

A NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF TRACE AMOUNTS OF TITANIUM(IV)

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Vinnakota Srilalitha¹, Aluru Raghavendra Guru Prasad^{2*},
Kakarla Raman Kumar³, Vahi Seshagiri⁴,
Lakshmana Rao Krishna Rao Ravindranath⁴

¹C.M.R. Institute of Technology, Hyderabad, A.P., India

²ICFAI Foundation for Higher Education, Hyderabad, A.P., India

³Malla Reddy College of Engineering, Hyderabad, A.P., India

⁴Sri Krishnadevaraya University, Anantapur, A.P., India

Abstract. *A new, rapid, simple, precise and extraction-free spectrophotometric method is proposed for the micro determination of titanium(IV) employing N'-(2-hydroxybenzylidene)-3-oxobutanehydrazide as a reagent. Under the optimum conditions established, the absorbance was found to increase linearly with the concentration of titanium(IV) in the range 1.757 to 17.57 $\mu\text{g mL}^{-1}$. The method parameters such as the molar absorptivity, Sandel sensitivity, stoichiometry of the complex, method detection limit and limit of quantification were reported. The reproducibility of the method was excellent and recoveries reported were ranging from 102 to 104%. The proposed method can be readily applied for the determination of titanium(IV) in synthetic mixtures and alloys.*

Key words: *spectrophotometry, titanium(IV), synthetic mixtures, alloys*

1. INTRODUCTION

Titanium is one of the important constituents of alloys. The combination of good strength, resistance to erosion and erosion-corrosion and high strength-to-weight ratio makes titanium suitable for many critical applications such as civilian and military air-frame parts, nuclear power plants, food processing plants, oil refinery heat exchangers, marine components and medical prostheses. In view of the increasing usage of titanium in different fields, it becomes necessary to develop simple and sensitive procedures for the analytical determination of titanium. Numerous methods were reported in the literature for the determination of titanium(IV) in trace levels [1-25]. Some of these methods involve tedious procedures and expensive instrumentation and are not feasible in a common laboratory. Many of these procedures have serious shortcomings, the most important

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* Corresponding author. E-mail: guruprasadar@yahoo.co.in.

being the interference of several elements [1-10]. Spectrophotometric techniques remain a frequent choice for routine analyses as they provide simple, accurate and inexpensive solutions when compared to other methods. Several spectrophotometric methods were reported in the literature for the analytical determination of titanium(IV) [11-25]. These methods adopt relatively complicated and time sensitive procedures or involve sensitive extraction steps prone to contamination at any stage of the analysis and hence require skilled analysts [11-25]. Unlike the procedures reported above [1-25], in this communication the authors propose a simple, sensitive and extraction free spectrophotometric method for the micro determination of titanium(IV).

2. MATERIAL AND METHODS

A Shimadzu UV-visible spectrophotometer (Model UV-160A) equipped with 1 cm matched quartz cells was used for absorbance measurements.

Double-distilled water and dimethylformamide were used throughout for the preparation of solutions. The buffer solutions were prepared by mixing 1 M hydrochloric acid and 1 M sodium acetate (pH 1.0-3.0) and 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.5-7.0). All chemicals and solvents used were of analytical reagent grade and were procured from Merck, India.

Required amount of potassium titanyl oxalate (Merck, India) was weighed into a Kjeldahl flask. Required amount of ammonium sulphate and concentrated sulphuric acid were added. The mixture was heated to boil and boiling was continued for 10 minutes. The solution was cooled, carefully transferred into the 100 mL standard flask and diluted to the mark with double distilled water. This serves as a stock solution ($1 \cdot 10^{-2}$ M) of titanium(IV). Working solutions were prepared by appropriate dilutions of the stock solution.

2.1. Synthesis of *N'*-(2-hydroxybenzylidene)-3-oxobutanohydrazide (HBOBH)

The hydrazone (HBOBH, *N'*-(2-hydroxybenzylidene)-3-oxobutanohydrazide, Fig. 1) of salicylaldehyde and acetoacetic acid hydrazide was synthesized by refluxing equimolar solutions of acetoacetic acid hydrazide and salicylaldehyde solutions prepared in aqueous methanol for two hours [26]. The contents were allowed to cool to the room temperature. The crude product obtained was filtered, washed with water, dried and recrystallised from hot aqueous methanol to get pure light yellowish crystals of *N'*-(2-hydroxybenzylidene)-3-oxobutanohydrazide. A solution of 0.01 M HBOBH prepared in dimethylformamide served as a stock solution. Acetoacetic acid hydrazide was synthesized by thoroughly shaking a mixture of equimolar quantities of hydrazine hydrochloride and acetoacetic acid in ice cold conditions. The crude compound obtained was recrystallised from ethanol to get pale yellow crystals (MP 107 °C).

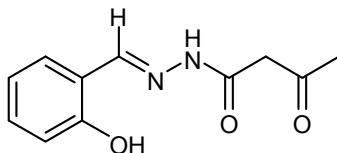


Fig. 1. Structural formula of *N'*-(2-hydroxybenzylidene)-3-oxobutanohydrazide

2.2. General experimental procedure

Aliquots of the metal ion solution of appropriate concentration, 5 mL of the buffer solution of required pH, 1 mL of HBOBH solution and 1 mL of dimethylformamide were transferred into a 10 mL volumetric flask. The solution was diluted to the mark with double-distilled water. The absorbance of the solution was measured at 500 nm against reagent blank.

2.3. Procedure for the preparation of the alloy sample

Required amount of the alloy sample (1. BCS-CRM 387, 2. BAS 387 and 3. Udimet 700) was dissolved in 2 mL of concentrated hydrochloric acid and 10 mL of concentrated nitric acid. The solution was evaporated to a small volume, 5 mL of 1:1 aqueous sulphuric acid was added and evaporated to dryness. The residue left over was extracted with 15 mL of water and carefully transferred into a 100 mL volumetric flask. The solution was made up to the mark with double-distilled water. This served as the stock solution.

3. RESULTS AND DISCUSSION

3.1. Complex formation

The titanium(IV) ions forms a reddish orange colored complex with HBOBH at pH 2. The complex shows an absorption maximum at 500 nm. The complex was instantaneously formed and was stable for at least six hours.

3.2. Optimization of experimental variables

The effect of pH on the intensity of the color reaction is shown in the Fig. 2. As seen from the Fig. 2, there is a slight increase in the absorbance with increasing pH from 1 to 2, whereas it has decreased in media of greater pH. Therefore the acetate buffer of pH 2 was optimal because of the higher sensitivity that could be achieved for the determination of titanium(IV). Hence further analytical investigations were carried out in buffer media of pH 2.

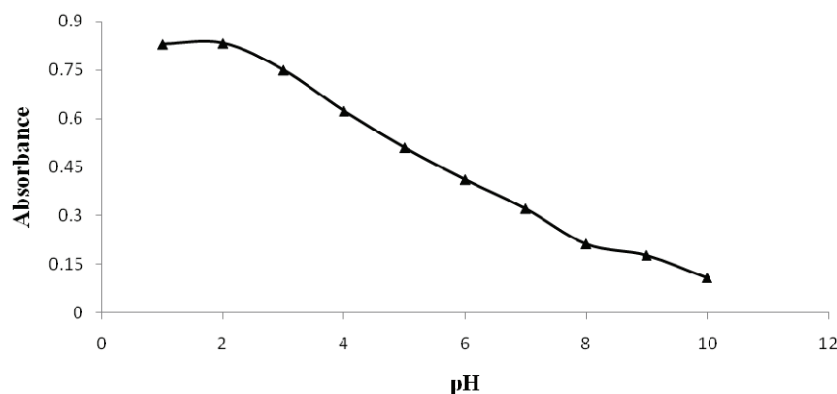


Fig. 2. The effect of pH on the absorbance of Ti(IV)-HBOBH complex ([Ti(IV)]= $1 \cdot 10^{-5}$ M; [HBOBH]= $1 \cdot 10^{-4}$ M, λ_{\max} =500 nm)

Figure 3 depicts the absorption spectra of a solution containing Ti(IV) and HBOBH, HBOBH and metal ions alone against the respective blank solutions. The figure revealed that the spectral profiles “a” and “b” were completely different from that of “c” and hence profile “c” was attributed to the complex formed between Ti(IV) and HBOBH. The complex solution has a maximum absorbance at 500 nm.

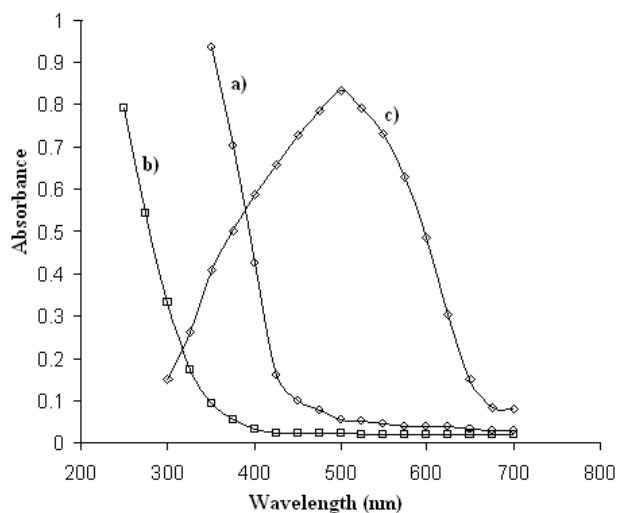


Fig. 3. Absorption spectra of a) HBOBH against water as blank, $[\text{HBOBH}] = 1 \cdot 10^{-4}$ M, pH 2; b) Ti(IV) against water as blank, $[\text{Ti(IV)}] = 1 \cdot 10^{-5}$ M, pH 2; c) Ti(IV)-HBOBH complex against a solution of reagent as blank, $[\text{Ti(IV)}] = 1 \cdot 10^{-5}$ M; $[\text{HBOBH}] = 1 \cdot 10^{-4}$ M, pH 2

The studies of the effect of concentration of the reagent reveal that a reagent excess of 40-fold was optimum for the complex formation. Hence, a 40-fold reagent excess was adopted for further investigations. However, the presence of excess of the reagent solution does not interfere with the color reaction.

3.3. Stoichiometry of the complex

The stoichiometry of the complex determined by Job's method of continuous variation [27] was found to be 1 : 2. The stoichiometry was further confirmed by mole ratio method [28]. The results are shown in the Figs 4 and 5, for Job's method and mole ratio method respectively. The stability constant of the complex determined by Job's method was $1.22 \cdot 10^{11}$. The tentative structure of Ti(IV)-HBOBH complex is given in the Fig. 6.

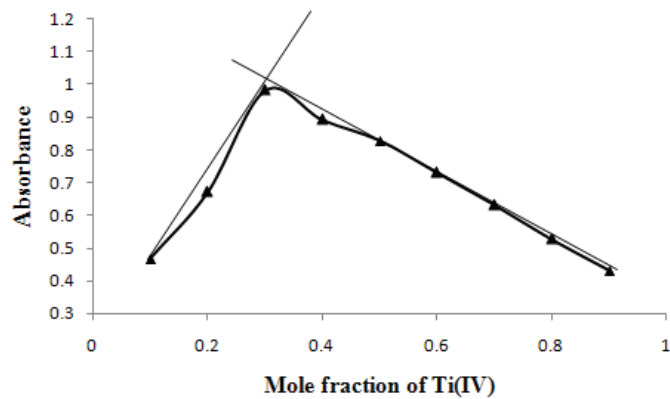


Fig. 4. Job's method of continuous variation ([HBOBH]=[Ti(IV)]= $1 \cdot 10^{-4}$ M, pH 2, λ_{\max} =500 nm)

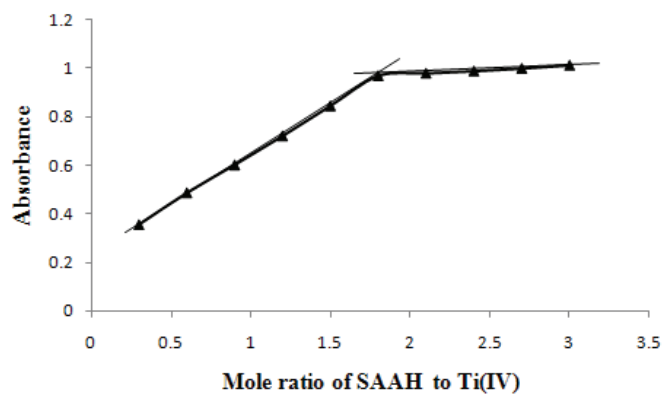


Fig. 5. Molar ratio method ([Ti(IV)]= $1 \cdot 10^{-4}$ M, different aliquots of HBOBH of concentration $1 \cdot 10^{-3}$ M, pH 2, λ_{\max} =500 nm)

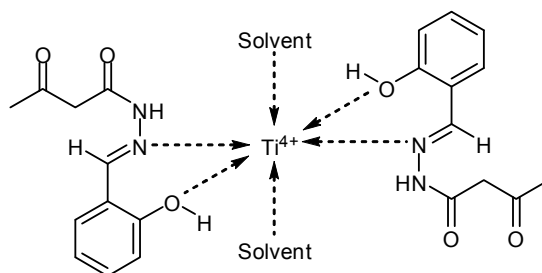


Fig. 6. Tentative structure of Ti(IV)-HBOBH complex

3.4. Construction of the calibration curve – analytical determination of Ti(IV)

A series of solutions containing different amounts of the metal ion were prepared as per the general experimental procedure. The absorbance of the solutions was measured at 500 nm. A calibration graph drawn between absorbance and the metal ion concentration indicates that Ti(IV) can be determined in the concentration range 1.757 to 17.57 $\mu\text{g mL}^{-1}$. The calibration graph is shown in the Fig. 7.

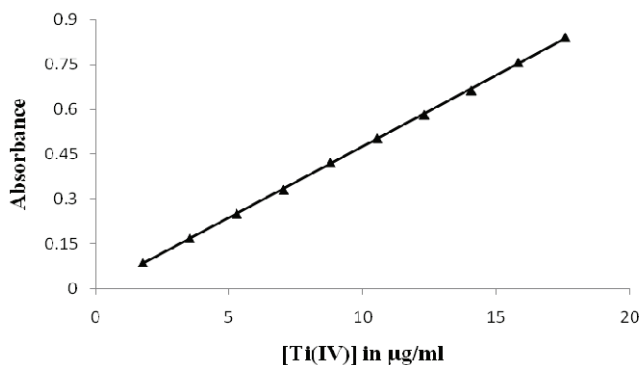


Fig. 7. Analytical determination of Ti(IV) ($[\text{HBOBH}] = 2 \cdot 10^{-3} \text{ M}$, pH 2, $\lambda_{\text{max}} = 500 \text{ nm}$)

3.5. Interference study

To assess the selectivity of the proposed method, the effect of foreign ions, urea and thiourea on the determination of titanium(IV) under the already established optimum conditions was studied by adding known quantities of the possibly interfering substance to a solution containing 0.72 ppm of titanium(IV). The tolerance limit was considered to be the amount that caused a $\pm 1\%$ deviation in the absorbance value. The results are shown in Table 1. It is evident from Table 1 that a large number of foreign substances did not interfere with the complex formation in the proposed method. However the tolerance limits of W(VI), Mo(VI), Mn(II) and Cu(II) were comparatively low.

Table 1. Effect of diverse ions, urea and thiourea on the determination of titanium(IV) ($[\text{Ti(IV)}] = 0.72 \text{ ppm}$)

Anion	Tolerance limit [ppm]	Cation	Tolerance limit [ppm]
Acetate	354.00	Ag(I)	80.90
Bromide	1198.70	Al(III)	20.98
Chloride	283.60	Bi(III)	208.98
Citrate	1890.00	Cu(II)	12.71
Fluoride	152.00	Hg(II)	20.06
Iodide	1269.00	Mo(VI)	9.59
Nitrate	496.00	Mn(II)	5.49
Oxalate	1232.00	Pb(II)	20.72
Phosphate	189.94	W(VI)	9.19
Tartrate	1776.00	Zn(II)	65.37
Thiocyanate	696.00		
Thiosulphate	1489.10		
Thiourea	608.96		
Urea	480.00		

3.6. A comparison with the already established methods

An advantage of the proposed method over the already reported ones is revealed in the following lines. As already mentioned, several methods were previously reported for the estimation of titanium(IV) at trace levels [1-25]. A review of the previously proposed spectrophotometric methods [11-25] is given in Table 2. The majority of these methods adopt relatively complicated and time consuming procedures or involve sensitive extraction steps prone to contamination at any stage of the analysis and hence, require skilled analysts [11-25]. Unlike the procedures listed in Table 2, the proposed method has the advantages of simplicity, selectivity and instantaneous analysis besides being accurate and precise. The photometric and analytical characteristics of the herein proposed method are shown in the Table 3.

Table 2. A review of the spectrophotometric methods to indicate the advantages of the proposed method

Reagent	λ_{\max} [nm]	Remarks	Molar absorptivity [L mol ⁻¹ cm ⁻¹]	Ref.
2,4-Dihydroxybenzaldehyde isonicotinoyl hydrazone	430 500	Narrow Beer's law range	$1.35 \cdot 10^4$	[15]
Cetyltrimethylammonium, cetylpyridinium or tetradecyldimethylbenzylammonium cation	420	Involves an extraction step	$(6-7) \cdot 10^4$	[16]
N ¹ -Hydroxy-N ¹ , N ² -diphenylbenzamidine and thiocyanate	400	Involves an extraction step; narrow Beer's law range	$2 \cdot 10^4$	[17]
2,3-Dihydroxynaphthalene	375	Involves extraction and re-extraction steps	$3.2 \cdot 10^4$	[18]
Thiocyanate and cetyltrimethylammonium bromide	421	Involves an extraction step	$1.1-1.0 \cdot 10^5$	[19]
Chlorpromazine hydrochloride	417	Involves an extraction step; narrow Beer's law range	$2.6 \cdot 10^4$	[20]
N-Pivaloyl-p-chloro-phenylhydroxylamine	380	Involves an extraction step	$5.3 \cdot 10^3$	[21]
N-Phenyllaurohydroxamic acid and phenylflurone	540	Involves an extraction step	$2.33 \cdot 10^5$	[22]
Mixed-ligand titanium(IV)-fluoride-alizarin complex	513	Involves an extraction step; narrow Beer's law range	$7.0 \cdot 10^4$	[23]
3-Hydroxy-2-methyl-1-(4-tolyl)-4-pyridone	355	Involves an extraction step; narrow Beer's law range	$1.6 \cdot 10^4$	[24]
2,6,7-Trihydroxyphenyl-fluorone derivatives, nitrilotriacetic acid and cetyltrimethylammonium bromide	576	Involves the formation of a quaternary complex	$1.9 \cdot 10^5$	[25]

Table 3. Photometric and analytical characteristics pertaining to the proposed method

Photometric characteristics		Analytical characteristics	
λ_{\max}	500 nm	Method detection limit	$0.385 \mu\text{g mL}^{-1}$
pH	2	Limit of quantification	$0.770 \mu\text{g mL}^{-1}$
Beer's law range	1.757 to $17.57 \mu\text{g mL}^{-1}$	Stability constant of the complex	$1.22 \cdot 10^{11}$
Molar absorptivity	$1.68 \cdot 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$	Recovery	102-104%
Sandell sensitivity	$0.00285 \mu\text{g cm}^{-2}$	Relative standard deviation	1.595
		([Ti(IV)] = $8.8 \mu\text{g mL}^{-1}$, n=10)	
		Regression Equation	$A = 0.0475C + 0.0005$
		Correlation Coefficient	0.9998

3.7. Applications

The proposed method has been applied for the determination of titanium(IV) in synthetic mixtures and the alloys containing Ti(IV). The data presented in the Table 4 and 5 indicate the accuracy and precision of the proposed method.

Table 4. Determination of titanium(IV) in synthetic mixtures

Titanium(IV) [$\mu\text{g mL}^{-1}$]		Recovery	RSD [%]
Taken	Found ^a		
3.5	3.627 \pm 0.092	103.63	3.539
8.8	9.109 \pm 0.104	103.51	1.595
15.8	16.121 \pm 0.17	102.03	1.473

^aThe value of t at 95% confidence level is 2.26

Table 5. Determination of titanium(IV) in alloy samples

S.No	Chemical composition of alloy sample [%]	Percentage of titanium(IV)		Error [%]
		Certified	Found	
1.	Ni=41.90; Fe=36.00; Cr=12.50; Mo=5.80; Ti=2.94; Al=0.24; Co=0.20; Cu=0.30	2.94	2.87	-0.07
2.	Ni=41.90; Fe=36.00; Cr=12.46; Mo=5.83; Ti=2.95; Si=0.28; Al=0.24; Co=0.21; Mn=0.08; Cu=0.032; C=0.03	2.95	2.90	-0.05
3.	Cr=15.00; Co=18.00; Al=4.30; Mo=5.21; C=0.08; B=0.003; Ti=3.50	3.50	3.40	-0.10

4. CONCLUSIONS

The article presents a new spectrophotometric method for the determination of trace amounts of titanium(IV). The major advantage of this method is that the color development was instantaneous and the method does not involve complicated procedures. Besides that the proposed method had a broad linear calibration range and is comparatively selective. The method has been successfully applied for the determination of titanium(IV) in synthetic mixtures containing Ti(IV) and alloy samples.

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NOVA SPEKTROFOTOMETRIJSKA METODA ZA ODREĐIVANJE TITANA(IV) U TRAGOVIMA

**Vinnakota Srilalitha, Aluru Raghavendra Guru Prasad,
Kakarla Raman Kumar, Vahi Seshagiri,
Lakshmana Rao Krishna Rao Ravindranath**

Predložena je nova, brza i precizana spektrofotometrijska metoda (koja ne zahteva ekstrakciju), zasnovana na primeni N'-(2-hidroksibenziliden)-3-oksobutanhidrazida (HBOBH) kao reagesa, za određivanje mikrokoličina titana(IV). Pod unapred određenim optimalnim uslovima, pokazano je da u opsegu od 1,757 do 17,57 $\mu\text{g mL}^{-1}$ apsorbanca linearno raste sa porastom koncentracije titana(IV). Utvrđeni su i parametri metode kao što su molarna apsorptivnost, Sendel-ova osetljivost, stehiometrija kompleksa, granica detekcije i granica kvantifikacije. Reprodutivnost metode je bila odlična, a "recovery" se kretao u opsegu od 102 do 104%. Predložena metoda je primenljiva za određivanje titana(IV) u sintetičkim smešama i legurama.

Ključne reči: spektrofotometrija, titan(IV), sintetičke smeše, legure