

Spectrophotometric determination of thorium(IV) using 3-hydroxy-2-(2'-thienyl)-4H-chromen-4-one

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A spectrophotometric method has been developed to determine thorium using 3-hydroxy-2-(2'-thienyl)-4H-chromen-4-one (HTC) which forms a 1:4 yellow complex in dilute acetic acid solution with λ_{max} at 430 nm. The method is free from the interference of a large number of metal ions of interest. Molar absorptivity and Sandell's sensitivity of the complex are $3.95 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0059 \mu\text{g cm}^{-2}$, respectively.

Since thorium often occurs naturally with rare earth elements, its separation from them and/or determination in their presence needs special attention. Also, thorium(IV) forms more stable complexes than the rare earths and this fact, in the present investigation, has been utilized to work out a spectrophotometric method for the trace determination of the former. Literature survey reveals that chromones and their derivatives give colour reactions¹⁻⁵ with transition metal ions even at quite low concentration levels and this behaviour of the reagent is extended further to cover thorium as well, employing 3-hydroxy-2-(2'-thienyl)-4H-chromen-4-one as a complexing agent and developing a method for microdetermination of thorium in aqueous medium, with the following details.

Experimental

Standard stock solution of thorium(IV) containing 1 mg mL^{-1} Th(IV) was prepared by dissolving an accurately weighed amount of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in distilled water. Working solutions at $\mu\text{g mL}^{-1}$ level were obtained by suitable dilutions.

Solutions of other metal ions were prepared by dissolving their commonly available "chemically pure" salts in distilled water or dilute hydrochloric or sulphuric acid.

3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one (HTC) was prepared⁶ in the laboratory and characterized. It was dissolved in ethanol to give 0.1% (m/v) solution. Acetic acid, 2 mol l^{-1} , was used. A UV-visible

spectrophotometer (Shimadzu-UV-140-02) was used for absorbance measurements.

To a solution containing $20 \mu\text{g}$ of Th(IV) in a 10 mL measuring flask, 1 mL (2M) CH_3COOH , and 1 mL 0.1% HTC were added and the volume was made up to the mark with distilled water. The absorbance measurements of the coloured species were taken at 430 nm against the similarly prepared reagent blank using 10 mm matched cells on a UV-visible spectrophotometer. To draw a standard curve, different microgram amounts of the metal ion were taken in each set and their corresponding absorbance values were noted and the graph was plotted between the two variables.

Results and discussion

It has been observed that thorium, in the tetravalent state, reacts with HTC forming a yellow complex in acidic medium at pH 3.3, whose absorption maximum lies at 430 nm. The absorbance measurements were taken in the aqueous phase as the resulting complex is non-extractable in nature.

Various factors affecting the absorbance of Th(IV)-HTC complex were studied. Under the same set of aqueous conditions, the absorbance of the complex is influenced by the nature of the acid. At 0.2N solution for different acids, the absorbance increases in the order H_2SO_4 , HCl, HNO_3 and CH_3COOH . Hence CH_3COOH was the preferred acid medium for the formation of Th(IV)-HTC complex. The absorbance increases with increase in acetic acid concentration and is maximum if the aqueous solution contains 0.95-1.05 mL of 2M CH_3COOH and shows a fall thereafter. In absence of HTC, the absorbance is nil. While it is 0.130 if 0.1 mL of HTC is there in solution and reaches a maximum value of 0.340 when 0.5-1.5 mL of 0.1% HTC are present in 10 mL aqueous volume. Further increase in HTC content, results in lowering of absorbance. It is evident from the study of different variables that for $20 \mu\text{g}$ Th(IV), 0.95-1.05 mL of 2 mol l^{-1} CH_3COOH , 0.5-1.5 mL of 0.1% HTC (in ethanol) at room temperature in a final 10 mL aqueous volume are the optimum conditions for the formation of the complex whose λ_{max} lies at 430 nm.

The absorption spectrum of Th(IV) complex against an analogously prepared blank shows maximum absorbance at 430 nm. The complex

Table I—Analysis of different samples by the proposed method

S.No	Composition of the sample Matrix ^a	Th(IV)	
		Added µg	Found µg
1	Ce(0.1)	10	10
2	Dy(0.5)	13	12
3	Pr(0.6)	15	14
4	Fe ^{II} (0.1)	10	10
5	Fe ^{III} (0.1)	13	13.8
6	Tb(0.5), Sm(0.1)	8	9
7	La(0.5), Eu(0.5)	11	10
8	Tb(0.5), Dy(0.5), Gd(0.5), Nd(0.5)	10	10
9	Cu(0.01), Ni(0.5), Mn(0.5)	15	14
10	Re(0.01), Ta(0.5), W(0.005)	5	6
11	Pt (0.01), Pd(0.001), As(0.5), Os(1)	20	19
12	Cr(0.05), Se(0.05), Ce(0.05)	11	10
13*	La(0.05), Ce(0.09), Pr(0.012), Nd(0.045), Sm(0.01)	5	5.8
14*	La(0.04), Ce(0.072), Pr(0.01), Nd(0.036), Sm(0.003)	20	19.4

*Corresponding to Australian Monazite.

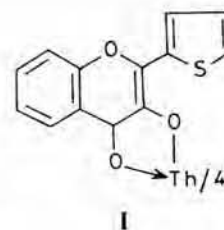
^aFigure in bracket indicates the amount of metal ion in mg

obeyed Beer's law range up to 0.0-5.0 µg Th mL⁻¹ and the optimum concentration range that can be measured accurately, as evaluated from Ringbom plot, was 1.1 to 3.5 µg Th mL⁻¹. Molar absorptivity and Sandell's sensitivity of the complex were 3.95×10⁴ L mol⁻¹ cm⁻¹ and 0.0059 µg Th cm⁻², respectively. For eight replicate determinations containing 20 µg thorium each time, the standard deviation was found to be ±0.006 when the absorbance measurements are effected within 15 min.

The ratio of Th to HTC in the complex was determined as 1:4 by Job's method of continuous variations^{7,8} employing their equimolar solutions. This ratio was further confirmed by the mole ratio method⁹. The probable structure of the complex is given in I.

Effect of diverse ions

The effect of diverse ions/complexing agents on the absorbance of the thorium complex was also studied. Sulphate, 30 mg; acetate, chloride, 20 mg each; nitrite, thiourea, 10 mg each; nitrate, thiocyanate, carbonate, bromide, iodide, 1 mg each; citrate, 0.1 mg; tartrate, sulphosalicylic acid, 0.05 mg each; added prior to the addition of the reagent to the aqueous phase in a final 10 mL volume do not affect the absorbance of the Th(IV)-HTC complex; whereas, oxalate, fluoride, EDTA, H₂O₂ (30%) cause interference by lowering absorbance. Preliminary



separation is required in case of phosphate as ammonium molybdophosphate. Re(VII), Os(VIII), 3 mg each; Co(II), Ni(II), Cu(II), Mn(II), As(III), Eu(III), Pr(III), Nd(III), Gd(III), Dy(III), Tb(III), Ta(V), Au(III), 1 mg each; Ce(IV), Se(IV), Cr(VI), Pd(II), W(VI), Fe(II), Cr(III), Y(III), Ce(III), Sm(III), Ho(III), La(III), 0.1 mg each; Ir(III), Pt(IV), 0.01 mg each; in 10 mL aqueous solution does not show any absorbance and are hence non-interfering. Fe(III), 0.1 mg/10 mL; U(VI), 0.5 mg/10 mL; and Zr(IV), 0.1 mg/10 mL; do not cause any interference if 1 mg of ascorbic acid is also present alongwith in aqueous solution in each case. However, Sb(III), Bi(III), Ti(IV), 0.1 mg each; cause interference.

The proposed method is simple, very sensitive and is free from the interference of a large number of metal ions. The validity of the method is tested by analyzing different samples of varying composition and also that of Australian Monazite as given in Table I. The proposed method of determination of thorium is free from the interference of a large number of metal ions which are of great analytical

importance so far as the determination of thorium is concerned and has an edge over some of the existing methods¹⁰⁻¹⁴ in respect of sensitivity, selectivity and accuracy. The method makes use of HTC as an analytical reagent for thorium for the first time.

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