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Spectrophotometric determination of titanium in industrial, pharmaceutical & soil samples using 3-hydroxy-2-(2′-furyl)-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′-furyl)-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 434nm. The method obeys Beer's law in the range 0.0-4.0 µg Ti ml^{-1} with molar absorbtivity and Sandell's sensitivity values of 1.55×10^4 l mol^{-1} $cm^{-1}$and 0.0031 µg Ti cm^{-2} respectively. The limit of detection, of the method is 0.0075 ppm. It is free from interference of a large number of cations and anions. Utilizing the proposed procedure, the analysis of various synthetic samples, soil, and pharmaceutical sample has been carried out to a greater degree of accuracy.

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

INTRODUCTION

Titanium is one of the most abundant elements, widely distributed in the earth's crust, all crystalline rocks and also detected in sea water. Many plants and animals are found to contain titanium in very low concentrations. [1]. It has excellent corrosion resistance property making it suitable for use in manufacture of stainless steel as a carbon and nitrogen stabilizing element to inhibit intergranular corrosion. Titanium dioxide, as a white pigment, is used in paints, lacquers, paper, floor coverings, rubber plastics, ceramics, coated fabrics and textiles.

Different analytical methods have been used in the past for the determination of titanium especially at trace levels, but, most of them are time-consuming, require costly instruments 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 being well known for their versatility, simplicity, less expensive equipment, high sensitivity and precision.

Many reagents have been used for spectrophotometric determination of titanium. Out of them diantipyrylmethane and thiocyanate [2], dichlorophenyl fluorone [3], dibromophenyl fluorone [4], 2,6-Dimercapto-4- Isopropyl phenol[5] 4-(2-thiazolylazo)-1,2,3-trihydroxy benzene [6] are highly sensitivity, but requiring prior separations from some elements and low Beer's law obedience; whereas, other methods using 5-bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydoxybenzoic hydrazone[7] slippery elm leaf [8] hydrogen peroxide[9], 2-(2-thiazolylazo)-p-cresol [10], 3,4-dihydroxy benzoic acid [11], promethazine hydrochloride and pyrogallol [12] mainly suffer due to lack of sensitivity.

literature data shows that most of methods have been reported in acid media, whereas there are only a few ones in alkaline conditions. 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′-furyl)-4*H*-chromen-4-one as a complexing agent for the metal ion. The proposed method is simple, sensitive, selective and also handles satisfactorily the analysis of a wide variety of samples including different soil, pharmaceutical and synthetic samples.

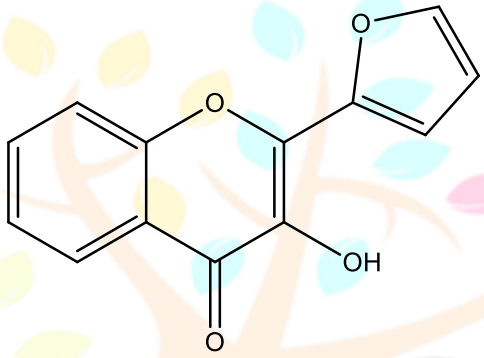
EXPERIMENTAL

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′-furyl)-4*H*-chromen-4-one, 'HFC' (0.1% m/v), is prepared [14] as under, characterized and dissolved in alcohol for use.



Preparation of 3-hydroxy-2-(2′-furyl)-4*H*-chromen-4-one**, 'HFC'**

To an ethanolic solution of 2-hydroxy-3′-(2′′-furyl) acrylophenone (2g in 20 ml), is added slowly an aqueous sodium hydroxide (10ml, 20%) at 0°C. This is followed by addition of hydrogen peroxide (8ml, 30%) dropwise to the resulting dark red slury with stirring, which is continued for 6 hrs. The light-yellow reaction mixture thus obtained is poured onto crushed ice and neutralized with dil. HCl. The yellow compound so obtained after crystallization from ethanol and water is HFC, m. pt. 169°C (lit. m.pt. 171°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 trasfered 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 ≤ 40µg Ti(IV) and/or other metal ions in a 100ml separatory funnel; add 0.35 ml $NaHCO_3$(1M), 1.0 ml 0.1% HFC (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 434 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.

RESULTS AND DISCUSSION

Absorption spectra

Ti (IV) reacts with HFC 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 433-436 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 434 nm.

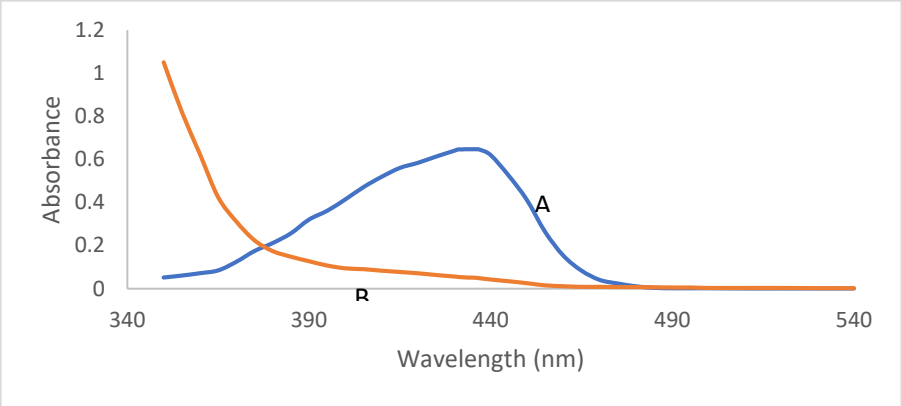


Fig.1 Absorption Spectrum of Ti (IV)-HFCcomplex

Conditions: 2µg Ti(IV)/ml, other conditions are same as described in procedure

Curve A- Absorbance of complex measured against reagent blank

Curve B- Absorbance of reagent blank measured against pure chloroform

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:

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 0.648 in $NaHCO_3$ solution; whereas, a downward trend in absorbance is observed with NH_4OH(0.380), CH_3COOH(0.356), Na_2CO_3(0.135), HCl(0.128), $HClO_4$(0.115), H_2SO_4(0.096), NaOH(0.084), H_3PO_4(0.078),. Hence, sodium bicarbonate provides a suitable medium for the system.

Sodium bicarbonate concentration

In absence of bicarbonate, the absorbance is just 0.315 which increases considerably on its addition and goes upto 0.492 when the solution contains 0.1 ml of $NaHCO_3$ (1M). It reaches a maximum value of 0.648 for 0.2-0.5ml (Table 1) and starts declining gradually on further addition. Thus 0.35 ml $NaHCO_3$ (1 M) is considered sufficient for working on the system.

Effect of HFC concentration

In absence of reagent, the absorbance is nil. A significant rise in absorbance value is noticed on addition of HFC. The absorbance is 0.235 when only 0.2 ml of reagent is used. It attains a maximum value of 0.648 for 0.8-1.5 ml of the reagent (Table 1) and starts decreasing though slowly thereafter. Thus, 1.0 ml HFC (0.1% 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 > isobutylmethyl ketone >1, 2-dichloroethane > dichloromethane > carbontetrachloride > isoamylacetate > toluene > benzene > xylene> iso-amylalcohol > diethyl ether. Chloroform is thus chosen as a suitable extractant for the complex.

Equilibration time

The absorbance of the complex is 0.325 on equilibrating just for 5 sec. It is maximum (0.648) and remains unchanged for an equilibration time of 10 sec. to 2 min. Thus, contact time of 30 sec. is enough for complete transfer of the complex to the organic phase (Table-1).

Stability of the complex

The metal complex is quite stable up to 10 hours with a constant absorbance value of 0.648 at 434 nm. This enables one to carry out safely the absorbance measurements.

Optimum conditions

For ≤ 40 µg Ti(IV), 0.2-0.5 ml of $NaHCO_3$ (1M), 0.8-1.5 ml of HFC (0.1% 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 434 nm.

Stoichiometry of the complex

The ratio of Ti to HFC 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; 414, 434 and 454nm by Job's method of continuous variation. The sharp break in the curves indicates a metal to ligand ratio of 1:1 in the extracted species. This is further supported by the mole ratio method.

Beer's law obedience

The method obeys Beer's law in the range 0.0-4.0µg Ti/ml with a molar absorptivity and Sandell's sensitivity values of 1.55×10^{4} L mol^{-1} cm^{-1} and 0.0031 µg Ti cm^{-2} respectively. The limit of detection of the method is 0.0075 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. Bromide, nitrate (75mg each); iodide, thiocynate, (50mg each); ascorbic acid, chloride (25mg each); tartrate (15mg); oxalate, citrate, aspirin(10mg); thiourea(5mg); bromate, sulphite, acetate (4mg each); sulfosalicylic acid (2mg); dithionite, potassium hydrogen sulphate (1mg each); are without effect. Fluoride, phosphate (1 mg each); decrease absorbance.

Na(I), K(I), Se(IV), Bi(III), 10mg each ; Re(VII), Cr(VI), Dy(III), Nd(III), Sb(III), Os(VIII), 5mg each; Tl(I), Pr(III), Y(III), Ho(III), La(III), 2mg each; As(III), Au(III), Zn(II), Mn(II) 1mg each; Sr(II), V(V), Ba(II), Sm(III), Ce(IV), Mo(VI), Co(II), 0.2mg each ; Hg(I), Pb(II), Cd(II), Eu(III), W(VI) 0.1mg; do not interfere. Cu (II) and Fe (III) increase absorbance. To mask Cu (II) and Fe (III) 0.1mg each, 10mg ascorbic acid is added prior to the addition of reagent.

Applications

The proposed method was applied successfuly for the determination of titanium (IV) in different pharmaceutical sample, soil sample and various synthetic samples(Table-2). The results obtained on applying the proposed procedure for the analysis of soil and pharmaceutical samples besides some other technical samples, are also in excellent agreement with the reference methods.

Conclusion

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. Further, the proposed method compares favorably well with the existing methods especially in respect of molar absorptivity and interferences.

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Table 1. Effect of various parameters on the absorbance of Ti (IV) - HFC complex

$NaHCO_3$ (IM),[a] ml	0.0	0.1	0.2-0.5	0.6	0.8	1.0	1.5
Absorbance	0.315	0.492	0.648	0.595	0.551	0.529	0.502
HFC[b],ml [0.1% (m/v) in alcohol]	0.0	0.2	0.5	0.8-1.5		2.0	2.5
Absorbance	0.000	0.235	0.472	0.648		0.621	0.605
Equilibration time[c], s	5	10	30	60	120		
Absorbance	0.325	0.648	0.648	0.648	0.648		

Conditions:

a) Ti, 20 µg; HFC (0.1% in alcohol), 2ml; aqueous volume = solvent volume =10ml; solvent = chloroform; equilibration time = 30 sec.; λ_{max}=434nm ; $NaHCO_3$ (1 M)= variable
b) $NaHCO_3$ (1 M), 0.35ml; other conditions are the same as in a) excepting variation in HFC (0.1%)
c) HFC (0.1%),1.0 ml ;other conditions are the same as in b) excepting variation in equilibration time

Table 2 -Analysis of different samples by the proposed method

S.No.	ple compostion	Ti(IV) added (µg)	Ti(IV) found (µg)#
1	Os^{VIII}(2), Cr^{VI}(2), Cr^{VI}(2)	10	10.20
2	Ce^{IV}(0.1),Tl^{I} (1), V^{V}(0.1)	15	15.65
3	Sb^{III}(2), Nd^{III}(2), Re^{VII}(5)	20	20.20
4	Dy^{III}(5), Bi^{III}(5), Nd^{III}(5)	25	24.90
5	Cr^{VI}(2), Mo^{VI}(0.1),Tl^{I} (1)	20	19.65
6	Y^{III}(2), Re^{VII}(2), Pr^{III}(2)	15	14.90
7	La^{III}(2), Sb^{III}(2), Mn^{II}(1)	20	19.80
8	Zn^{II}(1), Mn^{II}(1), Pr^{III}(2)	20	19.90
9	Soil sample	-	2.45
10.	Soil sample	10.00	12.60
11.	Pharmaceutical	-	6.65
12.	Pharmaceutical	10.00	16.50

* Figure in parentheses indicates the amount of the metal ion in mg
# Average of triplicate analysis

Table 3. 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*	*(i) 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*	*(i) 410nm (ii) 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*
4.	*Ti(IV), azopyrazolone*	*(i) 520nm (ii) --*	*5.0×10^3*	*?*	*Vladescu et al 1993*
5.	*Ti(IV),3,4-Dihydroxy benzoic acid*	*(i) 380nm (ii) 0.0-3.0*	*1.43×10^4*	*?*	*Ferreira et al. 1993*
6.	*Ti(IV), $NaHCO_3$ (0.035M), H, FC*	*(i) 434nm (ii) 0.0-4.0*	*1.55×10^4*	*Fe(III),Cu(II) (31 metal ions are non-interfering)*	*Proposed method*