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Spectrophotometric Determination of Titanium in Industrial and Soil Samples Using 3-Hydroxy-2-(2'-Thienyl)-4*H*-Chromen-4-One

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Abstract: A simple spectrophotometric method for the determination of titanium is developed using 3-hydroxy-2-(2'-thienyl)-4*H*-chromen-4-one as a complexing agent for the metal ion in slightly alkaline solution (pH 8.0-8.5). The resulting complex bears metal to ligand ratio of 1:1 whose absorption maximum lies at 430nm. The method obeys Beer's law in the range 0.0-5.0 µg Ti ml^{-1} with molar absorbtivity and Sandell's sensitivity values of 1.40×10^4 l mol^{-1} $cm^{-1}$and 0.0034 µg Ti cm^{-2} respectively. The limit of detection, of the method is 0.0086 ppm. The complex is stable for 24 hours. It is free from interference of a large number of cations and anions. Utilizing the proposed procedure, the analysis of various synthetic samples, soil, water and pharmaceutical sample has been carried out to a greater degree of accuracy.

Keywords: titanium, 3-hydroxy-2-(2'-thienyl)-4*H*-chromen-4-one, spectrophotometric determination.

I. Introduction

Titanium is one of the most abundant elements, widely distributed in the earth's crust.it is also detected in sea water. Many plants such as grains, vegetables, trees and shrubs are found to contain metal though in low concentrations. Trace amounts of titanium are also present in all forms of animal life [1]. Titanium metal is used in aircrafts where a high strength/weight ratio is important. It has excellent corrosion resistance, especially to sea water, and finds extensive use in the chemical processing industry. In addition, titanium dioxide, as a white pigment, is used in paints, lacquers, paper, floor coverings, rubber plastics, ceramics, coated fabrics and textiles.

Though several analytical techniques have been reported in the past are time-consuming, require prior separations involving lengthy procedures, and also have several other limitations restricting their use. Therefore, simple, highly sensitive and selective methods for microdetermination of elements are still in great demand and that is why spectrophotometric methods, even today are preferred amongst the most important instrumental methods of analysis, being well known for their versatility, sensitivity and precision.

Out of a wide variety of reagents employed for spectrophotometric determination of titanium, diantipyrylmethane and thiocyanate [2], dichlorophenyl fluorone [3], dibromophenyl fluorone [4], DBN-chlorophosphonazo [5], 2,6-Dimercapto-4-Isopropylphenol[6], 4-(2-thiazolylazo)-1,2,3-trihydroxy benzene [7] show high sensitivity, but these methods involves having serious interferences of other elements and also are of restricted use because of low Beer's law obedience; whereas, other methods using slippery elm leaf [8] hydrogen peroxide[9], 5- bromo-2-hydroxy-3-methoxybanzaldehyde-p-hydroxybenzoic hydrazone [10], 3,4-dihydroxy benzoic acid [11], promethazine hydrochloride and pyrogallol [12] mainly suffer due to lack of sensitivity.

It is also evident from literature that most of methods are in acid media. So, it is of much interest to develop methods in alkaline medium as is the case at present, while making use of 3-hydroxy-2-(2'-thienyl)4H-chromen-4-one as a complexing agent for the metal ion. The proposed method is simple, sensitive and free from the interference of a large number of foreign ions and also handles satisfactorily the analysis of a wide variety of samples including different synthetic, soil and pharmaceutical sample.

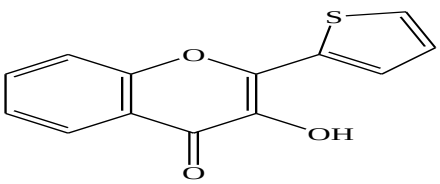
Experimental

Reagents:

A stock solution of titanium (IV) containing 1 mg ml^{-1} is prepared by dissolving an accurately weighed amount of $K_2[Ti(C_2O_4)_2O].2H_2O$ in minimum volume of dilute sulphuric acid and make it upto the mark in a 100ml volumetric flask before standardizing the metal ion gravimetrically [13]. Working solutions at µgml^{-1} level are made by suitable dilutions therefrom. Similarly, solutions of other metal ions at milligram level are prepared by dissolving their commonly available salts in distilled water or dilute acid.

Chloroform and alcohol used are of A.R. grade.

The reagent, 3-hydroxy-2-(2'-thienyl)-4*H*-chromen-4-one, 'HTC' (0.05% m/v), is prepared [14] as under, characterized and dissolved in alcohol for use.



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Preparation of HTC

Solutions of o-hydroxyacetophenone (4.08 g in 30 ml ethanol) and NaOH (4 g in 8 ml of 50% ethanol) are mixed and stirred (2 h, below 60°C) after adding thiophene-2-aldehyde (3.36 g) dropwise. The orange red mass (I, m.p. 100°C) thus obtained is neutralized with 0.2 mol/l HCl and crystallized from ethanol. Solutions of compound I (2 g in 20 ml methanol), NaOH (8 ml of 20% in methanol) and H_2O_2 (4ml) are mixed, stirred (2 h, below 10 °C) and neutralized with CH_3COOH. The yellow compound so obtained after crystallization from ethanol and water is HTC, m. pt. 199°C (lit. m.pt. 200°C).

Samples:

Various sample solutions were obtained by mixing solutions of Ti (IV) and other metal ions in a suitable proportion.

Pharmaceutical sample: For determination of titanium, the film coated paracetamol tablet (500mg) containing titanium was stirred for 10 min. in deionized water. The sample solution was quantitatively transferred to a 250 volumetric flask, diluted with deionized water, and then filtered through Whatman filter paper no. 41. The filtered solution was diluted with water to make it to 250ml. One ml of this sample is taken for the determination of titanium using the proposed method.

Soil sample: About 1g of air-dried homogenized soil sample was weighed and dissolved in conc. HCl. It was decomposed by heating to dryness on a sandbath. The residue was treated with 20-30 ml of water and the solution thus obtained was filtered into a 100 ml volumetric flask,which is makes upto the mark with deionized water. One ml of this sample is taken for the determination of titanium using the proposed method.

Procedure

To a sample solution containing ≤ 50µg Ti(IV) and/or other metal ions in a 100ml separatory funnel; add 0.30 ml $NaHCO_3$(1M), 2.0 ml 0.05% HTC (in alcohol) and the aqueous volume is made upto 10 ml with distilled water (pH= 8.0-8.5). The contents are gently mixed and then equilibrated once with an equal volume of chloroform for 30s. The two phases are allowed to separate and the yellow organic layer is filtered through a Whatman filter paper no. 41 (pre-treated with chloroform) into a 10 ml volumetric flask, which is filled upto the mark with pure chloroform. The absorbance of the yellow colored complex is measured at 430 nm against a similarly prepared reagent blank and the amount of titanium is determined from a standard curve obtained by plotting a graph between varying microamounts of the metal ion and their corresponding absorbance values obtained, as per procedure.

II. Results and Discussion

Absorption spectra

Ti (IV) reacts with HTC forming a yellow-colored species in slightly alkaline medium (pH=8.0-8.5 adjusted with $NaHCO_3$), which is quantitatively extracted into chloroform. Absorption maximum of the complex lies at 428-433 nm in the visible region, where the reagent blank shows hardly any absorbance (Fig.1). Hence, the absorbance measurements of the system are carried out at 430nm. The effect of various parameters on the formation and absorbance of the metal complex, while performing a single extraction with 10ml of chloroform each time, is studied systematically as under:

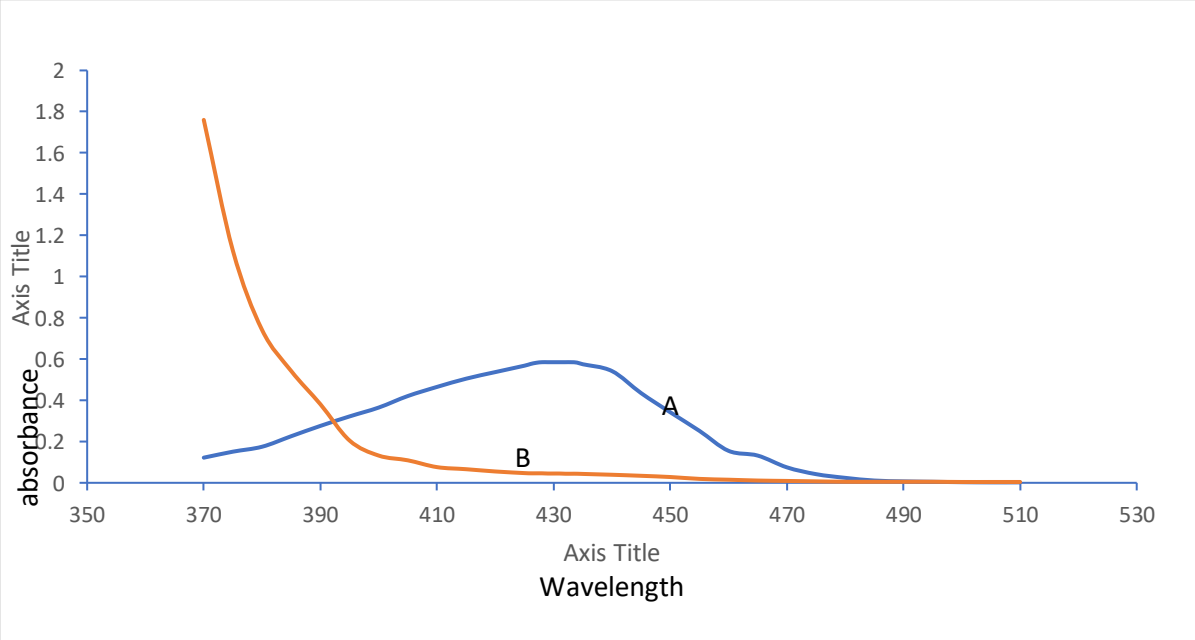

Fig.1 Absorption Spectrum of Ti (IV)-HT Ccomplex Conditions: 2µg Ti(IV)/ml, other conditions are same as described in procedure

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Curve A- Absorbance of complex measured against reagent blank

Curve B- Absorbance of reagent blank measured against pure chloroform

Choice of medium

Using 0.5ml of all 1N acids/bases, keeping other experimental conditions the same, in a final 10 ml aqueous volume, the absorbance of complex is found to be maximum at 0.585 in $NaHCO_3$ solution; whereas, a downward trend in absorbance is observed with CH_3COOH(0.440), $HClO_4$(0.255), NH_4OH(0.175), HCl(0.160), H_2SO_4(0.144), NaOH(0.078), H_3PO_4(0.055), Na_2CO_3(0.046). Hence, sodium bicarbonate provides a suitable medium for the system.

Sodium bicarbonate concentration

In absence of bicarbonate, the absorbance is just 0.330 which increases considerably on its addition and goes upto 0.455 when the solution contains 0.1 ml of $NaHCO_3$ (1M). It reaches a maximum value of 0.585 for 0.2-0.5ml and starts declining gradually on further addition. Thus 0.30 ml $NaHCO_3$ (1 M) is considered sufficient for working on the system.

Effect of HTC concentration

In absence of reagent, the absorbance is nil. A significant rise in absorbance value is noticed on addition of HTC. It attains a maximum value of 0.585 for 1.5-3.0 ml of the reagent and starts decreasing though slowly thereafter. Thus, 2.0 ml HTC (0.05% m/v in alcohol) is appropriate for the system.

Extractant

The extraction behaviour of the complex with various organic solvents in terms of absorbance is in the order: chloroform > 1, 2-dichloroethane > dichloromethane > carbontetrachloride > isobutylmethyl ketone > isoamylacetate > benzene > xylene> toluene > iso-amylalcohol > diethyl ether. Chloroform is thus chosen as a suitable extractant for the complex.

Equilibration time

The absorbance of the complex is 0.112 on equilibrating just for 5 sec. It is maximum (0.585) and remains unchanged for an equilibration time of 15 sec. to 3 min. Thus, contact time of 30 sec. is enough for complete transfer of the complex to the organic phase.

Stability of the complex

The metal complex is quite stable for 24 hours with a constant absorbance value of 0.585 at 430 nm. This enables one to carry out safely the absorbance measurements even a day after.

Optimum conditions

For ≤ 50 µg Ti(IV), 0.2-0.5 ml of $NaHCO_3$ (1M), 1.5-3.0 ml of HTC (0.05% m/v in alcohol) in a final 10ml aqueous solution, equilibrating once with an equal volume of chloroform for 30 sec., are the optimum conditions for the quantitative transfer of the metal complex to the organic phase, whose absorbance is measured at 430 nm.

Stoichiometry of the complex

The ratio of Ti to HTC in the extracted species is determined (in two different sets) using their equimolar solutions 4.177×10^{-4} M and 1.044×10^{-3} M respectively at three different wavelengths; 410, 430 and 450nm by Job's method of continuous variation. In this method, equimolar solution of 4.177×10^{-4} M for both Ti and HTC are mixed in different proportions (rest reagents remaining same as per procedure) and measuring absorbance. Mole fractions of Ti and corresponding absorbance value indicates a metal to ligand ratio of 1:1 in the extracted species. Similarly, in another set using equimolar solution of 1.044×10^{-3} M also confirms same. This is further supported by the mole ratio.

Beer's law obedience

The method obeys Beer's law in the range 0.0-5.0µg Ti/ml with a molar absorbtivity and Sandell's sensitivity values of 1.40×10^4 l mol^{-1} $cm^{-1}$and 0.0034 µg Ti cm^{-2} respectively. The limit of detection of the method is 0.0086 ppm calculated by $3S_b/m$ (where S_b is the standard deviation of 10 measurements of the blank and m is the slope of the calibration curve).

Effect of foreign ions

The influence of different anions, complexing agents and metal ions on the absorbance of the complex has been investigated under the proposed optimum conditions of the procedure. Chloride (100mg); nitrate (75mg); thiocyanate, bromide (50mg each); ascorbic acid, sulfosalicylic acid (30mg); tartrate (25mg); aspirin(10mg); thiourea(5mg) bromate, acetate(4mg each); oxalate (2mg); sulphite, dithionite, potassium hydrogen sulphate (2mg); are without effect. EDTA 'disodium salt', fluoride, phosphate (1 mg each); decrease absorbance.

Na(I), K(I), 10mg each ; Dy(III), Pr(III), Nd(III), Sb(III), Bi(III) 5mg each; Tl(I), Y(III), 2 mg each; Cr(VI),As(III), Au(III), Co(II) 1mg each; Sr(III), V(V), Ba(II), Sm(III), 0.2mg each ; Hg(I), Pb(II), Ce(IV), Cd(II), Se(IV), Mo(VI), 0.1mg; do not interfere. Cu

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(II) and Fe (III) increase absorbance. To mask Cu (II) and Fe (III) 0.1mg each, 20mg ascorbic acid is added prior to the addition of reagent.

Applications

The proposed method was applied successfully for the determination of titanium (IV) in different pharmaceutical sample, soil sample and various synthetic samples (Table-1). The results obtained on applying the proposed procedure for the analysis of soil and pharmaceutical samples are in in good agreement with amount added.

III. Conclusion

The optimum conditions of the formation and composition of the complex were established. The method worked out for the spectrophotometric determination of titanium (IV) in different pharmaceutical, soil and various synthetic samples is simple, highly selective and sensitive, with good reproducibility. The proposed method also compares favorably well with the existing methods especially in respect of molar absorptivity and interferences (Table-2).

Acknowledgements

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Table 1. Analysis of different samples by the proposed method

S.N.	Sample compostion*		Ti(IV) found (μg)#	RSD (%)
		Ti(IV) added (μg)		
1	Tl^{I} (1), Re^{VII}(1), Bi^{III}(1)	20	19.70±0.05	0.65
2	Ce^{IV}(0.1), Tl^{I} (0.1), Mo^{VI} (0.1)	15	14.80±0.10	0.95
3	Nd^{III}(2), Re^{VII}(2), Y^{III}(2)	25	24.65±0.07	0.89
4	Hg^{I}(0.1), Mo^{VI} (0.1), Cr^{VI}(0.1)	18	18.15±0.07	0.73
5	Y^{III}(2), Tl^{I} (1), Cr^{VI}(0.1)	12	11.79±0.21	1.18
6	Soil Sample	-	2.20±0.10	0.45
7	Soil Sample	5.00	7.25±0.15	0.70
8	Pharmaceutical	-	6.15±0.15	0.60
9	Pharmaceutical	5.00	11.10±0.10	0.70

* Figure in parentheses indicates the amount of the metal ion in mg

Average of triplicate analysis± standard deviation

Table 2. Comparison of the proposed method of determination of Titanium (IV) with some of the existing methods

S. No.	*Aqueous Conditions*	*(i) λ_{max}(nm)* *(ii) Beer's law range (μg ml^{-1})*	*Molar absorptivity (l $mol^{-1}cm^{-1}$)*	*Interfering metal ions*	*Ref.*
1.	Ti(IV), HCl (0.05M), slippery elm leaf	415nm (ii) 0.2-6.0	0.68×10^4	Fe(III),Zr(IV),Mo(VI)	Akbar et al. 2007
2.	Ti(IV), H_2SO_4 , Hydrogen peroxide	410nm 3.2-60.0	0.73×10^3	?	Ying et al. 2001
3.	Ti(IV), pH 2.0-2.6, CALX-S6	(i) 403nm (ii) 0.0-4.8	1.02×10^4	Mn(II),Ce(III, Zr(IV),	Nishida et al 1994

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4.	Ti(IV),3,4-Dihydroxy benzoic acid	(i) 380nm (ii) 0.0-3.0	1.43×10^4	?	Ferreira et al. 1993
5.	Ti(IV), $NaHCO_3$ (0.030M), HTC,	(i) 430nm (ii) 0.0-5.0	1.40×10^4	Fe(III),Cu(II) (23metal ions are non- interfering)	Proposed method

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