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Simultaneous spectrophotometric determination of Zirconium(IV) and Titanium(IV) Using 2-Hydroxynaphthaldehyde-P-Hydroxybenzoic Hydrozone

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Determination of zirconium(IV) by direct spectrophotometry and simultaneous determination of zirconium(IV) gives a yellow colour with 2-hydroxy naphthaldehyde-p-hydroxybenzoic hydrozone with 1:1 metal-reagent stoichiometry at pH 1. The complex shows an absorption maximum at 415 nm with molar absorptivity and the molar absorptivity and the Sandell's sensitivity of the method are $0.986 \pm 0.002 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0092 \mu\text{g/cm}^2$ respectively. Beer's law is obeyed in the range 0.456-4.56 $\mu\text{g/ml}$ at pH 1.0. Zirconium(IV) and titanium(IV) have been determined simultaneously by measuring the absorbance of the solution mixture at 415 and 405 nm respectively. The method has been applied for the simultaneous determination of zirconium(IV) and titanium(IV) in steel samples.

Keyword: Zirconium(IV), 2-Hydroxynaphthaldehyde-P-Hydroxybenzoic Hydrazone, Simultaneous spectrophotometric

1. Introduction

Benzoic hydrozones of carbonyl compounds has been used extensively for the spectrophotometric determination of metal ions in our laboratories [1-5]. Although several methods have been reported for the spectrophotometric determination of Zr(IV), they suffer from the drawbacks of zirconium(IV). Further, the method does not coexist in a number of industrially important alloys like Beta-C (titanium based alloy), no spectrophotometric method has been reported for the simultaneous determination of zirconium(IV) and titanium(IV) are determined simultaneously in alloy samples with good accuracy.

2. Material and methods

2.1 Chemicals

2-HNHBH was prepared by condensing 2-hydroxy-1naphthaldehyde and p-hydroxy benzoic hydrazide in methanol [11]. A solution of zirconium(IV) (0.01 M) was prepared by dissolving the 0.249 f of

hydrated zirconyl nitrate (A.R., B.D.H.) in 100 ml distilled water. The resulting zirconium(IV) solution was standardized gravimetrically. Titanium(IV) solution (0.01 M) was prepared by dissolving appropriate amount of $\text{K}_2\text{TiO}_2(\text{C}_2\text{O}_4)2\text{H}_2\text{O}$ in distilled water. The titanium content of the solution was determined gravimetrically [6]. The stock solutions were diluted as required.

Buffer solutions were prepared by mixing 1 M hydrochloric acid and 1 M sodium acetate (pH 1-3), and 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.5-7.0). The pH of these solutions was checked with a pH meter. All reagents used were of AR grade.

2.2 Instruments

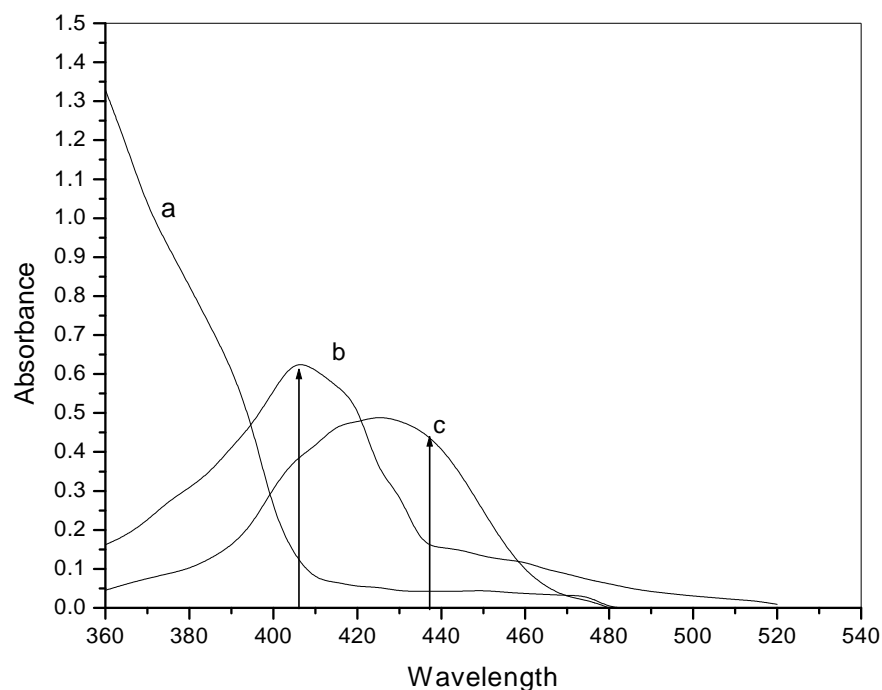
The absorbance and pH measurements were made with a Shimadzu UV-visible spectrophotometer (model UV-160A) fitted with 1 cm quartz cells and pH meter model LI 120 respectively.

Table 1: Effect of foreign ions on estimation of zirconium(IV) Amount of Zr(IV)=4.56 µg/ml pH=1.0

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
Tartrate	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

**Fig 5.4.1:** Absorption spectra of

a) 2-HNHBH system Vs buffer blank; b) Ti(IV)-2-HNHBH system Vs reagent blank; c) Zr(IV)-2-HNHBH Vs reagent blank

[Zr(IV)] = [Ti(VI)] = 5×10^{-4} M; pH 1.0; [2-HNHBH] = 5×10^{-3} M

Table 2: Simultaneous determination of Zr(IV) and Ti(IV) in synthetic mixtures

Amount taken ($\mu\text{g/ml}$)		Amount found* ($\mu\text{g/ml}$)		Relative error (%)	
Zr(IV)	Ti(IV)	Zr(IV)	Ti(IV)	Zr(IV)	Ti(IV)
0.912	2.395	0.908	2.338	+0.43	+2.3
0.912	1.916	0.918	1.902	-0.65	+0.73
0.912	0.718	0.902	0.726	+1.09	-1.1
0.912	0.958	0.906	0.948	+0.65	+1.04
0.912	0.479	0.916	0.470	-0.43	+1.8
1.824	0.479	1.814	0.472	+0.54	+1.4
3.648	0.479	3.634	0.476	+0.38	+0.62
5.472	0.479	5.422	0.475	+0.91	+0.83
7.296	0.479	7.224	0.477	+0.98	+0.41
9.12	0.479	9.2	0.475	-0.87	+0.83

2.3 Determination of zirconium (IV)

In case set of different 10 ml standard flasks, 5 ml of buffer solution (pH 1), 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.

2.4 Simultaneous determination of Zr(IV) and Ti(IV)

To 10 ml volumetric flasks, each containing buffer solution (5 ml, pH 1), 2-HNHBH (0.5 ml, 1×10^{-3} M) and aliquots of the mixture containing varying amounts of Zr(IV) and Ti(IV) were added. The volume was made up to the mark with DMF and the absorbencies were measured at 405 nm and 415 nm against reagent blank.

3. Results and discussion

The absorbance spectra of the reagent, Zr(IV)-2-HNHBH and Ti(IV)-2-HNHBH are given in fig.1. The yellow colored solution of shows absorbance maxima at 415 nm in pH 1. Titanium(IV) reacts with 2-HNHBH forming a brown colored complex with absorption maxima at 405 nm at pH 1.

The reagent shows appreciable absorbance at 300 nm and negligible absorbance at 415 nm. Hence all studies were carried out at 415 nm against reagent blank. Analytical studies were carried out at pH 1 as the interference from foreign ions was minimum at this pH. A 15 fold excess of the reagent

concentration was necessary for maximum absorbance. Beers law was obeyed in the range 0.456-4.56 $\mu\text{g/ml}$ of zirconium(IV). The molar absorptivity and Sandell's sensitivity was obtained as $0.986 \pm 0.002 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0092 \mu\text{g/cm}^2$ respectively. The standard deviation for ten determinations of 9.12 $\mu\text{g/ml}$ of Zr(IV) is ± 0.009 . The correlation coefficient (γ) for the experimental data was calculated 0.9977.

The stoichiometry of the complex was determined by Job's method and molar ratio method is found to be 1:1 (metal: reagent). The stability constant was determined by Job's method 2.87×10^6 . The tolerance limits of various diverse ions in the present method are given in Table 1. Tolerance limit was set as the amount of foreign ion that caused an error of $\pm 2\%$. It was observed that Cd(II) (300 $\mu\text{g/ml}$), Co(II) (130 $\mu\text{g/ml}$), Al(III) (40 $\mu\text{g/ml}$), V(V) (26 $\mu\text{g/ml}$) were tolerated in the presence of 1000 μg of thiosulphate.

At pH 1.0 the zirconium(IV)-2-HNHBH complex shows maximum absorbance at 438 nm and very low absorbance at 405 nm while titanium(IV)-2-HNHBH complex shows considerable absorbance at 405 nm (fig.1). Thus Zr(IV) and Ti(IV) can be determined simultaneously in a mixture by measuring absorbance at 405 and 415 nm.

Beer's law is obeyed for Zr(IV) in the range 0.912-9.12 $\mu\text{g/ml}$ at 438 nm and 0.912 to 3.648 $\mu\text{g/ml}$ at 405 nm. Ti(IV) obeys Beer's law in the range of 0.239 to 1.916 $\mu\text{g/ml}$ at 405 nm and 0.479 to 2.395 $\mu\text{g/ml}$ at 438 nm. The molar absorptivities for Ti(IV) are $0.51 \pm 0.002 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$ and $1.68 \pm 0.002 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$ at 438 nm and 405

nm respectively. The molar absorptivities for Zr(IV) are $0.496 \pm 0.002 \times 10^4$ lit mol⁻¹ cm⁻¹ and $0.938 \pm 0.002 \times 10^4$ lit mol⁻¹ cm⁻¹ at 438 nm and 405 nm respectively.

The absorbance of the solution mixture containing Ti(IV) and Zr(IV) complex species is recorded at 405 nm and 438 nm at pH 1.0. From these absorbance values the amount of Ti(IV) and Zr(IV) are calculated using the following simultaneous equations.

$$A_{405} = \epsilon_{405}^{Ti} C_{Ti} + \epsilon_{405}^{Zr} C_{Zr} \quad \dots\dots\dots 1$$

$$A_{438} = \epsilon_{438}^{Ti} C_{Ti} + \epsilon_{438}^{Zr} C_{Zr} \quad \dots\dots\dots 2$$

Converting concentrations into amounts (µg/ml) and solving the equation 1. and 2., we get,

$$Ti(IV) = \frac{A_{405} \epsilon_{438}^{Ti} - A_{438} \epsilon_{405}^{Zr}}{\epsilon_{405}^{Ti} \epsilon_{438}^{Zr} - \epsilon_{438}^{Ti} \epsilon_{405}^{Zr}} \times 47.9 \times 10^3 \quad \dots\dots 3.$$

$$Zr(IV) = \frac{A_{405} \epsilon_{405}^{Zr} - A_{438} \epsilon_{438}^{Ti}}{\epsilon_{405}^{Ti} \epsilon_{438}^{Zr} - \epsilon_{438}^{Ti} \epsilon_{405}^{Zr}} \times 91.2 \times 10^3 \quad \dots\dots 4.$$

Where A_{405} and A_{438} are the absorbance values of the solution mixture at 405 and 438 nm respectively. ϵ values represent the molar absorptivities of Ti(IV) and Zr(IV) complexes at the wavelengths specified. 47.87×10^3 and 91.2×10^3 are the factors to convert the concentrations into amounts for Ti(IV) and Zr(IV) respectively.

3.1 Application to real samples

Zirconium(IV) and titanium(IV) present in various alloy and steel were determined by the present method.

The alloy and steel sample solutions were prepared by the procedure reported by Buseve *et al.* [10]. The amount of zirconium(IV) present in the sample solutions was determined from the predetermined calibration plot. Zirconium(IV) and titanium(IV) present in alloy steel sample, titanium based alloy (Beta C), were calculated using Eqs. 3 & 4. The interference of Fe(III), Cd(II), Cu(II) was masked by adding 2 ml of thiosulphate. The amounts of

Zr(IV) and Ti(IV) were found to be 3.96 and 74.5 with relative errors of 1.0 and 0.66 respectively.

4. Conclusion

Titanium(IV) and zirconium(IV) are associated with each other in many alloys of industrial importance. Hence, their simultaneous determination is interesting. The proposed method for their simultaneous determination is simple, direct, rapid and highly selective. The method is easily applied for their simultaneous determination in steel samples.

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