

Trace Determination of Thorium with 6-Chloro-3-hydroxy-2-(2'-furyl)-4H-chromen-4-one as an Analytical Reagent

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A simple, rapid, highly sensitive and selective method for the spectrophotometric determination of micro amounts of thorium(IV) has been worked out using 6-chloro-3-hydroxy-2-(2'-furyl)-4H-chromen-4-one (CHFC) as a complexing agents in a acidified (CH_3COOH , pH 3.5) medium. The yellow complex shows a maximum absorbance at 425-435 nm. The method obeys Beer's law upto $3.5 \mu\text{g Th cm}^{-2}$. As many as 31 cations and 11 anions and/or complexing agents do not interfere. The method has good reproducibility and can be satisfactorily applied to the determination of thorium in samples corresponding to Australian monazite in composition.

Keywords: Thorium, 6-Chloro-3-hydroxy-2-(2'-furyl)-4H-chromen-4-one, Spectrophotometry.

INTRODUCTION

Thorium is a naturally occurring radioactive material discovered by Swedish chemist Jons Jakob Berzelius in 1828 and named as Thor, normally found in the environment, geological materials and nuclear fission products. Thorium is fertile rather than fissile, and can only be used as a fuel in conjunction with a fissile material such as recycled plutonium and is a worthwhile potential raw material for fissile nuclear fuel production for electricity production in power plants [1]. Thorium finds several applications in industries also like the manufacture of ceramics, lantern mantles, light lamps, welding electrodes, camera, telescope lenses and metals used in aerospace industry.

Thorium is a highly toxic heavy metal and its compounds are hazardous to environment. Humans when exposed to thorium have increased risk liver diseases [2]. In view of the extensive application and toxicity, the development of new methods for the monitoring, separation and preconcentration of thorium in various environmental samples is particular significant [3]. The analytical chemistry of thorium is complicated because of its similar behavior as that of other rare earths and in minerals it is usually associated with other rare earth metals. Different analytical techniques such as neutron activation analysis [4], inductively coupled plasma [5], chromatography [6], optical

sensor [7], electrochemistry [8] and spectrophotometry [9-16] have been reported for Th(IV) determination. Several conventional sample preparation techniques were performed to separate and preconcentrate Th(IV), such as liquid-liquid extraction (LLE) [17,18], solid-phase extraction (SPE) [19] and flotation [20] prior to its determination by different instruments. However, these methods are relatively expensive and consume large amounts of organic solvents or are tedious and time consuming. Various attempts have been made to modify the methods for determining thorium in microamounts spectrophotometrically so as to reduce the interference of various elements and to enhance the sensitivity of system in order to widen their scope.

From a survey of literature, it appears that there is a lot of scope for working out new methods and effecting amendments in the existing ones in view of the restrictions generally met within their applicability especially for reasons of their lower sensitivity and selectivity. Most of these aspects in various methods serve as impediments when trace amount of thorium in various samples are to be determined, thereby justifying the need for newer and/or modified procedures which are able to contain this problem to minimum. In the recent past, chromones and some of its derivatives [21-26] have undoubtedly been used for the microdetermination of some of the metal ions, but their application with respect to thorium has not received much attention.

In this work, an attempt is made to develop a highly sensitive and selective system for spectrophotometric determination of thorium. A new reagent, 6-chloro-3-hydroxy-2-(2'-furyl)-4H-chromen-4-one is introduced, which not only enhances the sensitivity ($\epsilon = 6.74 \times 10^4$) to a much higher value as compared to the existing complexes of thorium(IV), but also makes the method free from almost all the analytical important interfering elements. The procedure is simple, rapid and can be applied to the analysis of various kinds of thorium(IV) samples with satisfactory accuracy.

EXPERIMENTAL

Thorium (IV) solution: A stock solution of thorium (IV) (1 mg mL^{-1}) is prepared by dissolving an accurately weighed amount of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (s.d. fine-chem) in deionized water. Working solution at $\mu\text{g mL}^{-1}$ level was obtained by suitable dilutions.

Solutions of other metal ions of appropriate concentration were prepared by dissolving their commonly available salts (A.R.) in water or dilute acid and acetic acid (2 M) is used in this work.

6-Chloro-3-hydroxy-2-(2'-furyl)-4H-chromen-4-one (CHFC) is synthesized as per literature method [27] and its 0.1 % (w/v) solution in ethanol is used for analytical purpose. Yield 60 %, (m.w. $\text{C}_{13}\text{H}_6\text{O}_4\text{Cl}$; m.p.: 198°C); IR (KBr, ν_{max} , cm^{-1}): 3260 (OH) and 1635 (CO); $^1\text{H NMR}$ (90 MHz; CDCl_3): δ 12.80 (1H, br s, OH), 8.18 (1H, br s), 7.75 (2H, m), 7.58 (1H, m), 7.37 (1H, m) and 6.25 (1H, m). Elemental analysis calcd. (found) %: C, (58.43) 58.4; H, (2.67) 2.60.

Analytical samples: Synthetic samples are prepared by mixing solutions of thorium and other elements in suitable proportions. For absorbance measurements, a UV-Visible-140-02 spectrophotometer (Shimadzu, Japan) is used.

Procedure: To an aliquot containing $10 \mu\text{g}$ Th(IV) in a 10 mL measuring flask, added 1.0 mL of 2 M CH_3COOH and 1 mL of 0.1% CHFC and enough distilled water to make the aqueous volume 10 mL (pH 3.5). The absorbance measurements of the coloured species are taken at 430 nm against the similarly prepared reagent blank using 10 mm matched cells on a UV-Visible Spectrophotometer.

RESULTS AND DISCUSSION

It has been observed that thorium in the tetravalent state, reacted with 6-chloro-3-hydroxy-2-(2'-furyl)-4H-chromen-4-one (CHFC) reagent forming a yellow complex in acidic

medium, whose absorption maximum lies at 430 nm. Other acids *viz.* H_2SO_4 , H_3PO_4 , HCl , HClO_4 , a lower absorbance of the complex is observed, whereas in the medium the colour is found to be maximum and stable for 20 min. Hence, acetic acid provides a suitable medium. The absorption spectrum of the complex against a reagent blank exhibit a broad absorption band at 425-435 nm (Fig. 1). The spectrum of reagent blank against distilled water has shown an absorbance value of only around 0.010 nm. Thus, all the measurements are carried out at 430 nm against reagent blank.

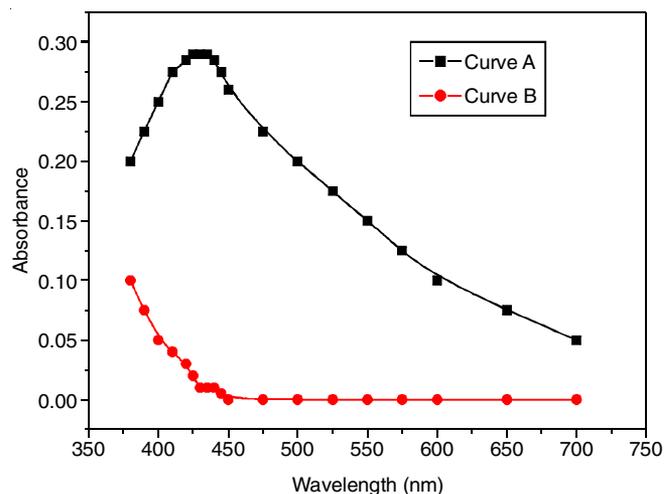


Fig. 1. Absorption spectrum of Th(IV)-CHFC complex; Curve A - Th(IV) complex measured against reagent blank, Curve B - Reagent blank measured against distilled water

Other operative parameters, which affect the absorbance of metal complex (temperature of aqueous phase, acid and CHFC concentration) are given in Table-1.

Effect of diverse ions: Under the optimum conditions of the procedure, ions and/or complexing agents added as their sodium or potassium salts in the aqueous phase ($\text{mg}/10 \text{ mL}$) such as sulphate, thiocyanate (30 mg each); chloride, nitrate, thiourea (20 mg each); acetate, bromide (10 mg each); iodide, nitrite, sulphosalicylic acid, carbonate (1 mg each); added initially to the aqueous phase do not affect the absorbance of Th(IV)-CHFC complex. Citrate, oxalate, EDTA, tartrate, fluoride, phosphate (1 mg each) and H_2O_2 (1 mL of 6 %) interfere by decreasing the absorbance value.

Among the cations, Os(VIII) (3 mg/10 mL); Co(II), Ni(II), Gd(III), Se(IV), Cu(II), Mn(II), As(III), Ce(IV), Au(III), Cr(VI), Rh(VII), Pd(II), Pt(IV), Ta(V), Cr(III) (1 mg/10 mL each);

TABLE-1
EFFECT OF VARIOUS PARAMETERS ON THE ABSORBANCE OF THORIUM COMPLEX

Acid (2 N) ^a	H_2SO_4	HNO_3	H_3PO_4	HClO_4	HCl	CH_3COOH
Absorbance	0.080	0.080	0.060	0.060	0.080	0.290
CH_3COOH (2 N) ^b mL	0	0.02	0.04	0.1-0.22	0.24	0.3
Absorbance	0.100	0.200	0.270	0.290	0.280	0.275
CHFC ^c , mL (0.1 % in ethanol)	0	0.1	0.2	0.4	0.5-1.5	1.7
Absorbance	0.000	0.100	0.200	0.275	0.290	0.275
					2.0	2.5
					0.250	0.200
						0.150

Experimental conditions: μg .

^aTh(IV) = $10 \mu\text{g}$, acid (2 N) = 1 mL, CHFC (0.001 % in acetone) = 1 mL, aqueous volume = 10 mL, λ_{max} = 435 nm, at room temperature.

^bTh(IV) = $10 \mu\text{g}$, CH_3COOH (2 N) = variable, CHFC (0.001 % in acetone) = 1 mL, aqueous volume = 10 mL, λ_{max} = 435 nm at room temperature.

^cTh(IV) = $10 \mu\text{g}$, acid (2 N) = 1 mL, CHFC (0.001 % in acetone) = variable, aqueous volume = 10 mL, λ_{max} = 435 nm at room temperature.

Tb(III), Dy(III), Yt(III), Sm(III), Ho(III), Nd(III), Ps(III), La(III), Ce(III), Eu(III), (0.1 mg/10 mL each); Ir(III), U(VI), Ru(III), W(VI) (0.01 mg/10 mL each) have no effect on the absorbance of the complex. However, Bi(III), Mo(VI) and Fe(III) ions interfered by colouring the aqueous phase.

Beer's law and sensitivity: Beer's law is valid in the concentration range of 0-3.5 $\mu\text{g Th(IV) mL}^{-1}$. However, the optimum range for the determination of thorium(IV), as evaluated from a Ringbom plot [28] (Fig. 2) is found to be 0.3-3.2 ppm. The molar absorptivity and Sandell's sensitivity of the system are 0.290 $\text{mL g}^{-1} \text{cm}^{-1}$ and 0.0034 $\mu\text{g Th(IV) cm}^{-2}$, respectively at 430 nm.

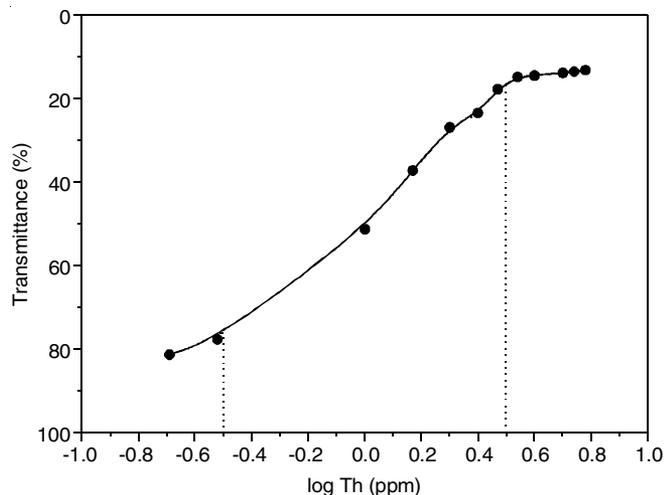


Fig. 2. Ringbom plot for Th(IV)-CHFC complex

Sandell's sensitivity (S) represents the number of microgram of determinand per mL of a solution having an absorbance (A) of 0.001 for a path length (l) of 1 cm, thus

$$S (\mu\text{g cm}^{-2}) = \frac{10^{-3}}{a}$$

where a is the specific absorptivity, and its value ($\text{mL g}^{-1} \text{cm}^{-1}$) corresponds to the absorbance of a 1 $\mu\text{g mL}^{-1}$ solution of the determinand in a cuvette with an optical path length of 1 cm.

Moreover,

$$a = \frac{\epsilon}{\text{Atomic weight of Th}} \times 1000$$

where ϵ is the molar absorptivity, which can be represented as follows:

$$\epsilon = \frac{A}{C \times l}$$

where c is the molar concentration of the determinand and l is the path length (1 cm).

Stoichiometry of complex: Equimolar solutions (0.0005 M) of Th(IV) and CHFC are utilized to determine the metal to ligand ratio by Job's method of continuous variation [29,30] (Fig. 3). The absorbance values are measured at two different wavelength 430 and 450 nm. The obtained curves are indicative of 1:4 stoichiometry in the aqueous species. This is further confirmed by mole ratio method [31] (Fig. 4) by using equimolar solutions of Th(IV) and CHFC (0.0005 M) and that of the reagent is varied from 0.0-3.0 mL. The graph is plotted between the

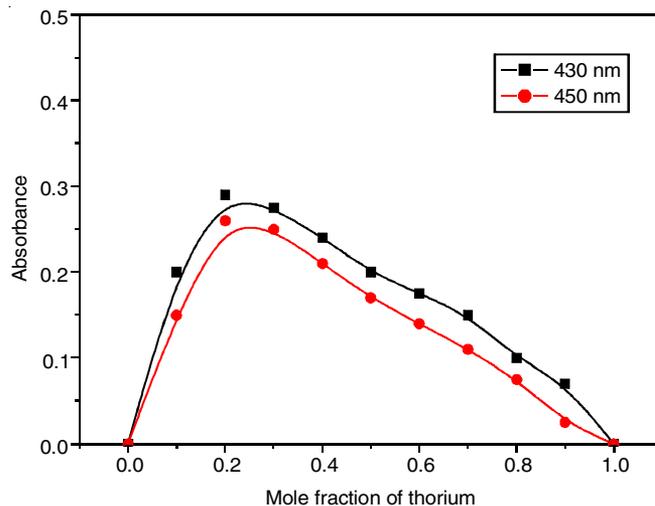


Fig. 3. Continuous variation of thorium and CHFC (Condition: Thorium = 0.0005 M ; CHFC = 0.0005 M)

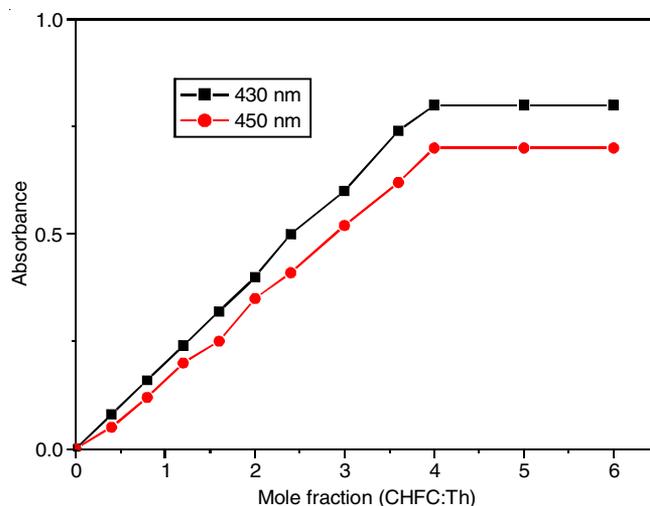
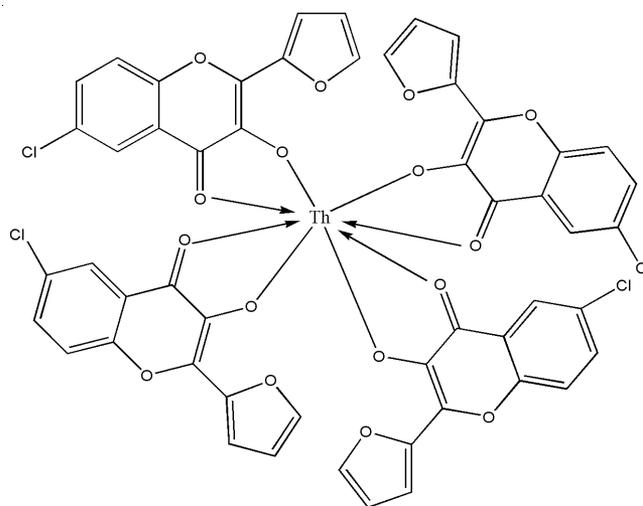


Fig. 4. Mole ratio method (Condition: Thorium = 0.5 mL, 0.0005 M; CHFC = 0.0005 M)

mole ratio of the reagent and the corresponding values at 430 and 450 nm. The probable structural formula of Th(IV)-CHFC complex in the aqueous solution may be represented as:



Structure of Th(IV)-CHFC complex

TABLE-2
ANALYSIS OF DIFFERENT SAMPLES BY THE PROPOSED METHOD

S. No.	Composition of the samples	Th(IV) added (μg)	Th(IV) found (μg)
1	Os (3)	10	11
2	Dy (1.0)	5	4
3	Ce ^{IV} (0.5)	15	14
4	Co (1.0), Ni (1.0), Cu (1.0)	25	25
5	Mn (1.0), As (1.0), Au (1.0)	10	11
6	Pd (1.0), Pt (1.0), Ta (1.0)	15	14
7	Y (0.05), Ho (0.05), Nd (0.05)	10	11
8	Gd (1.0), Eu (0.05), Ta (1.0)	15	14
9	Cr ^{III} (1.0), Cr ^{VI} (1.0), Re (1.0)	25	25
10	Nd (0.05), Pr (0.05), La (0.05)	10	11
11*	La (0.05), Ce ^{III} (0.09), Pr (0.012), Nd (0.045), Sm (0.01)	5	4
12*	La (0.04), Ce ^{III} (0.072), Pr (0.01), Nd (0.036), Sm (0.008)	10	11

*Samples corresponding to Australian monazite in composition; a) Values in bracket indicate the amount of metal ion in mg.

TABLE-3
COMPARISON OF THE PROPOSED METHOD OF DETERMINATION OF THORIUM(IV) WITH SOME OF THE EXISTING METHODS

Aqueous conditions	i) λ_{max} (nm) ii) Extractant	Molar absorptivity ($\text{l mol}^{-1} \text{cm}^{-1}$)	Interfering ions	Ref.
Th(IV), pH 5.8, semi xylenol orange	i) 510 nm ii) -	3.5×10^4	Ca(II), Sr(II), Mg(II), Mn(II), Bi(III), Al(III), Pb(II), Cu (II), Ni(II), Co(II), Zn(II), Cd(II), Fe(III), Cr(III)	[32]
Th(IV), Sodium benzoate and Aniline blue	i) 660 nm ii) -	3.16×10^3	-	[33]
Th(IV), pH 3.5, 4, 8-Diamino-1,5-dihydroxy anthraquinone-2,6-disulphonic acid	i) 685 nm ii) -	-	As ⁵⁺ , Au(III), UO ₂ ²⁺ , Al(III), Fe(III), Ba(II), Ca(II), Zn(II), F ⁻	[34]
Th(IV), 2,4-Dihydroxybenzaldehyde isonicotinoyl hydrazone	i) 390 nm ii) -	2.2×10^4	-	[35]
Th(IV), 1-amino-4-hydroxy anthraquinone	i) 590 nm ii) -	1.3×10^4	CN ⁻ ion has to be used as a masking agent for a large number of foreign ions.	[36]
Th(IV), pH 3.5, 6-chloro-3-hydroxy-2-(2'-furyl)-4H-chromen-4-one (CHFC)	i) 430 nm ii) -	6.74×10^4	Bi(III), Mo(VI), Fe(III) (31 cations are non-interfering)	Proposed method

Analytical applications: The applicability of proposed method is tested by carrying out satisfactorily analysis of various samples including the one of Australian monazite with corresponding composition and the result obtained are reproducible (Table-2). The procedure is simple rapid and free from the interference of a large number of metal ions. The present method is also compared well with some of the existing method [32-36] (Table-3) in respect of its sensitivity and selectivity. As seen from the comparable data, this method is found to be highly selectivity among the other reported methods.

Conclusion

A simple, rapid and sensitive system of spectrophotometric determination of thorium is developed with CHFC *i.e.* 6-chloro-3-hydroxy-2-(2'-furyl)-4H-chromen-4-one in acetic acid medium. The method is free from the interference of a large number of cations and anions. This method obeys Beer's law in the range 0-35 $\mu\text{g Th(VI)}/10 \text{ mL}$ and has a Sandell's sensitivity of 0.0034 $\mu\text{g Th(IV) cm}^{-2}$. The method is highly reproducible with a standard deviation of ± 0.002 . Stoichiometry of complex [Th(IV)-CHFC, 1:4] (metal to ligand) is also established.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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