1. A method for the determination of zirconium by first order derivative spectrophotometry is also proposed. The method is applied for the determination of zirconium in alloy steel samples.

Keywords: Substituted hydrazone, zirconium(IV), derivative spectrophotometry.

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INTRODUCTION

2-hydroxynaphthaldehyde-p-hydroxybenzoic hydrozone is used for the spectrophotometric determination of zirconium(IV). 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 zirconium(IV) in aqueous DMF forming a highly sensitive and stable yellow colored complex. This has been systematically studied both by direct and first derivative spectrophotometrically and the results are presented in this paper.

MATERIALS AND METHODS

Shimadzu UV-visible spectrophotometer model UV-160A and ELICO pH meter model LI 120 were employed for absorbance and pH measurements respectively. Suitable settings for first order derivative are as follows: spectra; band width5 nm; wavelength readability 0.1 nm increment, scan speed fast (nearly 2200 nm min^{-1}); wavelength accuracy ±0.5 cm with automatic wavelength correction and with 9 degrees of freedom.

2-hydroxynaphthaldehyde-p-hydroxybenzoic hydrozone: The reagent was prepared by condensing 2-hydroxy-1-naphthaldehyde and p-hydroxy benzoic hydrazide in methanol using a general procedure (m.p. 275°C)[1]. The structure of the reagent is as follows.

2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone
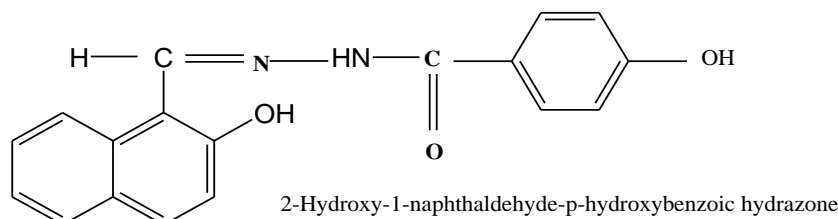
A freshly prepared solution in dimethylformamide is used in the studies

A 0.1-0.5 g of the alloy was dissolved in a mixture of 2 ml HCL and 10 ml HNO3. The resulting solution was evaporated to a small volume. To this 5 ml of 1:1 ($H_2O:H_2SO_4$) mixture was added and evaporated to dryness. The residue was dissolved in 15 ml of distilled water and filtered through Whatman filter paper No.41. The filtrate is collected in a 100 ml volumetric flask and made up to the mark with distilled water.

Zirconium solution (0.01 M): prepared by dissolving the 0.249 g of hydrated zirconyl nitrate (A.R., B.D.H.) in 100 ml distilled water. The resulting zirconium(IV) solution was standardized gravimetrically[5]. For the preparation of buffer solutions, 1 M HCL and 1 M sodium acetate (pH 1.0 to 3.0), 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.5 to 7.0) were used[5,7].

Direct spectrophotometry *:* In each set of different 10 ml standard flasks, 5 ml of buffer solution (pH 1.0), 3 ml of DMF and 0.5 ml of 2-HNHBH (1×10^{-3} M) were taken. Various amounts of zirconium(IV) were added to these flasks and made up to the mark with DMF. The absorbance was measured at 415 nm against the reagent blank. The calibration curve was prepared by plotting the absorbance against the amount of zirconium[1]..

First order derivative spectrophotometry: For the above solutions, first order derivative spectra were recorded with degrees of freedom 9 in the wavelength range from 400-500 nm. The derivative peak height was measured by peak-zero method at 448 nm. The peak height was plotted against the amount for zirconium to obtain the calibration curve. The calibration equations were calculated as $A_{415} = 0.1068C + 0.00296$ for zero order and $A_{448} = 0.00476C + 0.000061$ for the first order derivative data by fitting experimental data. The amount of zirconium present in the alloy sample was determined by the zero order first order derivative method and compared with the certified values.

RESULTS AND DISCUSSION

The absorption spectra of the reagent and the complex were recorded in wavelength region 400-500 nm at pH 1 (fig. 1). The complex shows absorbance maximum at 415 nm where reagent has a negligible absorbance. Hence analytical studies were made at 415 nm against reagent blank. The study of the effect of pH on the color intensity of the reaction mixture showed that maximum color was obtained at the pH 1.0. Thus analytical studies were carried out at pH 1.0 A 10-fold molar excess of 2-HNHBH was found necessary for maximum color development. The yellow color of Zr^{IV}-2-HNHBH complex was stable for more than 24 hours after heating 15 minutes at $60^{o}C$. Beer's law was obeyed in the range of 0.456-4.56 µg ml^{-1}. The molar absorptivity and Sandell's sensitivity was obtained as $0.986 \pm 0.002 \times 10^{4}$ 1 mol^{-1} cm^{-1} and 0.0092 µg/cm^{2} respectively. The standard deviation for ten determinations of 9.12 µg ml^{-1} of

Zr(IV)is±0.009. The correlation coefficient (γ) for the experimental data was calculated 0.9977[10].

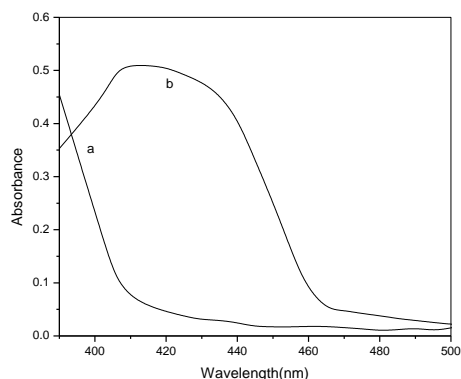**Fig.1** Absorption spectra of
a) 2-HNHBH Vs buffer blank   b) [Zr (IV)] – 2-HNHBH Vs reagent blank;
[Zr (IV)] = 5×10^{-4} M   [2-HNHBH] = 5×10^{-3} M; pH = 1.0

Effect of foreign ions: The effect of various cations and anions on the determination of Zr^{IV} 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. Cu^{II} and Fe^{III} can be masked up to 10-fold and 125-fold excess by adding 500 µ g of thiosulphate and 300 µ g of citrate respectively[2]. The composition if the complex was determined using Job's method as 1:1 and confirmed by mole-ratio method. The stability constant of the complex was calculated from Job's method and was obtained as 2.87×10^{6}[9]**.**

Determination of zirconium(IV) *by first order derivative spectrophotometry :* In the zero-order spectrophotometric determination of zirconium with 2-HNHBH, the commonly associated metal ions such as Ti^{IV}, Fe^{III} and Cu^{II} interferes and were masked by using masking agents[3]. The first derivative spectrophotometric method allows selective determination of Zr^{IV} in presence of these interfering ions without using masking agents.   The first derivative spectra of the Zr^{IV}-2-HNHBH complex with different concentrations of Zr^{IV} are 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 448 nm where many foreign ions do not interfere. Hence Zr^{IV} is determined by measuring the peak zero amplitude at 448 nm. Beer's law was obeyed in the range 0.456-4.56 µ g ml^{-1}.   Other statistical data for the present method are the standard deviation of the method for ten determinations of 9.12 µ g ml^{-1}. Zr^{IV} of was 0.008 and the correlation coefficient of the calibration equation is 0.999[8].
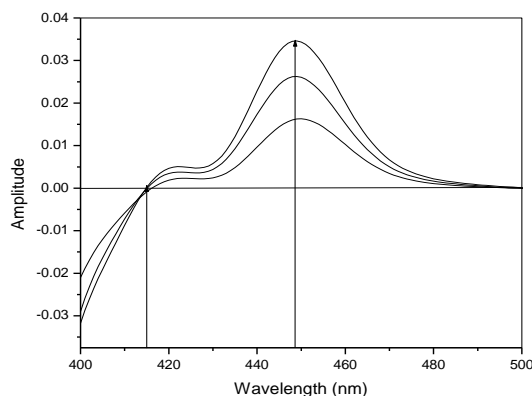

Fig.2.   First derivative spectra of Zr (IV)-2-HNHBH Vs reagent blankZr (IV) =a) 5.472 µg/ml; b) 7.296 µg/ml; c) 9.120 µ g ml^{-1}.

83

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 Zr^{IV} (Table 1) did not interfere in the first derivative method also. Further, their tolerance limits were in general higher than those of the zero order determination[6].

APPLICATIONS

The proposed method was employed for the determination of Zr^{IV} Zircaonyl -2[a]. The amount of zirconium 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 1.0, 0.5 ml of 0.5 M citrate solution (to mask iron), 2.5 ml of DMF and 1ml of $(1.0 \times 10^{-2} M)$ reagent solution. The contents of the flask are diluted 10 ml. the contents, if necessary, are filtered and the absorbance of the filtrate is measured at 4105 nm against the reagent blank and the amount of zirconium is calculated from the predetermined calibration plot. The derivative amplitude of the solution is measured at 448 nm[4].

CONCLUSIONS

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

Table 1

Ion	Tolerance Limit (μg/ml)	Ion	Tolerance Limit (μg/ml)
Thiosulphate	2310	Cd (II)	300
Ascorbate	1380	Co (II)	130
Iodide	1240	Hg (II)	120
Sulphate	940	Zn (II)	90
Carbonate	580	Pb (II)	80
Chloride	500	Mn (II)	60
Nitrate	460	Ce (IV)	50
Bromide	450	V (V)	26
Thiocyanate	410	Se (IV)	24
Phosphate	100	Tl (III)	22
EDTA	100	W (VI)	22
Citrate	50	Al (III)	40
Tartarate	40	Cr (VI)	10
Thiourea	20	Ni(II)	10

Oxalate	Interferes	Fe (III)#	3 ; 125#
Fluoride	Interferes	Ti (IV)#	Interferes
		Mo (VI)	Interferes
		Th (IV)	Interferes
		Cu (II)*	Interferes

*masked with thiosulphate ,# masked with citrate

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