

## Spectroscopy method for determination of Thorium with Azocalix[4]arene

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**Abstract**—A research of possible application of azocalixarene for evaluation of thorium content was described. Based on the complex of Ortho-Ester Tetra- Azophenylcalix[4]arene (TEAC) with Thorium(IV) in acetate buffer solution, the precision, reproducibility and interference of foreign metal ions were studied. From these results, a new method has been built to determine thorium. And this recommended method could be applied for determination of thorium concentration in some monazite ore with high confident results.

**Keywords:** Azocalixarene, Spectroscopy, Thorium, Complex, Molecular Mechanism, Calculation.

### I. INTRODUCTION

The compounds, which have a conjugated chromophore azo (-N=N-) group in *p*-positions are an important class of organic colorants and two or more aromatic rings [1,2]. Many interesting aspects of complexation of alkali and alkaline earth metal ions were reported by studying the absorption behavior of chromophoric groups. Among the azophenolic supramolecules, azocalix[4]arenes are especially attractive for their efficient ionophoric properties towards some of important guest ions such as  $\text{Ca}^{2+}$  or  $\text{K}^{+}$  ion [7]. There are relatively few reports on the design of sensor for transition metal ions as  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ , or  $\text{Fe}^{3+}$  [2,4,6,10]. A lead ion-selective electrode was made from calixarene carboxyphenyl azo derivative [3]. Besides, the extraction procedures were developed based on calixarene for metal cations like  $\text{Ag}^{+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  [4,18]. Moreover, the spectroscopic methods were used for determination of  $\text{Rh}^{3+}$ ,  $\text{Cu}^{2+}$  [22]. Last year, a new membranes containing *p*-(4-*n*-butylphenylazo)calix[4]arene as an electroactive material was used to fabricate a new cobalt (II)-selective sensor [8].

Thorium has traditionally been measured by radio-metric techniques, such as gamma spectroscopy [11] alpha spectroscopy, and neutron activation analysis (NAA) [12], or ICP-AES (atomic emission spectrometry), a non-radiometric

technique, offers low detection limits for many elements, but unfortunately is relatively poor for thorium [13], or ICP-MS [14, 23]. However, these methods are complicated and costly.

UV-VIS method is widely used for this purpose for its simplicity and rapidity in analysis. Chlorophosphonazo and arsenazo [15] type reagents are more frequently used as chromogenic reagents in the determination but these reagents are not often selective for Th(IV). Recently, we had also reported that TEAC formed a selective complex with Thorium ion in weak acid solution [24,25]. Herein, the analytical properties of the TEAC-Th complex were studied and a new spectroscopy method determination of thorium was developed.

### II. EXPERIMENTS

#### A. Apparatus and chemicals

Uv/Vis Lambda 25(Perkin Elmer), FT-IR: Bomen DA 8 spectrometer as KBr pellets (Canada) and  $^1\text{H}$ NMR spectroscopy: AVANCE- 600FT-MNR 600 MHz. (Germany). Fourier-transform Raman spectroscopy was carried out in the macroscopic mode with a specimen footprint of about 100 microns using a Bruker IFS 66 instrument with a FRA 106 Raman module.

#### B. Chemicals

All chemicals and solvents used were of analytical grade and used without further purification unless otherwise mentioned. Double-distilled and degasified water was used throughout,  $\text{HNO}_3$  65%, MeOH, MeCN,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_3$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{CH}_3\text{COOH}$ , NaOH  $\text{NaNO}_3$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ;  $\text{UO}_2(\text{NO}_3)_2$ ,  $\text{La}(\text{NO}_3)_3$ ,  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .

The reagent Ortho-Ester Tetraazophenyl Calixarene (TEAC) was synthesized and reported [5,7].

Absorption spectra were measured with Lambda 25 UV-visible recording spectrophotometer (USA). UV stock solutions of TEAC ( $10^{-3}$  M, in pure  $\text{CH}_3\text{OH}$ ) and metal

nitrate 1000mg/ml were prepared. The metal ion solution was diluted 10 and 100 times to give 100 and 10 mg/L solutions. Aliquots of metal ion solution were added to the TEAC solution, and the final concentration and composition of the solution were adjusted to the desired value by adding CH<sub>3</sub>OH +H<sub>2</sub>O (7:3 v/v)

### III. RESULTS AND DISCUSSION

#### A. Investigation the optimum conditions of complex.

The absorption peak of the reagent TEAC lies at 385 nm, corresponding  $\pi \rightarrow \pi^*$  transition of the -N=N- bond, which is in accordance with typical diazo spectra as observed by other workers [2,3] whereas the absorption peak of the TEAC-Th(IV) complex is located at 520 nm. Hence, a very large wavelength shift ( $\Delta\lambda= 135$  nm) is obtained. The maximum is observed absorbance of the complex is obtained in the pH range 4÷5. The Job's plot experiment was carried out by varying the concentration of both TEAC and Th(IV). The maximum absorbance was observed at a mole fraction of  $[TEAC]/([TEAC]+[Th(IV)])$  of about 0.5 corresponding to a TEAC-Th(IV) complex ratio of 1:1. So we had chosen these conditions for the following experiments.

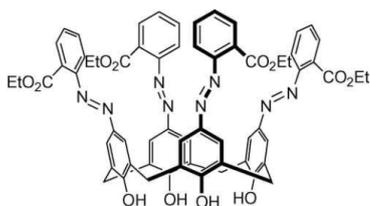


Figure 1. Structure of TEAC

#### B. FT-IR, HNMR and Raman spectra of complex

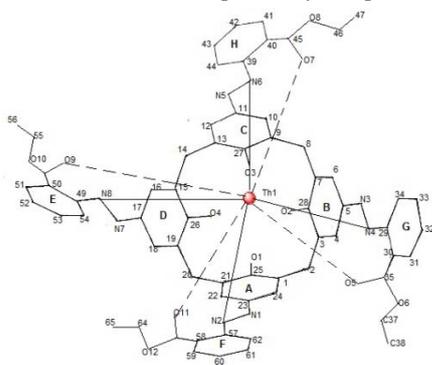


Figure 2. The numbering of complex

The FT-IR spectra of TEAC showed a weak band within the range 3450 cm<sup>-1</sup> corresponding to -OH. The low value indicated that the -OH groups were involved intra molecular hydrogen bonds, a weak band or shoulder located at 3165 cm<sup>-1</sup> which was assigned to aromatic C-H, and stretching vibration of the C=O (ester groups) leading to the band located at 1720cm<sup>-1</sup>, asymmetrical stretching vibration of the N=N group leading to the band located in the 1512 cm<sup>-1</sup> region. The TEAC may exist in two possible tautomeric

forms, namely an azo-enol and keto-hydrazo. The infrared spectra of this compound (in KBr) showed broad -OH bands around 3450 cm<sup>-1</sup> and C-O bands at 1159–1120 cm<sup>-1</sup>. It is suggested that this compound does not exist as the keto-hydrazo form in the solid state.

In the TEAC -Th(IV) complex, the stretching vibration of the N=N groups at 1512 cm<sup>-1</sup> and decreased and the new band observed at 1639 cm<sup>-1</sup> (-C=N) provided conclusive evidence concerning the bonding of nitrogen to the metal ion. So these phenomenon were important evidences to provide the interaction of TEAC with Th(IV) at azo region.

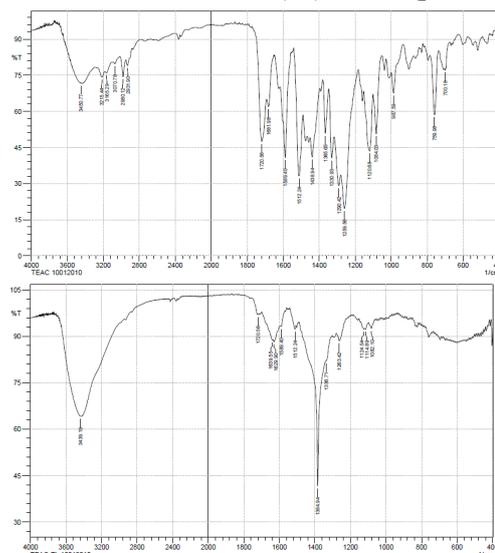


Figure 3. FT-IR spectra of TEAC (above) and TEAC-Th(IV)

The <sup>1</sup>HNMR spectrum of TEAC -Th(IV) showed a small downfield in the  $\delta$  values of the peaks occurred in the aromatic region of the calixarene protons. Therefore, the interaction of TEAC with Th(IV) may happen at the central annulus of reagent compound.

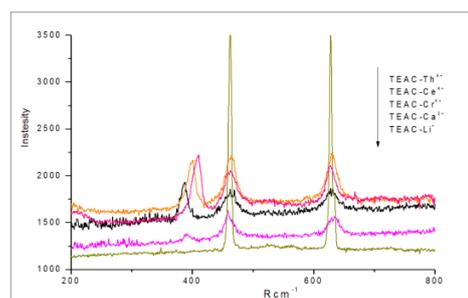


Figure 4. Raman spectra of TEAC complexes.

A new peak appeared at 405 cm<sup>-1</sup> in the Raman spectra of TEAC-Th(IV) so this phenomenon was equal to the bonds of Th(IV) with nitrogen atoms in the reagent.

#### C. The modeling of complex

Optimized geometry for the compound was calculated by using the MM method based on ArgusLab 4.01. The final

geometry energy (MM Bond, MM Angle, MM Dihedral, MM ImpTor, MM vdW MM Coulomb) of TEAC-Th4+ complex was (101.65 kcal/mol).

The Fig 1 showed the numbering scheme of TEAC complex. At the lower rim of the TEAC, the intramolecular hydrogen bonds between hydroxyl groups appeared. Based on these intramolecular hydrogen bonds, a second ring was formed to make the conformation more stable. These data are in good agreement with another azo calix[4]arenes[9]. In the complex, Thorium ion formed bonds with -NH-N=, hence the distances N(2)...N(6), N(4)...N(8) of complex are shorter than in TEAC free. After that, the QEq parameters were optimized for TEAC to represent the atomic charges by quantum chemical calculations with atom types for H, C, N and O atoms. The total QEq charges of azo region of TEAC are -1.598, -1.387. These significant showed that Thorium could form ionic bonds with nitrogen atoms via electrostatic effect.

The lightly shift of protons of aromatic region showed that the complex formation might happen at central annulus of reagent.

A new peak in the Raman spectra was raised at 400 cm<sup>-1</sup> to provide the existence of the bonds between Th and N.

The results calculation energy for complex by MM method in Arguslab 4.01 showed that Th(IV) might exist Th<sup>4+</sup> cation in the complex.

#### IV. APPLICATION FOR ANALYSIS

##### A. Effect of foreign species

Solutions 5 mg/L thorium and various amounts of 8 foreign ions were prepared and the procedure was followed for the determination of thorium. The tolerance limits (7% error maximum) are as follows: Fe<sup>3+</sup> (25mg/L); UO<sub>2</sub><sup>2+</sup> (20mg/L); Ce<sup>4+</sup> (15mg/L); Ti<sup>4+</sup> (15mg/L); La<sup>3+</sup> (15mg/L); Zr<sup>4+</sup> (20mg/L); Hf<sup>4+</sup> (20mg/L); Al<sup>3+</sup> (>30mg/L); and total ions (15mg/L). Most of the ions in the real sample have no reach at these investigated concentrations.

##### B. Linearity

Under the optimum conditions, Beer's law was obeyed in the range 0.6-5.0 mg/L of Th(IV), the linear regression equation was determined to be:  $A = 0.0855 \times C(\text{mg/L})$  of Th(IV) + 0.1061 ( $R^2 = 0.9903$ ,  $n = 5$ ). All detail was shown on the Fig. 5.

##### C. Precision of the method

The precision of the determination of thorium was evaluated under the optimum conditions mentioned above. For this purpose, we used four model sample solutions of with known concentration of thorium as follows: 2.0; 3.0; 4.0 and 5.0 mg/L, respectively. Model samples of thorium were added 8 ions above. Concentration of these ions was equivalent to concentration of these elements in monazite ore (see table 1).

TABLE I. EFFECT OF FOREIGN IONS ON THORIUM DETERMANATION

Metal ions	Tolerance Limit (mg/L)	Metal ions	Tolerance Limit (mg/L)
UO <sub>2</sub> <sup>2+</sup>	15	Al <sup>3+</sup>	30

La <sup>3+</sup>	10	Zr <sup>4+</sup>	15
Fe <sup>3+</sup>	20	Ce <sup>4+</sup>	10
Hf <sup>4+</sup>	15	Ti <sup>4+</sup>	10

Transfer 2ml of solution model sample into a 25 ml volumetric flask and add 5 ml buffer solution, and then add 1 ml of 10<sup>-3</sup>M TEAC solution. Dilute to the mark with mixture MeOH: H<sub>2</sub>O and mix well. Measure the absorbance at 520nm cell against water as blank.

The results showed on table II. It was found that the recovery thorium 100±7 at 95% confidence level, respectively. In conclusion, the precision of the method is very good, and the recovery of the analyzed is quantitative (>95%).

TABLE II. THE CONCENTRATION OF SOME METAL IONS IN MODEL SAMPLES

Samples	Th (mg/L) added	Concentrations of Th found (mg/L) <sup>(a)</sup>
N <sup>0</sup> 1	2	2.1 ± 0.1
N <sup>0</sup> 2	3	2.9 ± 0.2
N <sup>0</sup> 3	4	3.8 ± 0.2
N <sup>0</sup> 4	5	4.8 ± 0.3

(a) Average of five determinations

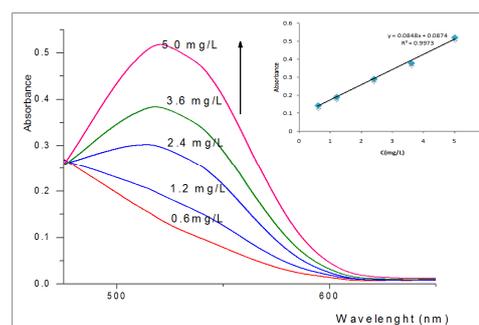


Figure 5. Changes in absorption spectra as a function of Th(IV) under optimum conditions

##### Collected samples

Samples were collected from Ha Tinh province, an area of central in Viet Nam. Before sampling all the equipment was cleaned according to standard cleaning procedures. After that the samples were dried at 105<sup>0</sup>C until the weight reached a constant value, they were ground in blender and kept in the clean polyethylene containers for elemental analysis.

##### Proposed procedure

Weigh accurately 0.500 g of monazite ore samples into a Platinum crucible and add 15- 20 ml of conc. HF+ H<sub>2</sub>SO<sub>4</sub>, evaporating the resulting solution to almost dryness and then dissolving the residue with dilute 0.1N HNO<sub>3</sub>. Add 0,2mL La(III) solution 1mg/ml, and use NH<sub>4</sub>OH dilute to adjust pH =2, and add 2mL 10 %, oxalic acid, filtrate the precipitate and wash by 1% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. After that, this precipitate is dissolved by conc. HNO<sub>3</sub>, Transfer the solution into a 25 ml volumetric flask, wash the beaker and dilute with water to mark.

Transfer 2ml of solution sample into a 25 ml volumetric flask and add 5 ml buffer solution and then add 1 ml of  $10^{-3}$  M TEAC solution. Dilute to the mark with mixture MeOH: H<sub>2</sub>O and mix well. Measure the absorbance at 520nm against water as blank.

#### D. Comparison with NAA method.

We also used NAA (neutron activation analysis) method to evaluate the content of thorium in these samples. The results were shown on the table III. The concentration of Th in monazite ore which were collected in some provinces of Viet Nam such as Ha Tinh, Hue, Binh Dinh, Phu Yen found a good agreement with previous literature [23]. However, these values were lower than in monazite of Korea and Australia [24]. The present results provided that the recommended method in this work were reliable and have good accuracy and precision.

TABLE III. DETERMINATION OF THORIUM IN MONAZITE ORE

Samples	Proposed method <sup>(b)</sup>	NAA Method
Monazite 1	2278,7 ± 190,2	2249,6 ± 256,7
Monazite 2	856,1 ± 79,1	842,6 ± 87,9
Monazite 3	1699,7 ± 124,2	1781,5 ± 145,6
Monazite 4	1285,8 ± 122,8	1289,6 ± 126,7
Monazite 5	1230,7 ± 118,2	1234,6 ± 119,9
Monazite 6	1189,5 ± 113,2	1192,5 ± 115,7

(b) Average of five determinations

#### V. CONCLUSIONS

Combining data from HNMR, IR, Raman, and UV-VIS spectra and using MM method for calculating energy, QEq charge, bonds length and bonds angels, we could propose the mechanism of complex formation.

The proposed method for the determination of Th(IV) with azocalixarene complexes provides a simple, easier and accurate for the investigation of this element in the rich sample as monazite ore. The method has been successfully applied to real samples.

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