

# Identification of titanium (IV) with 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrozone by applying direct and derivative spectrophotometry

G.Sumathi and T. Sreenivasulu Reddy\*

\*Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003 (A.P), India.

## ABSTRACT

Highly sensitive and selective direct spectrophotometric method is proposed for the identification of titanium in various real samples. 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone reacts with Ti(IV) forming an orange brown coloured soluble complex in aqueous dimethyl formamide which has a  $\lambda_{\max}$  at 405 nm in the pH range 1-6. The system obeyed Beer's law in the range 0.2395-2.395  $\mu$  g /ml of Ti(IV). Studies on effect of diverse ions showed almost all the anions, except Citrate, Fluoride and Ascorbate and a majority of the cations do not interfere. The interference from Fe(III), Mo(VI), Zr(IV), Th(IV) and Cu(II) was eliminated using suitable masking agents. The direct method was applied for the determination of titanium in steel and alloy samples.

**Key words:** *Ti(IV), direct spectrophotometric determination, 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone.*

## 1.Introduction

Titanium compounds are highly corrosion resistant to chloride solution including sea water, to nitric acid, to chlorine dioxide and other bleaching agents and to sulphur dioxide. Titanium is used as an alloy metal. Benzoic hydrozones of carbonyl compounds has been used extensively for the spectrophotometric determination of metal ions in our laboratories. Very few hydrazones are reported for the spectrophotometric determination of titanium. Among the sensitive methods reported, most of them involve extraction process and suffer from lack of selectivity. Classical methods using hydrogen peroxide and chromotropic acid suffer from the disadvantages of interferences and critical pH maintenance respectively.

2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrozone is used for the determination of titanium(VI). 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 titanium(VI) in aqueous DMF forming a highly sensitive and stable brown coloured complex. This has been systematically studied both by direct and first derivative spectrophotometrically and the results are presented in this paper.

## 2. MATERIALS AND METHODS

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 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<sup>-1</sup>); wave length accuracy ±0.5 nm 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. Titanium solution (0.01M):** 0.354 g of potassium titanium oxalate (AR) was weighed and transferred into a 100 ml volumetric flask. This is dissolved in distilled water and made up to the mark with distilled water to get 0.01 M solution. The solution was standardized and diluted as required.

**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<sup>-3</sup> M) were taken. Various amounts of titanium(VI) were added to these flasks and made up to the mark with DMF. The absorbance was measured at 405 nm against the reagent blank<sup>2-5</sup>. The calibration curve was prepared by plotting the absorbance against the amount of titanium.

**2.5. First order derivative spectrophotometry:** For the above solutions, first order derivative spectra were recorded with degrees of freedom 9 in the wavelength range from 360-540 nm. The derivative peak height was measured by peak-zero method at 415 nm. The calibration equations were calculated as  $A_{405} = 0.10689C + 0.00296$  for zero order and  $A_{415} = 0.00332C + 0.00184$  for the first order derivative data by fitting experimental data<sup>7-8</sup>. The amount of titanium present in the alloy sample 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 300-500 nm at pH 2.0 (fig.1). The complex shows absorbance maximum at 405 nm where reagent has a negligible absorbance. Hence analytical studies were made at 405 nm against reagent blank<sup>9</sup>. 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 brown colour of Ti<sup>IV</sup>-2-HNHBH complex was stable for more than 24 hours. Beer's law is obeyed in the range of 0.2395-2.395 μg/ml of Ti(IV). The molar absorptivity and Sandell's sensitivity are  $1.68 \times 10^4 \pm 0.002$  lit mol<sup>-1</sup> cm<sup>-1</sup> and 0.0028 μg/cm<sup>2</sup> respectively. The standard deviation of the method for ten determinations of 2.395 μg/ml of Ti(IV) is 0.011. The correlation coefficient (γ) of the calibration equation of the experimental data is 0.9977.

**3.2. Effect of foreign ions:** The effect of various cations and anions on the determination of Ti(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. 10 fold excess of Cu(II) is masked with thiosulphate and 100 fold excess of Fe(III) and 10 fold excess of Ti(IV) are masked with citrate<sup>10</sup>. The composition of 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  $4.51 \times 10^5$ .

**3.3. Determination of titanium(VI) by first order derivative spectrophotometry:** In the zero-order spectrophotometric determination of titanium with 2-HNHBH, the commonly associated metal ions such as  $\text{Mo}^{\text{VI}}$ ,  $\text{Zr}^{\text{IV}}$ ,  $\text{Cu}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  interferes and were masked by using masking agents. The first derivative spectrophotometric method allows selective determination of  $\text{Ti}^{\text{IV}}$  in presence of these interfering ions without using masking agents. The first derivative spectra of  $\text{Ti}^{\text{IV}}$  - 2-HNHBH complex with different concentrations of titanium 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 415 nm where many foreign ions do not interfere. Hence  $\text{Ti}^{\text{IV}}$  is determined by measuring the peak zero amplitude at 415 nm. The correlation coefficient of the experimental data is 0.9977. The standard deviation for the method for the determination of  $\mu\text{g/ml}$  of Ti (IV) is 0.009.

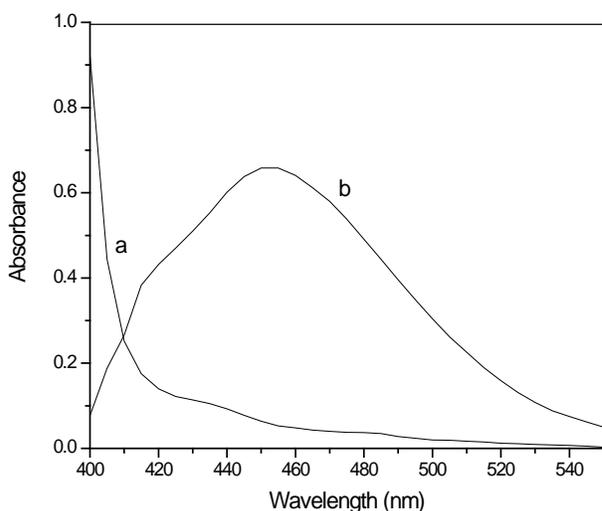


Fig.1. Absorption spectra of  
 a) 2-HNHBH Vs buffer blank                      b) [Ti(IV)] – 2-HNHBH Vs reagent blank  
 $[\text{Ti(IV)}] = 1.0 \times 10^{-3} \text{ M}$ ;  $[2\text{-HNHBH}] = 1.0 \times 10^{-2} \text{ M}$        $\text{pH} = 2.0$

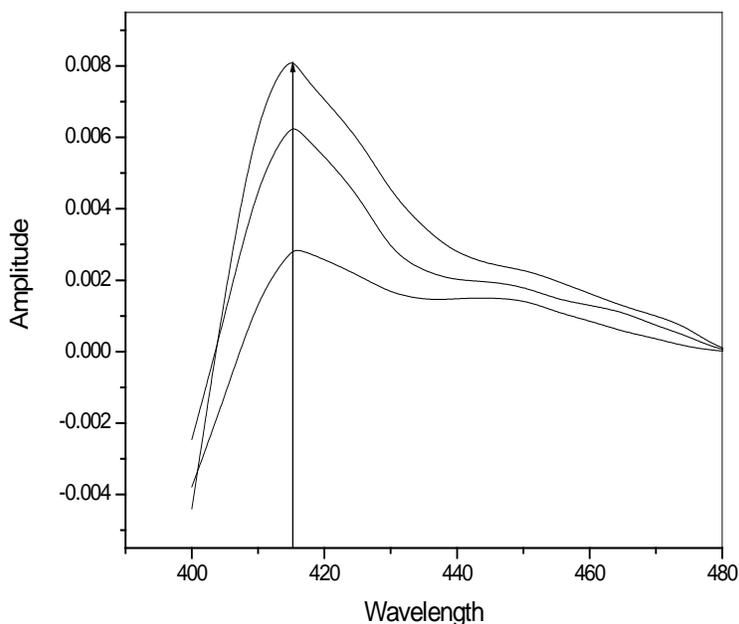


Fig.2. First derivative spectra of Ti (IV)-2-HNHBH Vs reagent blank  
 Ti (IV) =a) 0.7185 µg/ml; b) 1.437 µg/ml; c) 2.395 µg/ml; pH = 2.0

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 Ti(IV) (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.

#### 4. APPLICATIONS

The present method was employed for the determination of titanium based alloy. The amount of titanium 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 thiosulphate solution (to mask Cu), 2.5 ml of DMF and 1 ml of  $(1.0 \times 10^{-2} \text{ M})$  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 405 nm against the reagent blank and the amount of titanium is calculated from the predetermined calibration plot. The derivative amplitude of the solution is measured at 415 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 titanium(VI).

**Table 4.3.2**

**Tolerance limits of foreign ions**

Amount of Ti (IV) = 2.395 µg/ml pH = 2.0

<b>Ion</b>	<b>Tolerance limit (µg/ml)</b>	<b>Ion</b>	<b>Tolerance limit (µg/ml)</b>
Thiocyanate	2850	Ba (II)	5842
Oxalate	1500	Sr (II)	5450
Thiosulphate	1200	Zn(II)	600
Tartrate	1000	Cd (II)	310
Chloride	800	Hg (II)	195
Bromide	690	Co (II)	120
Nitrate	590	Ni (II)	100
Carbonate	460	Pb (II)	95
Sulphate	430	Cd (II)	82
Iodide	200	Cr (VI)	80
Phosphate	90	W (VI)	68
EDTA	50	Cu (II)*	63
Citrate	Interferes	Al(III)	60
Fluoride	Interferes	Mn (II)	50
Ascorbate	Interferes	Se (IV)	45
		Ag (I)	38
		V(V)	5
		Bi (III)	18
		Ce (IV)	10
		Ni (II)	5
		U (VI)	4
		Th(IV)	Interferes
		Mo (VI) <sup>#</sup>	Interferes
		Fe (III)	Interferes
		Zr (IV) <sup>#</sup>	Interferes

\*Masked with thiosulphate

#Masked with tartrate

## REFERENCES

- [1]. Vogel A.I, “A text book of quantitative inorganic analysis”, 4th Edn. ELBS and Longman **1978**, 488.
- [2]. Reddy V.K.; Reddy P.R.; Reddy T.S.;’ Journal of Analytical of Analytical Chemistry **55 (5)**, 435-439.(2000).
- [3]. Krishna Reddy, V., Mutta Reddy, S., Raveendra Reddy, P. and Srinivasulu Reddy, T., Chem. Anal. (Warsaw), **46**, 687 (2001).
- [4]. Nakamura Y., Nagai H., Kubota D., and Himene S., Benseki Pagaka, **1973**;22:1156.
- [5]. Muralimohan K, & Brahmajij Rao S, Analyt chim Acta, 120(1980) 353.
- [6]. Kuroda. R., Kurosaki. M. and Hayashibe. Y., Talanta, **36**, 6, 619-624 (1990).
- [7]. Mallikarjuna Rao K, Sreenivasulu Reddy T, & Brahmaji Rao S, J Indian Inst Sci, Jan 66, (1986), 38.
- [8]. Glenn, A.L.,J.Pharm. Parmacol., **12**:595 (1960).
- [9]. Gopala Krishna D, Devanna N., Chandrasekhar K.B., Int.J.Chem Tech Res.(2011), 3,(1),506-515.
- [10]. Muralikrishna V., Sivaramakrishna, Akella **Asian Journal of Chemistry 13 (1)**, 289-29 (2001).
- [11]. Wang. Z., Zheng. Z. and Liu, P., *Fenxi Huaxue*. **16(11)**, Bacjcover (Ch) (1988).