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Research Article

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Direct spectrophotometric determination of titanium(IV) with 5-bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoic hydrazone

Madhavi Devireddy, B. Saritha, A. Giri and T. Sreenivasulu Reddy*

Department of Chemistry, Sri Krishnadevaraya University, Anantapur(A.P), India

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ABSTRACT

5-Bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoichydrazone reacts with Ti(IV) forming thick orange coloured soluble complex in aqueous dimethyl formamide in the pH range 2.0-7.0. It has a λ_{max} *at 390 nm. Studies were carriedout at pH-4.0.The method obeys Beer's law in the range 0.241 to 2.87 μg /ml. The molar absorptivity is* 1.44×10^{4} *l* $mol^{-1}cm^{-1}$ *and Sandell's sensitivity is 0.0033* $\mu g/cm^{2}$*. The standard deviation of the method for ten determinations of 1.197 μg/ml of Ti(IV) is* 9.04×10^{-3}*. The correlation coefficient (γ) of the calibration equation of the experimental data is 0.9998. The effect of various diverse ions is studied. The formula of the complex is 1:1 and its stability constant is* 2.25×10^{5}*. Based on the above , a rapid, simple, sensitive and selective direct spectrophotometric method has been developed. The method developed was used for the determination of Ti(IV) in alloy and steel samples. The results are in good agreement with the certified values.*

Key words: Ti(IV), Direct spectrophotometric determination, 5-BHMBHBH.

INTRODUCTION

Metallic titanium is well known for its excellent corrosion resistance. It is as strong as steel. Titanium is one of the important constituents of alloys. It is a lighter but heavier than aluminium. These properties make titanium highly resistant to the usual kinds of metal fatigue[1] Titanium finds critical applications in civilian and military air frame parts, food processing plants, nuclear power plants and marine components. It has several medical applications such as preparation of arthritis hips, knee joints and dental implants[2]. Titanium exists in nature in its most stable oxidation state of +4. Titanium dioxide is an extensively used as a white pigment in printing ink, ceramics and cosmetics. Ferro titanium is used as a scavenger to remove oxygen, hydrogen and nitrogen in steel industry. Several analytical techniques such as flame spectrometry[3-5], x-ray fluroscence, Stripping voltametry[6], flow injection[7], kinetic spectrophotometry[8-9], AAS, ICP-AES[10], ICP-MS, and spectrophotometry[11-35] have been used for the determination of Ti(IV). Spectrophotometric techniques remain preferred because they are cheaper, easier to handle and provides good sensitivity other techniques involve costly instrumentation. Many of the spectrophotometric methods reported involve relatively complicated and time sensitive procedures, or involve extraction steps[36].

Hence there is a need for the development of new sensitive, simple, spectrophotometric methods for the determination of Ti(IV) at micro levels. A survey of literature reveal that several hydrazones are available for the spectrophotometric determination of Ti(IV)[37-43]. As already stated they involve extraction steps. The potentiality of hydrazones as analytical spectrophotometric reagents have been reviewed by Singh et.al[44]. Literature survey reveal that no para hydroxy benzoic hydrazones are employed for the spectrophotometric determination of Ti(IV).

The present paper reports a sensitive, rapid, direct spectrophotometric method for the determination of Ti(IV) for the micro level which was successively employed in many real samples, such as alloy and steel, tap water etc.

EXPERIMENTAL SECTION

The reagent,5-bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoichydrazone was synthesized in the laboratory by condensing 5-Bromo-2-hydroxy-3-methoxybenzaldehyde and p-hydroxybenzoichydrazone. A 0.01 M DMF solution of the reagent is used in the studies.

0.01M stock solution of Ti(IV) was prepared by dissolving requisite amount of potassium titanium oxalate(AR) in distilled water and standardized volumetrically[45]. The working solutions were prepared by diluting the stock solutions with distilled water. Buffer solutions of pH 5.0 were prepared by mixing 0.2M sodium acetate and 0.2 M acetic acid in suitable proportions and the pH was adjusted by a pH meter.

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.

General Procedure:

To 5 ml of buffer solution (pH 4.0) 0.5 ml of 5-BHMBHBH (1 x 10^{-2}M) in DMF,1.5 ml of DMF were taken in each of a set of 10 ml volumetric flasks, varying amounts of Ti(IV) were added and diluted to the mark in 10 ml volumetric flasks with distilled water. The absorbance of these solutions was measured at 390 nm against reagent blank and plotted against the amount of titanium. A straight line is obtained which corresponds to the equation A_{390}= 0.3035C+ 0.00354. (C is the amount of copper in µg/ml).

RESULTS AND DISCUSSION

5-bromo-2-hydroxy-3-methoxybenzaldehyde-4-hydroxybenzoichydrazone was used for the spectrophotometric determination of the titanium(IV). Titanium(IV) reacts with 5-BHMBHBH in the pH range 2.0- 7.0 to form thick orange coloured complex. The absorption spectra of 5-BHMBHBH and its titanium(IV) complex under the optimum conditions were recorded in the range 370- 500 nm and shown in Figure1. The titanium(IV)-5-BHMBHBH complex shows maximum absorbance at 390 nm, where the reagent has negligible absorbance and constant in the pH range 3.0- 5.0. The analytical measurements were made at pH 4.0 as at this pH the interference due to diverse ions is minimum. The absorbance is The colour formation is instantaneous. It is stable for 48 hours. The order of addition of various constituents such as the buffer, the metal ion, the reagent has no effect on the maximum intensity of the colour reaction. A six fold molar excess of the reagent is sufficient to produce maximum absorbance. The formula of the complex was ascertained from jobs and molar ratio methods as 1:1. The stability constant of the complex is 2.25×10^5.

Analytical characteristics of [Fe(III)-5-BHMBHBH] and the effect of foreign ions:

The molar absorptivity, Beer's law range, detection limit, determination limit etc., are shown in the Table-1. The data indicate that the method is highly sensitive.

The effect of various foreign ions on the absorbance of the experimental solution containing 1.197 µg/ml of Fe(III) was studied and the results are presented in Table.2. All the anions studied except phosphate, oxalate, citrate and EDTA do not interfere even if they are present in more than 100 fold excess. Many cations except Mo(VI), Cu(II) do not interfere in the determination of Ti(IV) even in more than 10 fold excess. However 20 fold excess of Fe(III) and 50 fold excess of Cu(II) could be masked using phosphate and thiosulphate respectively.

Applications:

The present method for the determination titanium(IV) is applied to alloy and steel samples and tap water. The following general procedure is adopted for the analysis of titanium(IV) in the above sample solutions.

a) Determination of Ti(IV) in alloy and steel sample:
The alloy sample was brought into solution by the procedure An aliquot of the sample was analysed by the following procedure.

1gm of the alloy sample was dissolved in a mixture of 2ml of concentrated hydrochloric acid and 10ml of concentrated nitric acid. The solution was evaporated to a small volume. 5ml of 1:1 sulfuric acid were added and the solution was evaporated to dryness. The residue left over was extracted with 15ml of water and the solution was diluted to 100ml with double distilled water. This serves as the stock solution. The stock solution was appropriately diluted and analyzed by the general procedure. The results are given in table-3.

b) Determination of Ti(IV) in Water samples :
The water samples were collected from different parts of anantapur district. (A.P. India) and treated as follows.

1 litre of the water sample was taken in a 2 litre beaker and evaporated slowly 225 ml. 5 ml of H_2O_2 were added and evaporated to dryness in a china dish. filtered. It was then dissolved in 20 ml of water and transferred quantitatively into a 100 ml volumetric flask and made up to the mark with distilled water. An aliquot the sample was analysed by the following procedure. The results are given in table-4.

Table -1 Analytical characteristics of [Ti(IV) – 5-BHMBHBH]

Parameter	Direct method (390nm)
Beer's law range (μg/m l)	0.241 - 2.87
Molar absorptivity (L mol^{-1}cm^{-1})	1.44 × 10^4
Sandell's sensitivity (μg/c m^2)	0.0033
Correlation coefficient (γ)	0.9998
Standard deviation	0.00273
Y- intercept(b)	0.0035
Detection limit(μg/m l)	0.026
Composition (Metal : Ligand)	1:1
Stability constant(ß)	2.25 × 10^5

Table - 2 Tolerance limits of foreign ions
Amount of Ti (IV) = 1.197μg/ml pH = 4.0

Ion	Tolerance limit (μg/ml)	Ion	Tolerance limit (μg/ml)
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)	12
Nitrate	590	Ni (II)	12
Carbonate	460	Pb (II)	9
Sulphate	430	Cd (II)	82
Iodide	200	Cr (VI)	8
Phosphate	90	W (VI)	8
EDTA	50	Cu (II)*	63
Citrate	Interferes	Al(III)	6
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
		Mo (VI)$^{\#}$	59
		Fe (III)**	50
		Zr (IV)$^{\#}$	16

** Masked with thiosulphate; # Masked with tartarate;* ** *Masked with phosphate*

Table -3 Determination of titanium in alloy and steel samples

Cobalt-based high Temperature alloy[a]	Composition (%) certified	Composition (%) found	Error (%)
(i) Udimet – 500	2.90	2.86	-1.38
(ii) Udimet-700	3.50	3.48	-0.57
(iii)Titanium based alloy[b]	70.14	70.10	-0.06

******Average of five determinations*

Composition of samples (%) as follows:

i. Co 18.5: Cr 18: Mo 4.8: Al 2.9: Ti 2.9: C 0.08: B 0.006: Zr 0.05;
ii. Co 18; Mo 5.21; Cr 1.5; Al 4.3; Ti 3.5; C 0.08; B 0.003
iii. Ti 70.14; Ni 15.03; Cu 14.83;

Table -4 Determination of titanium in tap water

Sample No.	Ti(IV) added	Ti(IV) Found*		Error (%)
		Present method	AAS method	
1	5.0	5.05	5.01	-0.79
2	10.0	10.11	9.99	-1.20
3	15.0	15.12	15.01	-0.73

**Average of five determinations*

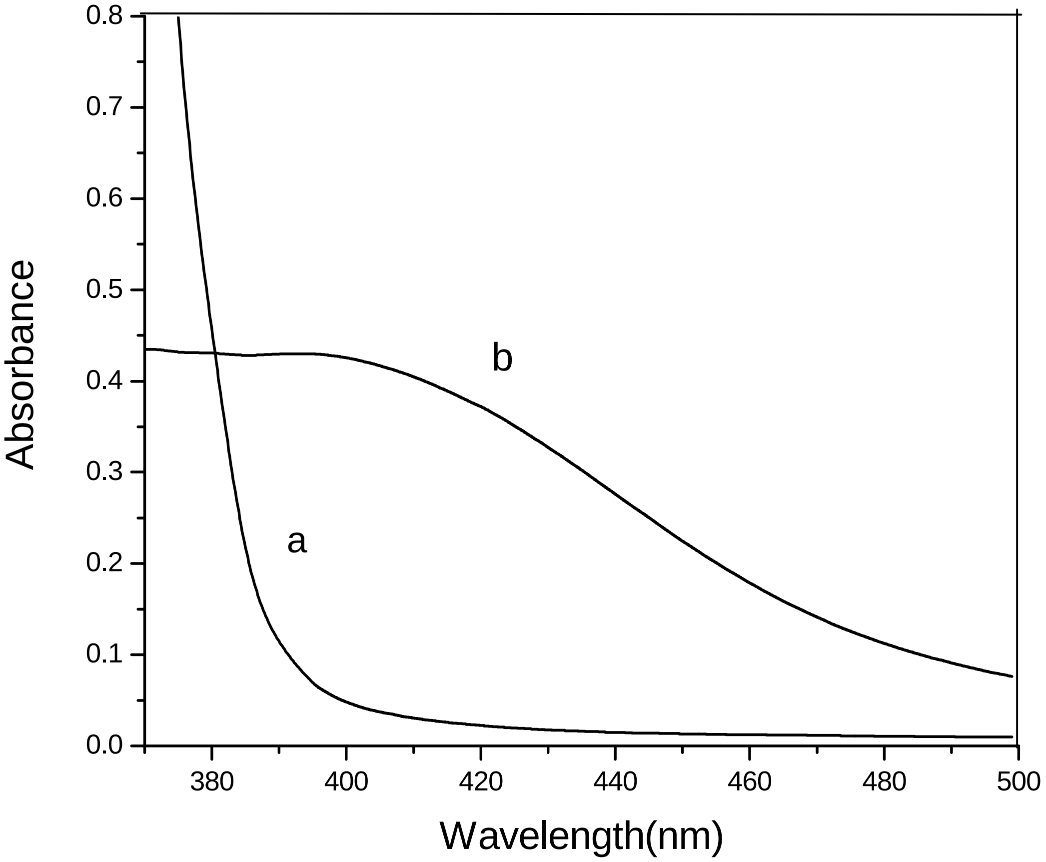

Fig.1. Absorption spectra of
a) 5-BHMBHBH Vs buffer blank
b) [Ti (IV)] – 5-BHMBHBH Vs reagent blank
[Ti (IV)] = 1.0 x10^{-4} M: [5-BHMBHBH] = 1.0 × 10^{-2} M
pH = 4.0

CONCLUSION

The present direct spectrophotometric method determination for the Ti(IV) using 5-BHMBHBH is a new simple , highly sensitive and selective method. It can be easily applied for the determination of Ti(IV) in alloy and steel samples. Although many sophisticated techniques such as pulse polarography, HPLC, AAS, ICP-AES, ICP-MS, etc. are available for the determination of titanium(IV) at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement for consumables and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in laboratories of developing countries with limited budget. The sensitivity in terms of molar absorptivity and precision in terms of relative standard deviation of the present method are very reliable for the determination of titanium(IV) in real samples.

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