

## Micro Level Determination of Titanium Using 6-Chloro-3-hydroxy-2-(2'-furyl)-4-oxo-4*H*-1-benzopyran as Analytical Reagent

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**Abstract:** An extractive spectrophotometric method is developed for the trace determination of titanium with 6-chloro-3-hydroxy-2-(2'-furyl)-4-oxo-4*H*-1-benzopyran (CHFB) in presence of sodium sulphite in acidic medium which was extracted into dichloromethane and shows maximum absorbance at 432 nm. Beer's law is obeyed in the range 0.0 to 2.5  $\mu\text{g}$  of Ti  $\text{mL}^{-1}$  having molar absorptivity, specific absorptivity and Sandell's sensitivity value of  $1.659 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ,  $0.346 \text{ mLg}^{-1}\text{cm}^{-1}$  and  $0.00289 \mu\text{g}$  of Ti(IV)  $\text{cm}^{-2}$  respectively at 432 nm. The limit of detection of the method is 0.017 ppm. The method is free from the interferences of a large number of cations of major analytical importance such as Pr(III), Ba(II), Mn(II), V(V), Ca(II), La(III), Cr(VI), Se(IV), Bi(III), Re(VII), Ce(IV), Sb(III), W(VI), Tl(I), Cd(II), Rh(III), Be(II), Sr(II) and platinum metals. Nitrate, chloride, sulphate, acetate, iodide, bromide and thiourea do not interfere. The applicability of the method was tested by analyzing satisfactorily a wide variety of samples with good reproducibility.

**Keywords:** Titanium, Extraction, 6-Chloro-3-hydroxy-2-(2'-furyl)-4-oxo-4*H*-1-benzopyran, Spectrophotometry

### Introduction

A variety of benzopyran reagents employed for spectrophotometric determination of titanium<sup>1-3</sup> have undoubtedly been used for the micro determination of some of the metal ions, but these methods require prior separations from seriously interfering elements and are of restricted use due to low sensitivity. In view of aforesaid aspect, an attempt has been made to introduce 6-chloro-3-hydroxy-2-(2'-furyl)-4-oxo-4*H*-1-benzopyran (CHFB) for the complexation of titanium in acetic acid medium in presence of sulphite effecting quantitative extraction into dichloromethane which not only give a rapid and highly reproducible system but also provides a highly sensitive and selective spectrophotometric determination of titanium in trace amounts.

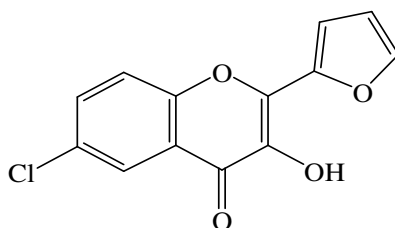
### Experimental

A stock solution of titanium(IV) containing 1 mg  $\text{mL}^{-1}$  is obtained by dissolving an accurately weighed amount of  $\text{K}_2[\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$  in minimum volume of HCl and make

up the volume up to 100 mL in a volumetric flask before standardizing the metal ion gravimetrically<sup>4</sup>. Working solutions of the metal ion of required  $\mu\text{g mL}^{-1}$  level are made by proportionate dilutions.

Solutions of other metal ions at the  $\text{mg mL}^{-1}$  level were prepared by dissolving their commonly available sodium or potassium salts 'C.P grade' in distilled water or dilute acid. Sulphite solution, 5% is prepared by dissolving 5 g of sodium sulphite (A.R) in 100 mL distilled water. Dichloromethane (A. R. grade) was used for the system.

A UV-Visible spectrophotometer (Elico SL-177) with 10 mm matched cells was used for the routine absorbance measurements and spectral studies. The reagent 6-chloro-3-hydroxy-2-(2'-furyl)-4-oxo-4H-1-benzopyran (Figure 1) (CHFB, m.pt. 198 °C), was synthesized by the literature method<sup>5-6</sup> and dissolved in alcohol to get 0.05% (w/v) solution.



**Figure 1.** 6-Chloro-3-hydroxy-2-(2'-furyl)-4-oxo-4H-1-benzopyran (CHFB)

### Synthetic samples

Synthetic sample solutions were obtained by mixing solutions of Ti(IV) and other metal ions in a suitable proportion with compositions as shown in Table 1.

**Table 1.** Analysis of samples by the proposed method

S.No.	Sample composition*	Ti(IV) added, $\mu\text{g}$	Ti(IV) found, $\mu\text{g}$ #
1	$\text{Se}^{\text{IV}}(0.1)$ , $\text{Mg}^{\text{II}}(0.1)$ , $\text{Bi}^{\text{III}}(0.1)$ ,	25	25.33
2	$\text{Re}^{\text{VII}}(0.1)$ , $\text{V}^{\text{V}}(0.1)$ , $\text{Sr}^{\text{II}}(1.0)$ ,	10	10.05
3	$\text{Sb}^{\text{III}}(0.1)$ , $\text{Be}^{\text{II}}(0.2)$ , $\text{Mn}^{\text{II}}(1.0)$	15	14.95
4	$\text{Cd}^{\text{II}}(1.0)$ , $\text{Ce}^{\text{IV}}(1.0)$ , $\text{Hg}^{\text{I}}(0.1)$	20	20.45
5	$\text{Re}^{\text{VII}}(1.0)$ , $\text{Cd}^{\text{II}}(1.0)$ , $\text{Ag}^{\text{I}}(0.1)$	30	29.05
6	$\text{V}^{\text{V}}(0.1)$ , $\text{Mg}^{\text{II}}(1.0)$ , $\text{Ag}^{\text{I}}(0.1)$	10	10.39
7	$\text{Hg}^{\text{II}}(0.1)$ , $\text{Re}^{\text{VII}}(1.0)$ , $\text{Bi}^{\text{III}}(0.1)$	10	9.85
8	$\text{Mg}^{\text{II}}(1.0)$ , $\text{Ce}^{\text{IV}}(1.0)$ , $\text{Se}^{\text{IV}}(0.1)$	20	10.09
9	$\text{Rh}^{\text{III}}(0.1)$ , $\text{Re}^{\text{VII}}(0.1)$ , $\text{Ca}^{\text{II}}(0.1)$	15	15.09
10	$\text{Sb}^{\text{III}}(0.1)$ , $\text{Ca}^{\text{II}}(0.1)$ , $\text{Se}^{\text{IV}}(0.1)$	25	24.86
11	Reverberatory flue dust, 50 $\mu\text{g}$	10	9.98
12	Tap Water	25	25.02

\*Figure in parenthesis indicates the amount of the metal in mg, #Average of triplicate analysis

### Reverberatory flue dust

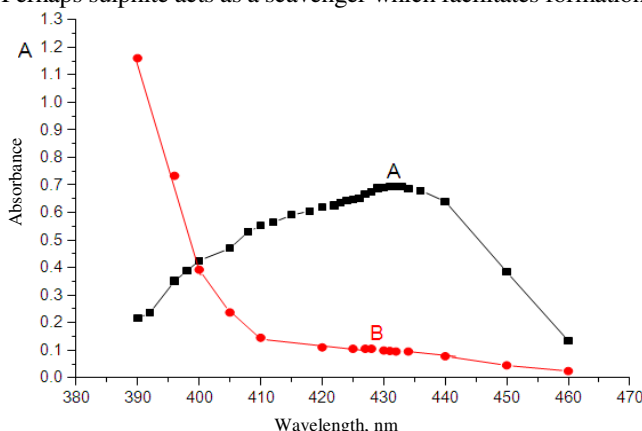
A weighed amount of flue dust from copper manufacture was mixed with a known amount of titanium and dried in an oven. After fusion of the sample with sodium peroxide (approximately eight times the weight of the sample), the leach was neutralized carefully with conc.  $\text{H}_2\text{SO}_4$  and the solution was made 100 mL with distilled water and adjusted at pH ~7 to determine titanium by the proposed method.

### Procedure

To a sample solution containing  $\leq 25 \mu\text{g}$  Ti(IV) and/or other metal ions in a 100 mL separating funnel; 0.5 mL  $\text{CH}_3\text{COOH}$  (1 M), 2 mL sulphite solution (5% in distilled water), 2 mL 0.05% CHFB (in alcohol) were added and aqueous volume was made up to 10 mL with distilled water. The contents were gently mixed and then equilibrated once with equal volume of dichloromethane for 30 s. The two phases were allowed to separate and the yellow organic layer was filtered through a Whatmann filter paper no. 41 (pre-treated with dichloromethane) into a 10 mL volumetric flask, which was filled up to the mark with pure dichloromethane. The absorbance of the yellow coloured complex was measured at 432 nm against a similarly prepared reagent blank and the amount of titanium was determined from a standard curve obtained by plotting a graph (Figure 2) between varying micro amounts of the metal ion and their corresponding absorbance values, as per procedure.

### Results and Discussion

Ti(IV) reacts with CHFB forming a yellow coloured species in presence of sulphite solution, which is quantitatively extracted into dichloromethane. Absorption maximum of the complex lies at 430-434 nm in the visible region, where the reagent blank shows hardly any absorbance (Figure 2). Hence, the absorbance measurements of the system were carried out at 432 nm. Keeping concentration same for the acids at 0.1 N, the absorbance values are decrease in the order  $\text{CH}_3\text{COOH} > \text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$ . Without sulphite, the absorbance is quite low (0.185) while reaches to 0.315 for 0.5 mL on addition of sulphite and become maximum (0.546) for 1.8-2.5 mL. Perhaps sulphite acts as a scavenger which facilitates formation of the complex.



**Figure 2.** Absorption spectrum of Ti(IV) CHFB complex in dichloromethane [Conditions:  $2.5 \mu\text{g}$  of Ti(IV)/mL, other conditions are the same as described in the procedure section. Curve A- Absorbance of complex measured against reagent blank. Curve B- Absorbance of reagent blank measured against dichloromethane]

#### Effect of diverse ions

Under the optimum conditions of the procedure containing  $25 \mu\text{g}$  of Ti(IV), the ions complexing agents added as their sodium or potassium salts in 10 mL aqueous phase such as thiourea (100 mg); iodide (75 mg); chloride (35 mg); sulphate, nitrate (15 mg each); sulfosalicylic acid (10 mg); ascorbic acid, acetate, thiocyanate (5 mg each); oxalate, aspirin (2 mg each); bromide (1 mg); are non-interfering. But citrate, EDTA 'disodium salt' and phosphate (1 mg each); decrease absorbance.

Similarly, the effect of different metal ions on the absorbance of the complex was studied by measuring absorbance of 25  $\mu\text{g}$  titanium in presence of these ions added to the aqueous phase (in 10 mL final volume) before the addition of acid. Dysprosium(III), neodymium(III), gadolinium(III), cerium(IV), ytterbium(III), manganese(II) (10 mg each); strontium(II), thallium(I), cadmium(II), samarium(III) (5 mg each); rhenium(VII), selenium(IV), mercury(II), magnesium(II) (1 mg each); antimony(III), calcium(II), beryllium(II), bismuth(III) (0.5 mg each); vanadium(V), silver(I), arsenic(III), mercury(I), europium(III), rhodium(III), barium(II) (0.1 mg each); do not interfere. Copper (II) (0.1 mg) can be masked with 25 mg thiourea respectively.

### *Spectral characteristics*

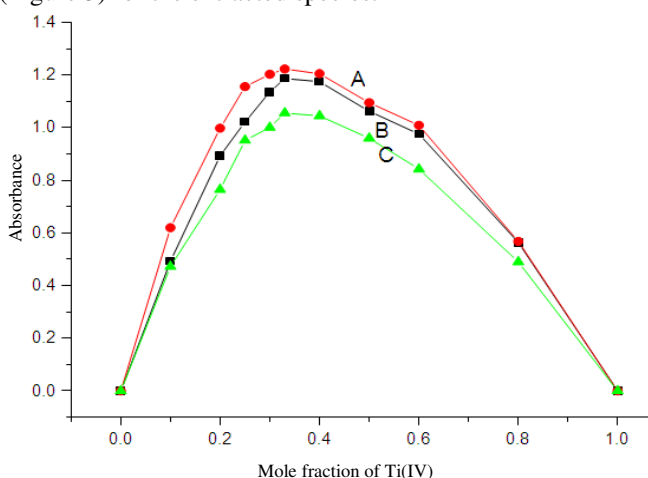
The method obeys Beer's law in the range 0.0-2.5  $\mu\text{g}$  of  $\text{Ti(IV)}$   $\text{mL}^{-1}$  however, the optimum concentration range that can be measured, as evaluated from Ringbom's plot<sup>7</sup> is 0.55-2.13  $\mu\text{g}$  of  $\text{Ti/mL}$ . The molar absorptivity, specific absorptivity and Sandell's sensitivity values of the complex at 432 nm are  $1.659 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ,  $0.346 \text{ mL g}^{-1} \text{ cm}^{-1}$  and  $0.00289 \mu\text{g of Ti(IV) cm}^{-2}$ , respectively. The linear regression equation is  $Y=0.331X+0.015$  ( $Y$ = absorbance,  $X$ =  $\mu\text{g}$  of  $\text{Ti(IV) mL}^{-1}$ ) and correlation coefficient,  $r = 0.9996$ . The limit of detection of the method is 0.017 ppm. The reproducibility of the method was tested by performing ten sets of experiments keeping the same (2  $\mu\text{g}$  of  $\text{Ti mL}^{-1}$ ) amount of metal ion each time; the standard deviation and relative standard deviation of the method found are 0.0018 and 0.257% respectively.

### *Stoichiometry of complex*

Stoichiometry of  $\text{Ti(IV)}$  CHFB complex is established by Job's method of continuous variation<sup>8</sup>, as modified by Vosburgh and Cooper<sup>9</sup> is found to be 1:2. This is further confirmed by mole ratio method<sup>10</sup>. The details are given below:

### *Job's method of continuous variation*

Equimolar solution of titanium and CHFB ( $4.177 \times 10^{-4} \text{ M}$ ) of  $\text{Ti(IV)}$  and CHFB were mixed and the absorbance corresponding to different mole fractions of titanium are measured at three different wavelengths, namely 420, 432 and 440 nm, the curve indicate 1:2 stoichiometry (Figure 3) for the extracted species.



**Figure 3.** Job's method of continuous variation of  $\text{Ti(IV)}$  CHFB complex  
Curve A- 432 nm, Curve B- 420 nm and Curve C- 440 nm

### *Mole ratio method*

Equimolar solution of Ti(IV) and CHFB ( $4.177 \times 10^{-4}$  M) were prepared. Keeping the concentration of metal ion constant (1.0 mL of  $4.177 \times 10^{-4}$  M), the volume of the reagent CHFB was varied in each case. The absorbance in each case was measured at three wavelengths namely 420, 432 and 440 nm as per procedure. The plot of absorbance *versus* mole ratio of the two components shows a clear break at 1:2 Ti-CHFB ratio.

### **Conclusion**

The method is simple, highly selective and sensitive, with good reproducibility. It is satisfactory for the analysis of a wide variety of samples including reverberatory flue dust and the results obtained are in agreement with the amount of metal ion initially added.

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