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Determination of titanium and vanadium with 2,4-Dihydroxy acetophenone isonicotinoylhydrazone by Direct and derivative spectrophotometric method

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ABSTRACT

A simple and sensitive spectrophotometric method is developed for the determination of titanium in and vanadium in aqueous medium. The metal ions form a red coloured complex with 2'4-Dihydroxyacetophenone isonicotinoylhydrazone(RPINH) in the pH range 1-7. The complex shows absorption maximum at λ_{max} *490nm and 400nm respectively. The molar absorptivity and sandell's sensitivity of the method are* 1.0×10^4 $Lmol^{-1}$ cm^{-1} *and* 0.0048 μgcm^{-2} *and* 8.9×10^3 $Lmol^{-1}$ cm^{-1} *and* 0.0056 μg cm^{-2} *respectively. Beer's law is obeyed in the range of 0.47-3.35* μg ml^{-1} *and 0.255 – 3.056* μg ml^{-1} *respectively. A method for the determination of titanium and vanadium by first order derivative spectrophotometry is also proposed. The methods have been employed successfully for the determination of titanium and vanadium in several water, alloy and steel samples.*

Key words: Spectrophotometry, Titanium, vanadium, 2'4-Dihydroxyacetophenone isonicotinoyl hydrazone**,** Water, Alloy and steel samples.

INTRODUCTION

Titanium exists in nature in its most and common oxidation state as titanium (IV). 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. Titanium alloys are principally used for aircrafts and missiles, where light weight strength and ability to withstand extremes of temperature are important. Its capacity for joining with bone and other tissue-Osseo integration makes it suitable for medical applications, such as total replacement of arthritis hips, knee joints, facial treatment and dental implants [1-2].

Titanium dioxide is also used as white pigment in paints. The paint, pigment, paper and pulp industries discharge a very high amount of titanium. Most of the reagents used for extraction, separation and determination of titanium shows serious interference to vanadium, molybdenum, zirconium, iron, etc., [3-5].

Vanadium is an important element in environmental and biological studies. Vanadium in trace amounts (ng/ml) is an essential element for normal cell growth but can be toxic when present at higher, concentration [6]. The toxicity of vanadium is dependent on its oxidation state [7-8], V(V) as vanadate is more toxic than V(IV), present as vanadyl ions. Vanadium compounds are toxic to human beings and animals. It inhibits biosynthesis of cholesterol in mammals. Atmospheric pollution by this element leads to lung diseases. Due to its toxicity, the determination of vanadium is very important. Some types of samples e.g. tap water [9] and ultrapure [10], require ultra trace determination of vanadium.

Vanadium chemicals are used in a variety of applications. Such as in ceramics, catalysts and electronics equipment, in liquid – phase oxidation reactions and as sodium or ammonium vanadates in fuel gas scrubbers. Vanadium also plays an important role in biochemistry and physiology. Its role in physiological systems includes normalization sugar levels, participation in various enzyme systems as an inhibitor and a co-factor and catalysis of the oxidation of various amines [11-12]. Although vanadium can exist in oxidation states from II to V in aqueous solutions. Most methods have concentrated on its determination in the IV and V states.

The analytical application of hydrazone derivatives for the spectrophotometric determination of metal ions has been reviewed by R.B. Singh et al [13]. A thorough literary survey has revealed that a few number of hydrazones are available for the spectrophotometric and extractive spectrophotometric determination of titanium(IV) [14-21]. Among the sensitive methods reported, most of them involve extraction processes [22-28] and suffer from lack of selectivity. Classical methods using hydrogen peroxide [29] and chromotropic acid [30] suffer from the disadvantages of interference and critical pH maintenance respectively. It indicates that the potentiality of hydrazones is not fully utilized.

Current techniques for trace determination of vanadium include catalytic analysis[6,31], neutron activation analysis [NAA] [32] atomic absorption spectrometry (AAS) [33], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [34] and ICP mass spectrometry [35]. However, many of these methods require laborious procedures for pre-concentration. Disadvantages of ICP-MS and NAA include the high cost of instrumentation. Among the most sensitive methods for the determination of vanadium are those based on its ability to catalyze the oxidation of various organic dyes [36-40].

2-Methyl isonicotinic acid salicylalhydrazone is employed for the direct spectrophotometric determination of vanadium by Dudarev [41] et al. Sreenivasulu Reddy [42] et. al. studied the colour reaction between vanadium(IV) and RPINH spectrophotometrically in the pH range 3.0 – 6.0. The complex formed by V(V) in acidic 50% aqueous ethanol medium with acetone isonicotinoylhydrazone and 4-hydroxybenzaldehyde isonicotinoylhydrazone are used for spectrophotometric determination of V(V) [43]. Of the different hydrazones employed as analytical reagents for the spectrophotometric determination of vanadium isonicotinoyl hydrazones are very scarcely used.

This paper describes the simple, rapid, sensitive, selective and direct spectrophotometric determination of micro amounts of titanium and vanadium are reported in aqueous medium as their RPINH complexes and a first order derivative spectrophotometric method is described for the determination of these two metals in which interference seen with the zero order method is eliminated.

Derivative spectrophotometry is a very useful approach for determining the concentration of single components in mixture with over lapping spectra as it eliminates much of the interference. It has recently been used to eliminate interference during spectrophotometric analysis [44-47]. It has been widely used in pharmaceutical analysis, amino acid and protein analysis, clinical chemistry, environmental analysis etc., [48]. But less often in inorganic analysis [49, 50]

MATERIALS AND METHODS

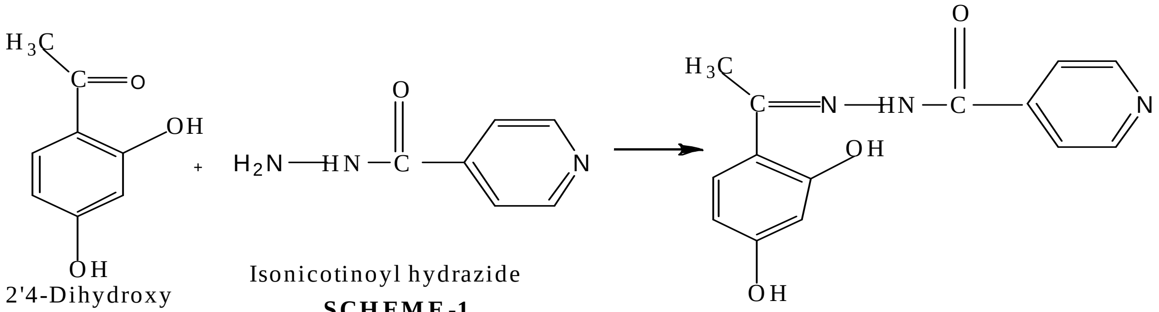
A Shimadzu 160A UV visible spectrophotometer equipped with 1.0 cm quartz cells and Elico Model LI-120 pH meter were used for absorbance and pH measurements in present study. Suitable settings for first-order derivative are as follows: special band width 2nm; wave length readability , 0.1 nm increment ; scan speed fast (nearly 3600 nm min^{-1}); wave accuracy ± 0.5 nm with automatic wave length correction; recorder; computer controlled thermal graphic printer with cathode ray tube, and with nine degrees of freedom in the wave length range 800-400nm. The reactions of some important metal ions were tested at different pH values. The absorbance was measured in 350-600 nm range against the reagent blank.

Reagent and solutions

All chemicals used were of analytical-reagent grade of the highest purity available procured from Merck. Doubly distilled de-ionized water was used throughout the experiment. Glass vessels were cleaned soaking in acidified solutions of $K_2Cr_2O_7$ followed by washing with con. HNO_3 and were rinsed several times with high purity de-ionized water.

1.1 Preparation of 2’4-Dihydroxyacetophenone isonicotinoylhydrazone(RPINH):

The reagent (RPINH) Resacetophenone isonicotinoyl hydrazone is prepared by refluxing a mixture of equal volumes of equimolar solutions of isonicotinoyl hydrazide and resacetophenone in aqueous methanol. One or two pellets of sodium hydroxide are added to assist condensation. The refluxing is continued for about 3 hours such that the reaction mixture turns yellow. The contents are then cooled and the yellow solid separated is washed with water and with cold dilute aqueous methanol. The yellow solid is recrystallized from methanol or dimethyl formamide in presence of norrit. Yellow needle shaped crystals decomposing between 267-271^0 C are formed, yild is 4.8 g; as shown in Scheme 1.



2'4-Dihydroxy acetophenone

Isonicotinoyl hydrazide

SCHEME-1

2'4-Dihydroxyacetophenone isonicotinoylhydrazone(RPINH)

A 0.01 M solution in DMF is used in the studies.

The compound was characterized by IR and ^{1}H-NMR spectral data.

2.2 RPINH solution

The reagent, 2'4-Dihydroxyacetophenone isonicotinoylhydrazone solution (0.01M) was prepared by dissolving 0.0677g of the compound in dimethylformamide (DMF) in 25-ml standard flask. The reagent solution is stable for at least 12h. Fresh reagent solution is prepared every time before use.

2.3 Titanium (IV) solution

This was prepared by dissolving the requisite quantity of $K_2TiO(C_2O_4)_2.2H_2O$ (AR,BDH) is dissolved in double distilled water in a 100 ml volumetric flask to get 1x10^{-2}M solution and standardized. The stock solution is suitably diluted to get the required concentration.

2.4 Vanadium (IV) solution

A stock solution (1000 µg/ml) of vanadium (IV) is prepared by dissolving 0.2393g of $(VO)_2$ $SO_4.4H_2O$ (Merck) in water and adding H_2SO_4 to about pH 7.0 and diluting to the mark in a 100ml standard flask.

2.5 Buffer solutions

For the preparation of buffer solutions, 1M HCl and 1M sodium acetate (pH 1-3), and 0.2 M acetic acid and 0.2 M Sodium acetate (pH 3.2 – 7) were used.

2.6 Preparation of alloy sample solutions:

A 0.1 - 0.5 g of alloy sample is dissolved in a mixture of 2 ml HCl and 10 ml $HN0_3$. The resulting solution is evaporated to a small volume. To this 5 ml of 1:1 H_2O : H_2SO_4, mixture is added and evaporated to dryness. The residue is dissolved in 15 ml of distilled water and filtered through Whattman filter paper No. 41. The filtrate is collected in a 100 ml volumetric flask and made up to the mark with distilled water. The solution is further diluted as required.

The amount of titanium present in the sample solutions was calculated from the predetermined calibration plots. In zero order spectrophotometry. 1 ml of 1M ascorbic acid was added to mask iron(III).

2.7 Preparation of river water sample:

20ml of sample is mixed with 0.5ml of 0.1M urea and heated at 90^{o}c for 20 min. Then 0.3ml of Ag^+ (5 x 10^{-3}M) and 2ml of methanol (0.125M) are added and the solution diluted to 50ml with water. The proposed method is applied to the determination of vanadium in a river water sample by following the procedure.

A known aliquot of the sample of river water is added to a 10ml of volumetric flask containing 5ml buffer, (pH 4.0) solution, 1.5ml of DMF and 0.5ml of the reagent (1 x 10^{-2}M) solution and made up to the mark with distilled water and the absorbance measured at 400 nm against the reagent blank. The amount of V (IV) is determined from the pre determined calibration plot and the results are presented in table. 4.

2. Recommended Procedure

i) Direct spectrophotometry of Ti(IV) and V(IV), (Zero Order):

In each of a set of different 10 ml standard flasks, 5 ml of buffer solution (pH 1.5) various volumes of 5x10^{-5}M Titanium (IV) and 4.0 x 10^{-5}M (pH 4.0) Vanadium (IV) solution, 1 ml of n-butanol, 1ml of dimethylformamide (DMF) and 2 ml of RPINH (1x10^{-2}M) in DMF were added and made up to the mark with distilled water. The absorbance was measured at 490 nm for Ti (IV), at 400nm for V (IV) against reagent blank. The calibration curves were prepared by plotting the absorbance against the amount of titanium and vanadium.

ii)First Order derivative spectrophotometry:

For the above solutions, first order spectra (Fig1a & 1b.) were recorded with a scan speed of fast nearly 2400nm min^{-1}, slit width 1 nm, with degree of freedom 9, in the wave length range from 400–650 nm. The derivative peak heights were measured by peak-zero method at 545 nm for Ti (IV) and at 470nm for V (IV). The peak heights were plotted against the amount of titanium and vanadium to obtain the calibration curves.

The calibration graphs follow the straight line equation $y = mx + b$ where x is the concentration of the solution, y is the measured absorbance or peak height. And m and b are constants. By substituting the corresponding experimental data in to the above equation, calibration equations were calculated as $y = 0.2084x + 0.0018$ for the zero order data and $y = 0.0359x – 0.0009$ for the derivative data for Ti (IV) and $y = 0.1847x + 0.0071$for zero order and $y = 0.01213x – 0.0001$ for the derivative data for V (IV).

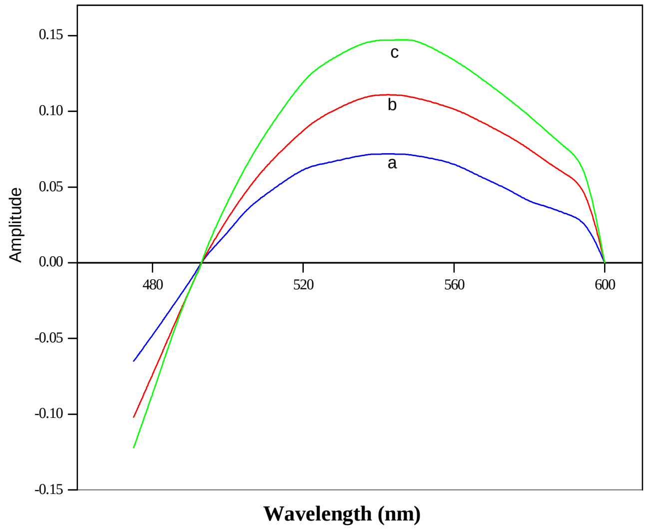


Fig. 1.a. First derivative spectra of Ti (IV) – RPINH Vs reagent blank [Ti (IV)] = (a) 2.0 x 10^{-5}M (b) 3.0 x 10^{-5}M (c) 4.0 x 10^{-5}M

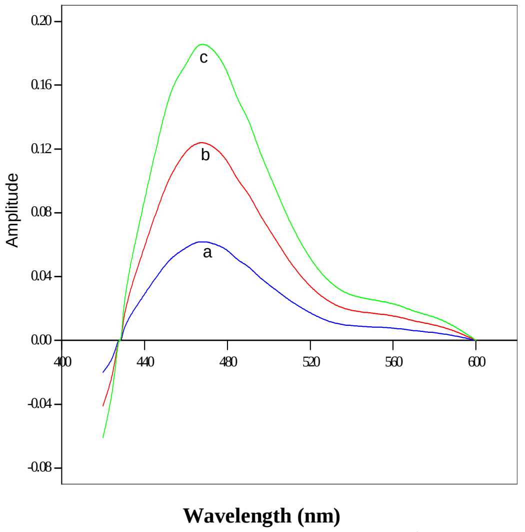


Fig. 1.b. First derivative spectra of V (V) – RPINH Vs reagent blank [V (IV)] = (a) 1.0 x 10^{-5}M (b) 2.0 x 10^{-5}M (c) 3.0 x 10^{-5}M

RESULTS AND DISCUSSION

2.1 *Absorption Spectra:*

The absorption spectra of the reagent solution against the complex were recorded in the wavelength range 350-700nm at pH 1.5 and 4 for Ti(IV) and V(IV) respectively against the buffer solution and reagent blank, respectively (Fig-2.a, & 2.b). The complexes have an absorption maximum at 490 nm and 400nm respectively. The reagent has no absorbance at 490 nm and 400nm. Hence, analytical studies are made at 490 and 400 nm for Ti (IV) and V (IV) respectively.

2.2 Effect pH

The study of the effect of pH on the colour intensity of the reaction mixture showed that maximum colour is obtained in the pH range 1.0 to 2.0. And 2.0 to 5.0 for Ti (IV) and V (IV) respectively. Hence, pH 1.5 and 4.0 are selected for further studies as minimum interference due to foreign ions is observed at this pH.

2.3 Effect of RPINH concentration:

The studies revealed that a 20 fold molar excess of RPINH is essential for complete and constant colour development. Excess of the reagent has no effect on absorbance of the complex.

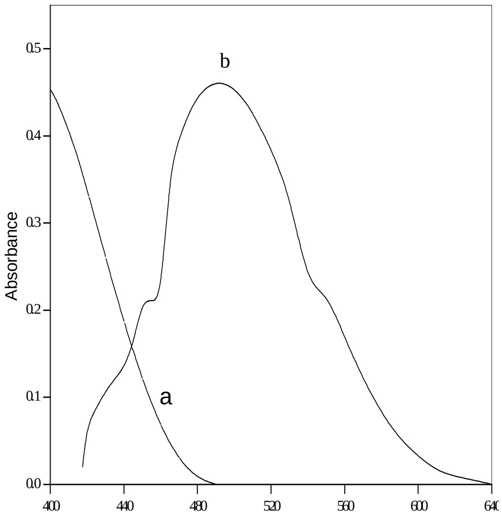


Fig. 2.a. Absorption spectra of
a) RPINH Vs buffer blank
b)[Ti (IV)] - RPINH Vs reagent blank
[Ti (IV)] = 5.0 x 10^{-5}M[RPINH] = 1.0 x 10^{-3}M

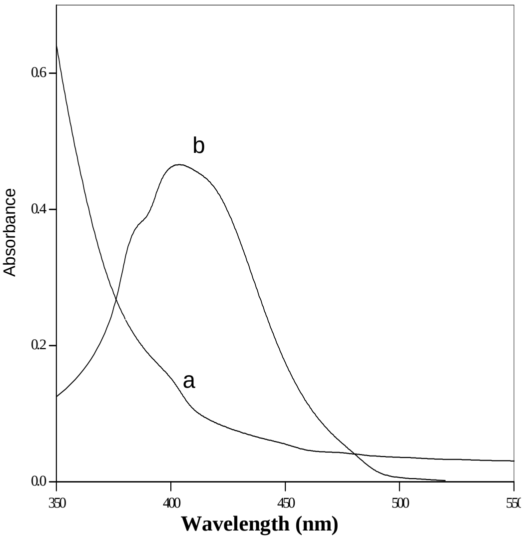


Fig.2.b. Absorption spectra of
a) RPINH Vs buffer blank
b)[V(IV)] - RPINH Vs reagent blank
[V(IV)] = 5.0 x 10^{-5}M : [RPINH] = 1.0 x 10^{-3}M

2.4 Effect of solvent:
The variation in the intensity of the colour of the reaction mixture with different volumes of DMF and n-butanol is studied and observed that the red precipitate of the Ti(IV)- RPINH complex dissolves in 20% aqueous DMF. But there is a decrease in the colour intensity of the complex. The intensity of the colour is stabilized by adding 1 ml of n- butanol to the reaction mixture. Hence further studies were carried out in a 5%(v/v) and 15% (v/v) n-butanol mixture.

2.5 Effect of time on colour development and stability of the colour:
The colour reaction between Ti (IV), V (IV) and RPINH were instantaneous at room temperature and remains constant for more than eight hours.

2.6 Order of addition of reactants:
The order of addition of the constituent solutions [buffer solution, n- butanol, DMF, metal ion solution and the reagent solution] has no effect on the absorbance of the experimental solution. However, n- butanol and DMF are added to the flask prior to the addition of the reagent solution to avoid its precipitation.

2.7 Adherence of the system to Beer's law
From the calibration plot, it is observed that in the present methods Beer's law is obeyed (Fig.3.a & 3.b) in the concentration range 0.47 – 3.35µg ml^{-1} of Ti (IV) and 0.255 – 3.056 µg ml^{-1} of V(IV). The molar absorptivity and Sandell's sensitivity are 1.00 x 10^{4} ± 0.03.l $mo1^{-1}cm^{-1}$ and 0.0048 µg cm^{-2} and 8.9 x 10^{3} $Lmol^{-1}$ cm^{-1} and 0.0056 µg cm^{-2} respectively.

Other statistical data derived from the present methods are as follows, the standard deviation of the method for ten determinations of 2.39µg ml^{-1} of Ti(IV) is 0.0333 and 2.547 µg ml^{-1} of V(IV) is 0.0058.

The correlation coefficient (γ) of the calibration equation of the experimental data is 0.9996 for both the metal ions. The effective range of concentration for accurate determination of Ti(IV) and V(IV) as ascertained from Ringbom's plot are 0.72- 2.87µg ml^{-1} and 0.382 – 3.317 µg ml^{-1} respectively.

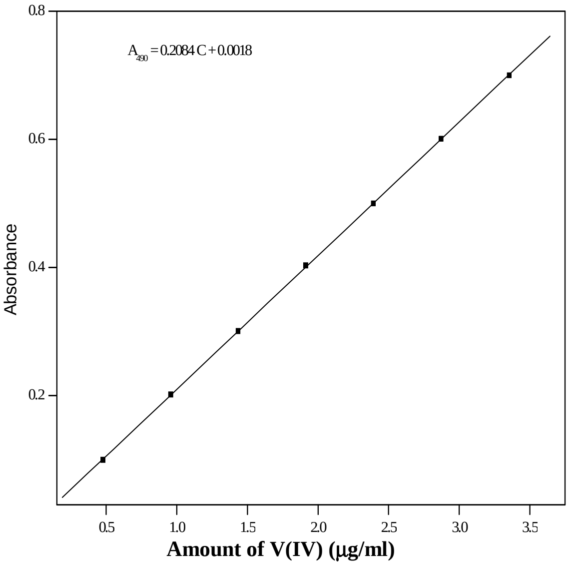


Fig.3.a. Absorbance Vs Amount of Ti (IV) (µg/ml)
[RPINH] = 1.0 x 10^{-3}M pH = 1.5 ; Wavelength = 490nm

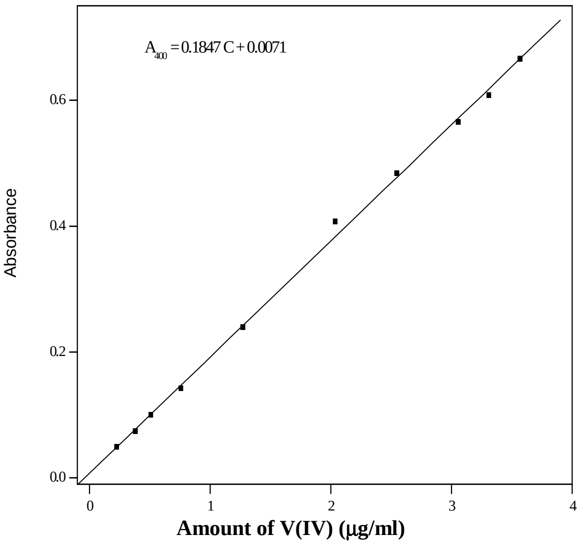


Fig.3.b. Absorbance Vs Amount of V(IV) (µg/ml)
[RPINH] = 1.0 x 10^{-3}M pH = 4.0 ; Wavelength = 400nm

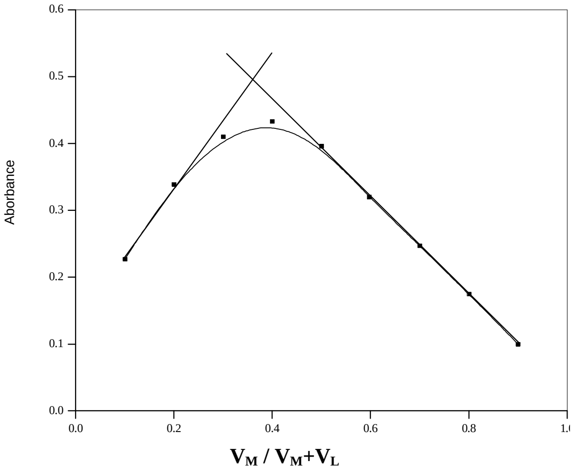


Fig. 4.a. Job's curve
[Ti (IV)] = [RPINH] = 1.5 x 10^{-5}M
Wavelength = 490nm

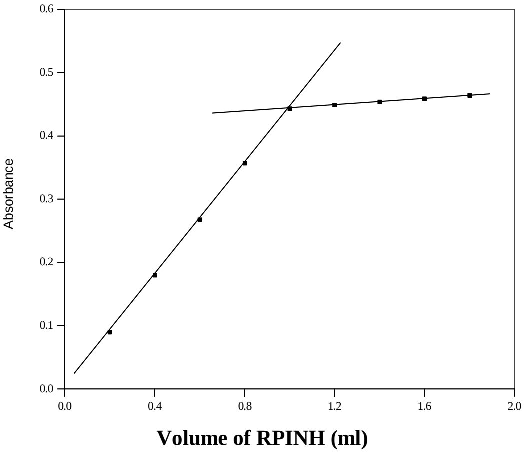


Fig.4.b. Mole ratio plot
[Ti (IV)] = [RPINH] = 1.5 x 10^{-5}M
Volume of Ti (IV) = 0.5 ml
Wavelength = 490 nm

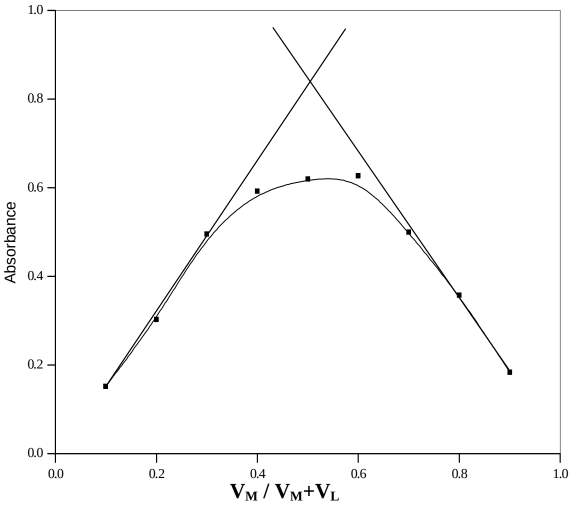


Fig. 5.a Job's curve
[V(IV)] = [RPINH] = 7.5 x 10^{-5}M
Wavelength = 400nm

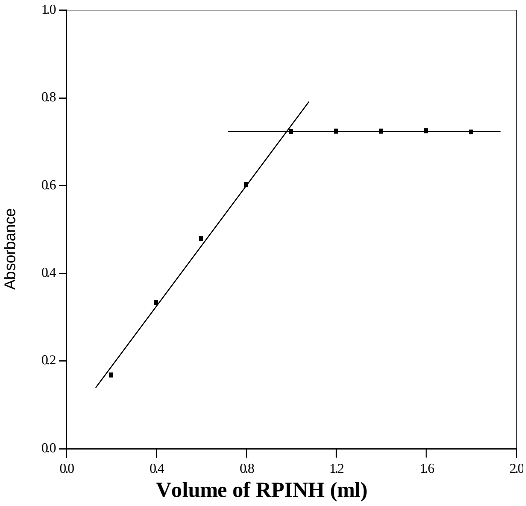


Fig. 5.b. Mole ratio plot
[V(IV)] = [RPINH] = 7.5 x 10^{-5}M
Volume of V(IV) = 1ml
Wavelength = 400 nm

2.8 Composition and stability constant of the complexes:

The composition of the complexes are determined by Job's continuous variation method (Fig. 4.a. & 4a.) and mole ratio method (Fig. 5.b. & 5.b.) and found to be 1:2 (Ti (IV): RPINH) and 1:1 [V(lV) : RPINH]. The stability constants β as calculated from the jobs method for Ti (IV) and V (IV) are found to be 1.98 x 10^{10} and 2.9 x 10^{7} respectively.

2.9 Effect of foreign ions:

The effect of various cations and anions which are generally associated with the metal ion on the determination of Ti(IV) and V(IV) were studied by measuring the absorbance of the metal complexes containing 2.35 µg/ml of Ti(IV) and 2.55 µg/ml of V(IV) respectively in solution. The colour reactions were developed as described in the standard procedure. An error of ± 2% in the absorbance or amplitude reading in the case of derivative methods considered tolerable. The data is given in table .1.

Table .1 Tolerance limits of foreign ions in the determination of 2.35 and 2.55 µg ml^{-1} of Ti(IV) and V(IV) respectively

Ion	Tolerance limit(µg/ml) Ti(IV).	Tolerance limi(µg/ml) V(IV).	Ion	Tolerance limit (µg/ml) Ti(IV).	Tolerance limit (µg/ml) V(IV).
Ascorbic acid	17620	174	K(I), Ba(II)	1500	70
Iodate	8710	635	Zn(II), Co(II)	653	35
Bromate	4200		Mg(II), Ca(II), Na(I)	500	25
Nitrate	3190	310	Ce(IV)	200	15
Thiocyanate	2900	58	Ni(II)	120	6
Borate	2000		Mn(II), Hg(II), Pb(II)	109	100
Citrate	1900	100	Cr(III)	100, (52)[b]	3[c,d]
Tartrate	1800	190	Ti(IV)	-	96
Iodide	1280	635	Cd(II)	60	12
Oxalate	920	90	Zr(IV), W(VI)	20	
Thiourea	761	80	Al(III)	14	Interfere
Carbonate	700	300	Ag(I)	6	110
Hypo	510	51	Pd(II)	5.3	2
Phosphate	96	50	Mo(V)	5, (30)[d]	Interfere
Fluoride	19	10	U(VI)	4	25
Suiphate		490	Cu(II)	3, (6.5)[c],(65.4) [a]	
			Th(IV)	3	
			V(V)	3, (5.1) [a]	
			Fe(III)	(2.7), 30[ab]	Interfere

'a' masked with 1740µg/ml of ascorbic acid
'b' masked with 900 µg/ml of citrate
'c' masked with 761 µg/ml of thiourea
'd' masked with 800 µg/ml of tartrate

3. Applications:

Analysis of alloys and steel samples. Titanium present in various alloy and steel samples and vanadium present in river water samples were determined by the zero-order and first-order derivative methods. Tables 2-4

Table 2 Determination of titanium in alloy and steel samples

Sample	Amount taken (µg ml^{-1})	Amount found * (µg ml^{-1})	Error %
Nickel-based high temperature alloy[a] (I) Udimet – 500	0.51	0.50	-1.96
	1.02	1.03	+0.98
	1.53	1.55	+1.30
(II) Udimet – 700	1.00	1.00	-
	1.50	1.49	-0.67
	2.00	2.02	+1.00
Titanium based alloy[b]	0.62	0.64	+3.22
	1.20	1.25	+0.61
	1.86	1.87	+0.54
BAS No. 387[C]	0.50	0.51	+2.00
	1.00	1.02	±2.00
	2.00	2.01	±0.50
Low alloy steel[d]	0.70	0.71	+1.42
	1.40	1.39	±0.71
	2.10	2.09	-0.48

** Average of seven 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.
c. Ni, 41.9; 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, 0.0321; C, 0.03.
d. C, 0.1; Cr, 0.1; Cu, 0.30; W, 0.1; Mo, 0.1; Fe, 99; Ti, 0.10

Table 3 Determination of Ti(IV) in fly ash

Sample	Amount of Ti(IV) μg ml^{-1}		Error (%)
	AAS method	*Present method	
Fly ash	1.20	1.08	-1.66
	2.40	2.36	+1.66
	3.60	3.55	-1.40

**Average of seven determinations*

Table 4. Determination of vanadium in river water

V(IV) added (μg ml^{-1})	Total V(IV) found* (μg ml^{-1})	Error (%)
0.0	2.0	-
1.0	2.92	2.7
1.5	3.51	0.3
2.0	3.90	2.5
2.5	4.46	0.9

**Average seven determinations.*

The data obtained on samples spiked with vanadium(IV) (table 4) show good recoveries.

Comparison with other methods:

The present method is compared with the standard hydrogen peroxide method. Chromotropic acid method and other hydrazone methods and the results are presented in Table.4. The rapidity of color development with RPINH is an advantage in analyzing various samples, in which titanium(IV) can vary over a wide range. When compared to the other existing methods (15-30 and 45-51). The developed method retains specific interaction of titanium(IV) with RPINH to form a colored complex and has good sensitivity at room temperature without the need of extraction. The uses of organic solvents which were generally toxic were avoided in this proposed method. The proposed method has significant advantage over the other spectrophotometric methods in terms of simplicity and sensitivity. This proposed method has good precision and accuracy. The first derivative spectra of the solution are recorded and the amplitude is measured at 545 nm. The first order derivative spectrophotomdetric method eliminates the interference of V(V), Cu(II), Zr(IV), Mo(VI), U(VI), and Th(IV).which causes problems in the zero order method. The only interfering cation, Fe(III), is easily masked, up to 1000-fold, with ascorbic acid. Thus the first order derivative method is selective for the determination of Ti(IV) in the presence of ascorbic acid.

Table 5. Comparison of the present method with other spectrophotometric methods for the determination of titanium (IV) Comparison with other hydrazone methods

Reagent	Molar absorptivity (x10^4 l mol^{-1} cm^{-1})	**λ_{max} (nm)**	pH	M:L	Beer's law range (μgml^{-1})	Ref
RPINH	1.0	490	1.5	1:2	0.47-3.35	**Present Method**
Hydrogen Peroxide	0.07	-	Acid	-	-	29
Chromic acid	1.7	-	3.5	-	-	30
Acyl hydrazones of aromatic carbonyl compounds	0.7-1.4	-	2.0-6.0	1:1	-	19
2-methyl isonicotinic salicylal hydrazone	-	425	1.0-2.5	1:2		42
Hydrazo-T	-	525	1.5-2.5	-	0.1-2.0	17
Diphenylglyoxal bis 2- hydroxyl-benzoyl), hydrazone	1.5	500	0.1N H_2SO_4	1:3	0.5-2.5	9
Pyridoxal-3-hydroxy-2-naphthylhydrazone	-	430	2-7		0.5-0.7	15
Pyridoxal nicotinoyl hydrazone	0.69	410	2.1-2.3	1:1	-	32
1,2 cyclohexane dione bis(benzoyl) hydrazine	1.0	477	1.75-3.0	1:2s	-	33
2,4 Di hydroxy benzaldehyde isonicotinoyl hydrazone	1.35	500	102-3.5	1:2	0.90-2.15	34
Pyridoxal salicylal hydrazone	0.39	450	0.9-2.5	1:1	1.0-10	35
Orthovanillinisonicotinoyl hydrazone	0.44	450	2.0	-	2.0-10.0	36

CONCLUSION

The results of the present direct and derivative methods were compared with those of some of the already reported methods in the case of Ti and presented in table 5. The comparison shows that both the direct and derivative methods proposed are more sensitive than majority of the reported methods. Further, the derivative methods are found to be more selective than large number of the reported method. The data may bring awareness among the public.

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