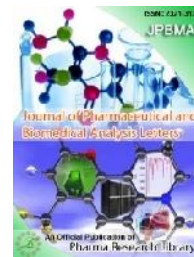




# International Journal of Medicine and Pharmaceutical Research

Journal Home Page: [www.pharmaresearchlibrary.com/ijmpr](http://www.pharmaresearchlibrary.com/ijmpr)



## RESEARCH ARTICLE

### A New Non-Extractive Spectrophotometric Method for the Determination of trace Quantities of titanium (IV)

Dr. Srinivas Jagarlapudi\*, Dr. V. Suryanarayana Rao, A. Ravi Kumar, Panchumarthi Srinivas, CH. Sunil Babu

Obvez Labs Pvt. Ltd. Plot No. 22 & 23, ALEAP Industrial Area, Pragathi Nagar, Hyderabad, Telangana-500090, India

#### ABSTRACT

The reaction between Ti (IV) and 3, 4-Dihydroxybenzaldehyde isonicotinoyl hydrazone (3, 4-DHBINH) has been investigated in sodium acetate and acetic acid buffers. A highly sensitive and simple procedure for the determination of Ti (IV) is suggested. The orange coloured complex shows maximum absorption at 420 nm in a buffer solution of pH6.0. The composition of the complex is 1:1 (M: L). Beer's law is obeyed in the range 0.478 µg/ml to 2.394 µg/ml. The molar absorptivity and Sandell's sensitivity are calculated as  $1.4933 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.00317 \mu\text{g/cm}^2$  respectively.

**Keywords:** 3,4-Dihydroxybenzaldehyde isonicotinoyl hydrazone, titanium(IV), spectrophotometry.

#### ARTICLE INFO

##### Corresponding Author

**Dr. Srinivas Jagarlapudi**

Obvez Labs Pvt. Ltd. Plot No. 22 & 23,  
ALEAP Industrial Area, Pragathi Nagar,  
Hyderabad, Telangana-500090, India  
MS-ID: JPBMAL3893



PAPER-QR CODE

**ARTICLE HISTORY:** Received 11 May 2019, Accepted 29 June 2019, Available Online 18 January 2019

**Copyright** ©2019 Srinivas Jagarlapudi, et al. Production and hosting by Pharma Research Library. All rights reserved.

This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

**Citation:** Srinivas Jagarlapudi, et al. A New Non-Extractive Spectrophotometric Method for the Determination of trace Quantities of titanium (IV). *J. Pharm, Biomed. A. Lett.*, 2019, 7(2): 48-52.

#### CONTENTS

1. Introduction . . . . .	48
2. Materials and Methods. . . . .	49
3. Results and Discussion. . . . .	49
4. Conclusion . . . . .	51
5. References. . . . .	51

#### 1. Introduction

Titanium exists in nature in its most common oxidation state as titanium (IV). The lower oxidation states are quite readily oxidized to titanium (IV) by air, water or other reagents. Titanium compounds are highly corrosion resistant to chloride solution, sea water, nitric acid, chlorine dioxide, sulphur dioxide and to other bleaching agents.

Journal of Pharmaceutical and Biomedical Analysis Letters

Titanium is used as an alloy metal. Many organic compounds of titanium such as phthalates, oxalates, gluconates, tetraethylate and butyl titanate are widely synthesized and used extensively. Titanium is a constituent of a number of azodyes. The analytical applications of hydrazone derivatives for the spectrophotometric

determination of metal ions have been reviewed by R.B. Singh et al<sup>1</sup>. Very few hydrazones are reported for the spectrophotometric determination of titanium<sup>2-5</sup>. Among the sensitive methods reported, most of them involve extraction processes<sup>6-12</sup> and suffer from lack of selectivity. Classical methods using hydrogen peroxide<sup>13</sup> and chromotropic acid<sup>14</sup> suffer from the disadvantages of interference and critical pH maintenance respectively. Srilalitha et al<sup>15</sup> described a method for the spectrophotometric determination of titanium with **2N'-(2-hydroxybenzylidene)-3-oxobutanhydrazide (HBOBH)**, Cejar et al<sup>16</sup> determined titanium with pyridoxal nicotinoyl hydrazone. V. Vojkovi, V.A. Zivci<sup>17</sup> is used thiocyanate complex to determine Ti (IV) spectrophotometrically. The survey of literature shows that isonicotinoyl hydrazones are not widely employed for the determination of titanium. Hence, spectrophotometric investigations are made with 3,4-dihydroxybenzaldehyde isonicotinoyl hydrazone for the determination of Ti (IV). The results obtained are presented in this research article.

## 2. Materials and Methods

### General Methods.

3,4-dihydroxybenzaldehyde and isonicotinic acid was purchased from sigma Aldrich (Milwaukee, WI, USA). Methanol and dimethyl formamide (DMF) of analytical grade quality were purchased from qualigens (Mumbai, Maharashtra, India). Titanium alloys (Udimet-500, 700) were purchased from sigma Aldrich and used without further purification. For all absorption measurements, an ELICO SL-164 double beam U.V. Visible spectrophotometer is used. pH measurements were made by using an ELICO LI 160 digital pH meter.

### Synthesis of 3, 4-DHBINH:

The 3,4-DHBINH was prepared by equimolar reactions of 3,4-dihydroxybenzaldehyde (0.500g; 3.6 mmol), isonicotinic acidhydrazide (0.496g ; 3.6 mmol) in methanol through refluxing for 3hrs. It was allowed to stand at room temperature until the yellow colour crystals were formed. The yellow colour crystals were dried and used for the complex preparation.

### Preparation of Ti (IV) sample solution:

Stock solutions of 0.01 M titanium (IV) was prepared by dissolving appropriate quantity of analytical grade potassium titanyl oxalate (Merck India) in double distilled water and standardized. Lower concentrations were prepared by diluting the stock solutions. The 5 ml of buffer solution of pH 6.0, 1 ml of Ti (IV) ( $1.0 \times 10^{-3}$ M) and 1.0 ml of reagent ( $1.0 \times 10^{-2}$ M) were taken in a 10 ml standard flask. The contents of the flask were made up to the mark with double distilled water. Solutions were shaken well for homogeneous appearance. Blank solution was prepared without metal ion. 0.01M solution of 3, 4-DHBINH was prepared by dissolving appropriate quantity in DMF.

### Preparation of titanium alloy sample:

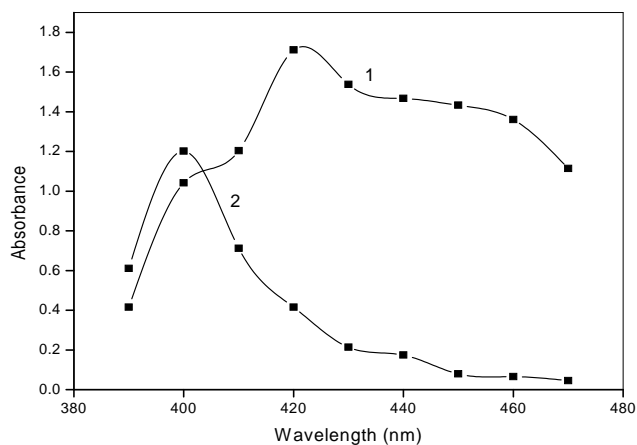
Required amount of the alloy sample (1. Udimet 500, 2. Udimet700) was dissolved in 2 mL of concentrated hydrochloric acid and 10 mL of concentrated nitric acid. The solution was evaporated to a small volume; 5 mL of 1:1 aqueous sulphuric acid was added and evaporated to

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. A suitable aliquot of the sample solution is added to a 10 ml standard flask containing 5ml of buffer solution of pH 6.0 1ml of 0.1M tartrate or 1 ml of 0.1M hypo [to mask Mo(VI) or Cu(II)] and 1 ml of the reagent ( $1.0 \times 10^{-2}$ M) solution and made up to the mark with distilled water. The absorbance of the solution is measured at 420 nm against the reagent blank. The absorbance values are referred to the predetermined calibration plot at 420 nm to compute the amount of titanium (IV) present in the sample.

## 3. Results and Discussion

### Absorption spectra

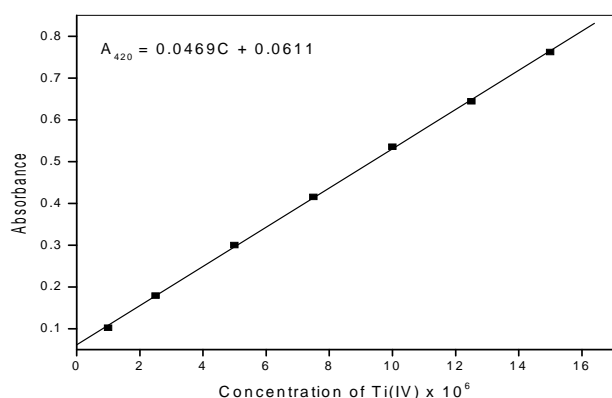
The complexes formed a very intense and dark coloured solution and thus, very low concentrations have been used. Absorption spectrum of the complex against 3,4-DHBINH as blank and 3,4-DHBINH against buffer as blank were recorded in the wavelength ranging from 350 to 500 nm. Since the complex showed maximum absorbance (max = 420 nm) at pH 6.0. Hence, pH 6.0 is selected for all experimental studies. At this wavelength 3, 4-DHBINH has low absorbance which is shown in fig. 1. The effect of 3,4-DHBINH concentration on absorbance spectra was also studied by varying amounts of 3,4-DHBINH with fixed amount of Ti(IV). It was also observed that 10 fold excess of reagent is sufficient for complete color development, and there was no substantial change in the absorbance values even when adding excess amount of reagent. The stability of the complexes was evaluated by the effect of time on complexation and addition of organic solvents to the complex solution. complex solution containing fixed concentration of Ti(IV) and 3,4-DHBINH, measuring the absorbance for every 10 min and after the addition of every organic solvent. There were no appreciable change in absorbance for more than an hour and after the addition of any organic solvent, which indicates the stability of complex.



**Fig .1:** Absorption Spectrum of Ti(IV) and 3,4-DHBINH System; Curve 1: Ti(IV) and 3,4-DHBINH Vs reagent blank ; Curve 2: 3,4-DHBINH-System Vs buffer blank. [Ti(IV)] =  $1 \times 10^{-4}$ M; [3,4-DHBINH] =  $1 \times 10^{-3}$ M

**Beer's law**

We tested whether the present method obeys Beer's law by varying the volumes of Ti(IV) solutions in the range 0.478  $\mu\text{g/ml}$  to 2.394  $\mu\text{g/ml}$ . Blank solutions were prepared without metal ion and the absorbance values were measured at 420 nm against blank and 3,4-DHBINH. A linear relationship was found between the absorbance ( $A_{\text{max}}$ ) and the concentration of the metal ion complex in the concentration range 0.478  $\mu\text{g/ml}$  to 2.394  $\mu\text{g/ml}$ . The experimental data referred into straight line equation  $A = mc + b$ , Where A is the measured absorbance, c is the concentration of metal ion in mol/l, m is angular coefficient, and b is y-intercept. The relationship were obtained as  $A_{420} = 0.0469C + 0.0611$ . The other statistical parameters were also calculated by applying various statistical methods. For example, the molar absorptivity and Sandell's sensitivity are calculated as  $1.4933 \times 10^4 \text{L mol}^{-1} \text{cm}^{-1}$ ,  $0.00317 \mu\text{g cm}^{-2}$  respectively.



**Fig .2:** Beer's law range of Ti (IV) and 3, 4-DHBINH System; [Ti (IV)] =  $1 \times 10^6 \text{M}$ ; [3, 4-DHBINH] =  $1 \times 10^{-4} \text{M}$

**Composition of the complex:**

The composition of Ti (IV) – 3, 4-DHBINH complex is found to be 1:1. It was determined by studying jobs method

& mole ratio method. The stability constant calculated by the Job's method is  $11.75 \times 10^3$ .

**Effect of diverse ions**

Under optimum conditions the effect of diverse ions on determination of Ti (IV) is studied. The tolerance limit of a diverse ion was taken as the amount of diverse ion required to cause an error of  $\pm 2\%$  in the absorbance. The tolerance limits of various diverse ions in the determination of 0.2394  $\mu\text{g/ml}$  titanium are shown in table 1.

**Applications****Procedure**

A suitable aliquot of the sample solution is added to a 10 ml standard flask containing 5ml of buffer solution of pH 6.0 1ml of 0.1M tartrate or 1 ml of 0.1M hypo [to mask Mo(VI) or Cu(II)] and 1 ml of the reagent ( $1.0 \times 10^{-2} \text{M}$ ) solution and made up to the mark with distilled water. The absorbance of the solution is measured at 420 nm against the reagent blank. The absorbance values are referred to the predetermined calibration plot at 420 nm to compute the amount of titanium (IV) present in the sample. The results are tabulated in table 2.

**Antimicrobial and Antifungal Activity of Ti (IV)-3, 4-DHBINH:**

In this method antimicrobial and anti fungal activities of titanium (IV) – 3, 4-DHBINH complex is studied. Agar diffusion method<sup>18</sup> and tube dilution<sup>19</sup> methods are used for biological studies. Microorganism belongs to gram negative and gram positive bacteria such as *E-coli*, *Pseudomonas aureginosa*, *Basillus subtilis*, *Streptococci* were used to examine antibacterial activity of palladium complex and results are incorporated in Table 3 & 4. In similar lines antifungal activity for *Aspergillus niger*, *Penicillium notatum*, is determined and results are shown in Table 5 and compared with standard.

**Antibacterial**

Antibacterial study was carried out by agar diffusion method using streptomycin as standard. Activity studies of the compounds on each organism were done in triplicate, and the average has been considered.

**Table 1:** Effect of diverse ions (Ti (IV) = 0.2394  $\mu\text{g/ml}$ )

Diverse ion	Tolerance limit ( $\mu\text{g/ml}$ )	Diverse ion	Tolerance limit ( $\mu\text{g/ml}$ )	Diverse ion	Tolerance limit ( $\mu\text{g/ml}$ )
Fluoride	200	Mo (VI)	2.5	Ni (II)	3
Chloride	270	Pb (II)	27	Ag (I)	5
Citrate	1920				
iodide	1190	W (VI)	15	Hg (II)	18
nitrate	420	Co (II)	3	Mg (I)	1
Acetate	310	Cr (VI)	3	Th (IV)	9
oxalate	1235	Cu (II)	13.5	-	-
Phosphate	175	Fe (II)	4	-	-
tartarate	1785				
thiosulphate	1448	-	-	-	-

**Table 2:** Determination of titanium in alloys

Alloy <sup>a</sup>	Composition (%) certified	Composition (%) found*	Recovery (%)
(i) Udimet-500	2.90	2.86	98.6
(ii) Udimet-700	3.50	3.52	100.6
(iii) Titanium based alloy <sup>b</sup>	70.14	70.01	99.8

\*Average of five determinations.

Composition of samples (%) as follows:

- a. i. Cr, 18; Co, 18.5; Al, 2.9; Mo, 4.8; C, 0.08; B, 0.006; Zr, 0.05; Ti, 2.9;  
 a. ii. Cr, 15; Co, 18; Al, 4.3; Mo, 5.21; C, 0.08; B, 0.003; Ti, 3.5;  
 b. Ti, 70.14; Ni, 15.03; Cu, 14.83;

**Table - 3**

Compound	Diameter of Zone of Inhibition in mm					
	<i>Pseudomonas aureginosa</i>			<i>E-Coli</i>		
	200 µg/0.1 ml	400 µg/0.1 ml	800 µg/0.1 ml	200 µg/0.1 ml	400 µg/0.1 ml	800 µg/0.1 ml
<b>Ti (IV) 3,4-DHBINH</b>	10	13	15	11	16	18
<b>Std</b>	24	-	-	30	-	-

STD : Streptomycin

Solvent : DMF

**Table - 4**

Compound	Diameter of Zone of Inhibition in mm					
	<i>Bacillus subtilis</i>			<i>Streptococci</i>		
	200 µg/0.1 ml	400 µg/0.1 ml	800 µg/0.1 ml	200 µg/0.1 ml	400 µg/0.1 ml	800 µg/0.1 ml
<b>Ti (IV) 3,4-DHBINH</b>	--	11	13	14	13	15
<b>Std</b>	22	-	-	28	-	-

STD : Streptomycin

Solvent : DMF

--- : Not active

**Table - 5**

Compound	Diameter of Inhibition Zone in mm					
	<i>Aspergillus niger</i>			<i>Penicillium notatum</i>		
	60 µg/0.1 ml	120 µg/0.1 ml	400 µg/0.1 ml	60 µg/0.1 ml	120 µg/0.1 ml	400 µg/0.1 ml
<b>Ti (IV) 3,4-DHBINH</b>	12	14	17	13	15	18
<b>Std</b>	20	-	-	23	-	-

STD : Griseofulvin

Solvent : DMF

----- : Not active

#### 4. Conclusion

In summary we have synthesized 1:1(metal: ligand) of titanium (IV) complexes with 3,4-DHBINH as a new complexing reagent. This method shows simplicity, adequate selectivity, precision and accuracy with low operating cost compared to other analytical procedures. The effect of time and organic solvent was determined by measuring absorbance. We proved that the analytical procedure obeys beer's law even at low concentrations. Hence this method is non-extractive it requires simple sample preparation. The above metal ligand complex shown antibacterial and fungal activity indicates the biological importance. By using our present method, further studies to determine various metal ions are currently in progress.

#### 5. References

- [1] Singh, R.B.; Jain, P. and Singh, R.P. *Talanta* **29**, 77-84 (1982).
- [2] I. Lopez-Garcia, I. Arnau-Jerez, N. Campillo and M. Hernandez-Cordoba, Determination of tin and titanium in soils, sediments and sludges using electrothermal atomic absorption spectrometry

with slurry sample introduction, *Talanta*, **62** (2), 413-419 (2004).

- [3] Y.K. Agrawal and S. Sudhakar, Extractive spectrophotometric and inductively coupled plasma atomic emission spectrophotometric determination of titanium by using dibenzo-18-crown-6, *Talanta*, **57** (1), 97-104 (2002).
- [4] F.S. Kika and D.G. Themelis, Selective stopped-flow sequential injection method for the spectrophotometric determination of titanium in dental implant and natural Moroccan phosphate rock, *Talanta*, **71** (3), 1405-1410 (2007).
- [5] Dolgorev, A.V *Zh Analit. Khim*, **28**, 1093 (1973).
- [6] P.K. Tarafder and R. Thakur, Micelle mediated extraction of titanium and its ultra-trace determination in silicate rocks, *Talanta*, **75** (1), 326-331 (2008).
- [7] B. Tamhina and V. Vojkovi, Extraction and spectrophotometric determination of titanium (IV) with 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone, *Microchimica Acta*, **88** (1-2), 135-145 (1986).

- [8] R.L. Nunez, M.C. Mochon and A.G. Perez, Extraction and spectrophotometric determination of titanium (IV) with alizarin and fluoride, *Talanta*, **33** (7), 587-591 (1986).
- [9] Moro Garcia R; Sanchez Uria, J.E. and Arribas, s; Imeno, *J. Quin, Anal*; **30**, 385-388 (1976).
- [10] Dzymbo, L.N; Matenkova, I.N; and Pochianova, V.N; *Zn. Anal. Khim*; **27**, 2386-2391 (1972).
- [11] O. Babaiah, C.K. Rao, T.S. Reddy and V.K. Reddy, *Talanta*, **43** (4), 551-558 (1996).
- [12] Tananaiko, M.M. and Nebylits, Kaya, S.V. *Zavodsk Lab*, **28**, 263 (1962).
- [13] Y. Xiong, Z.-r. Zhou and F.-h. Wu, *Journal of China University of Mining and Technology*, **17** (3), 418-423 (2007).
- [14] R. Purohit and S. Devi, *Analyst*, **117** (7), 1175-1177 (1992).
- [15] Vinnakota Srilalitha; Aluru Rahavendra Guru Prasad et al *Factauniversitatis; Physics, Chemistry and Technology* Vol. 8, No 1, 2010.
- [16] Cejas, M.A; Gomez, Hens, A. and Valcarcel, *M.Quim. Anal*; **3**, 164 (spain) (1984).
- [17] V. Vojkovi , V.A. Zivci and V. Druskovi , *Spectroscopy Letters*, **37** (4), 401-420 (2004).
- [18] Cremer, A., *Microbiological methods*, 6<sup>th</sup> eds. *Butterworth co., Ltd.*, pp. 235 -241.
- [19] Robert Cruickshank, R, Duguid, J.P., Marmion, R.H.A. Swain, *Medicinal microbiology*, Vol. 2, 12<sup>th</sup> eds. Edinburgh, London, 1975, p. 170.