Spectroscopic Determination of Thorium Based on Azophenylcalix[4]arene

TRAN QUANG HIEU[1], NGUYEN NGOC TUAN[2] and LE VAN TAN[3,*]

[1]Saigon Technology University, 180 Cao Lo, Ward 4, District 8, Ho Chi Minh City, Vietnam
[2]Dalat Nuclear Research Institute, Dalat City, Vietnam
[3]Ho Chi Minh City Industrial University, 12 Nguyen Van Bao Street, Ward 4, Go Vap Disc., Ho Chi Minh City, Vietnam

*Corresponding author: Fax: +84 8 38946268; Tel: +84 8 38940390; E-mail: tanhuaf@yahoo.com; lvtantqp@yahoo.com

The work describes a new 1:1 complex of *o*-ester tetra azophenyl calix[4]arene (TEAC) with Th(IV) at pH 4-5 has found. The FTIR, H NMR, Raman spectra of calix[4]arene and its Th(IV) complex had also checked. Based on complex formation, a new method has been developed to determine thorium in monazite sand. The sand samples are decomposed by mixed acid (conc. H_2SO_4 and HF) in platinum crucible, after cooling, the residue was dissolved in dilute HCl and thorium is separated together with the lanthanides in the form of oxalate from zirconium, iron and the phosphate ion. The oxalate precipitate is dissolved in concentration nitric acid. After that, Th(IV) will be formed complex with *o*-ester tetra azophenyl calix[4]arene in acetate buffer solution. The absorbance of complex solution was measured at 520 nm against water as blank.

Key Words: Azocalixarene, Spectroscopy, Thorium, Complex, Monazite.

INTRODUCTION

Azocalixarenes, which have a conjugated chromophore azo (-N=N-) group in *p*-positions. These compounds are important class of organic colourants and consist of at least a conjugated chromophore azo (-N=N-) group 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 behaviour 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 Ca^{2+} or K^+ ion[3]. There are relatively few reports on the complexation with Cr^{3+}, Ni^{2+} or Pb^{2+} ion[4-7]. A lead ion-selective electrode was made from calixarene carboxyphenyl azo derivative[8]. Besides, the extraction procedures were developed based on calixarene for metal cations[9] as Ag^+, Zn^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+}. Moreover, the spectroscopic methods[10] were also used for determination of Rh^{3+} and Cu^{2+}. Recently, a new membranes containing *p*-(4-*n*-butylphenylazo)calix[4]arene as an electro active material was used to fabricate a new cobalt (II)-selective sensor[11].

Determination of thorium, a first member of 5*f*-actinide series, is an important way for research and quality control in geology and metallurgy and in the application of this element. Thorium has traditionally been measured by radio-metric techniques, such as γ-spectroscopy[12] α spectroscopy and neutron activation analysis (NAA)[13,14] or ICP-AES (atomic emission spectrometry), a non-radiometric technique, offers low detection limits for many elements, but unfortunately is relatively poor for thorium[15] or ICP-MS[16,17]. However, these methods are complicated and costly. Spectrophotometry method is widely used for this purpose for its simplicity and rapidity in analysis. N-Hydroxy-N,N'-diphenylbenzamidine and thorin type reagents are more frequently used as chromogenic reagents in the determination but these reagents are not often selective for Th(IV)[18]. Recently, we had reported that *o*-ester tetra azophenyl calix[4]arene (TEAC) formed a selective complex with thorium ion in weak acid solution[19]. In the work presented here, the analytical properties of the TEAC-Th complex were studied and a new spectroscopy method determination of thorium was developed.
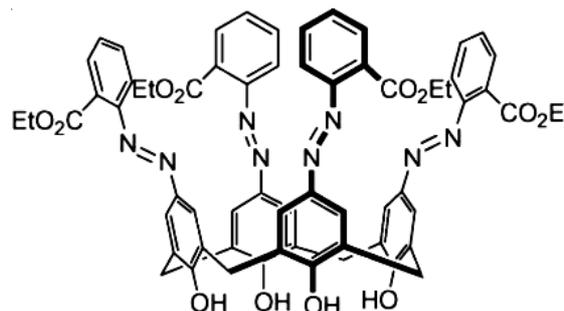
Structural of *o*-ester tetra azophenyl calix[4]arene

EXPERIMENTAL

UV/vis Lamda 25 (Perkin-Elmer), FT-IR: Bomen DA 8 spectrometer as KBr pellets (Canada) and ^{1}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.

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, HNO_3 65 %, MeOH, MeCN, $Pb(NO_3)_2$, $Cr(NO_3)_3$, $Ni(NO_3)_2$, CH_3COOH, NaOH, $NaNO_3$, $Th(NO_3)_4 \cdot 5H_2O$; $UO_2(NO_3)_2$, $La(NO_3)_3$, $Sm(NO_3)_3 \cdot 6H_2O$, PA, Merck. The reagent TEAC was synthesized as reported[6].

Absorption spectra were measured with Lambda 25 UV-visible recording spectrophotometer (USA). UV stock solutions of TEAC (10^{-3} M, in pure CH_3OH) and metal nitrate 1000 mg/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 $CH_3OH + H_2O$ (7:3 v/v).

Samples were collected from some central provinces of Viet Nam such as Ha Tinh (HT), Binh Dinh (BD), Phu Yen (PY). Before sampling all the equipment was cleaned according to standard cleaning procedures. After that the samples were dried at 105 ºC until the weight reached a constant value, they were ground in blender and kept in the clean polyethylene containers for elemental analysis.

RESULTS AND DISCUSSION

Investigation the optimum conditions of complex: The experiments have been undertaken in order to find proper reaction conditions. The absorption spectra of the reagent TEAC and its TEAC-Th(IV) complex under the optimum conditions are shown in Fig. 1. In the figure, curve 'a' and 'b→n' are the spectra of TEAC and TEAC-Th(IV) complex, respectively against water blank. As the observation, the maximum absorption peak of the reagent TEAC lies at 385 nm, corresponding π→π* transition of the -N= N- bond, which are in accordance with typical diazo spectra as observed by
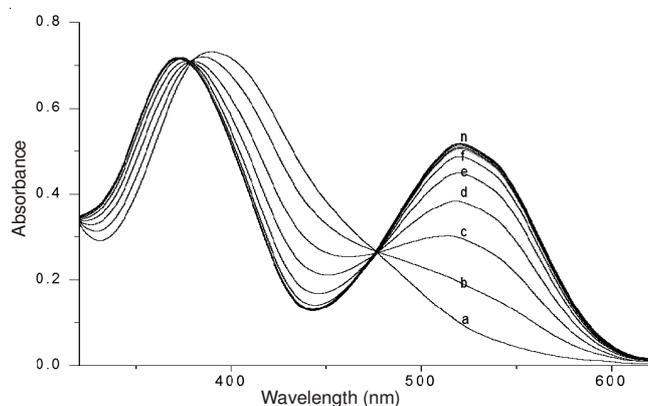

Fig. 1. Absorption spectra of TEAC and TEAC-Th(IV) against water blank (a) 2×10^{-5} M of TEAC and TEAC-Th(IV) complex: b→n (15-250 µg of Th(IV)/25 mL) at pH = 4.5

other workers[5,6], whereas the absorption peak of the TEAC-Th(IV) complex is located at 520 nm. Hence, a very large wavelength change (λ = 135 nm) is obtained.

Thorium(IV) tends to form hydrate precipitate in basic solution, so TEAC-Th (IV) complex was investigated in acid solution. The absorption spectra of TEAC-Th(IV) complex was obtained in the pH range 2.5-6.0. To maintain optimum conditions, appropriate concentrations of reagent TEAC (2.0×10^{-5} mol L^{-1}) and Th(IV) (2.0×10^{-5} mol L^{-1}) were chosen. The effect of pH on the absorbance of TEAC-Th(IV) at 520 nm was checked and the absorbance maximum is obtained in the pH range 4-5, so pH condition of 4.5, which was chosen for the following experiments. Different pH values were obtained by varying the relative amounts of NaOAc and HOAc and confirmed by a digital pH-meter. The stability of complex were checked and we found that the absorption peak at 520 nm of TEAC-Th(IV) appeared only 10s after the addition of Th(IV) to the TEAC reagent, the equilibrium was attained in *ca.* 2 min. From these characteristics, it is proposed that TEAC could be a significant chromogenic ionophore for the recognition of Th(IV) ion, suitable for practical application.

For the complexation ratio between the host and metal ions, the Job's plot experiment was carried out by varying the concentration of both host and metal ions. 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.

FT-IR, H NMR and Raman spectra: The FT-IR spectra of TEAC showed a weak band within the range 3450 cm^{-1} 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^{-1} which was assigned to aromatic C-H and stretching vibration of the C=O (ester groups) leading to the band located at 1720 cm^{-1}, asymmetrical stretching vibration of the N=N group leading to the band located in the 1512 cm^{-1} 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^{-1} and C-O bands at 1159-1120 cm^{-1}. 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^{-1} decreased and the new band observed at 1639 cm^{-1} (-C=N) and 576.12 cm^{-1} (Th-N) provided conclusive evidence concerning the bonding of nitrogen to the metal ion. So these phenomena were important evidences to provide the interaction of TEAC with Th(IV) at azo region.

The ^{1}H NMR spectrum of TEAC -Th(IV) showed a small downfield in the δ 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. And a new peak appeared at 405 cm^{-1} in the Raman spectra of TEAC-Th(IV) complex so this phenomenon could be atributed to the bonds of Th(IV) with nitrogen atoms in the reagent.

Effect of foreign ions: Solutions of 60 µg/25 mL of thorium and various amounts of foriegn ions were prepared and the procedure was followed for the determination of thorium. The tolerance limits (7 % error maximum) are as follows: Cu^{2+},

Zn^{2+}, Ni^{2+}, Ti^{4+}, (0.06-1.2) mg; Fe^{3+}, Cr^{3+} (0.06-1.5) mg; Hf^{4+}, Zr^{4+}, UO_2^{2+}, Ce^{4+} (0.06-0.9) mg; La^{3+}, Sm^{3+} (0.06-1.2) mg; acetate, NO_3^-, PO_4^{3-} in the range (1.0-5.0) mg. Most of the ions in the real samples have no reach at these investigated concentrations. However, the content of Zr , Hf, Ti and Fe are often high in the soil or monazite sand, hence we have to mask the influent of these ions by precipitation of thorium along with the lanthanides as oxalate by the addition oxalic acid (Table-1).

TABLE-1
EFFECT OF SOME FOREIGN IONS
ON THORIUM DETERMINATION

Ions	Concentration (μg/25 mL)	Ions	Concentration (μg/25 mL)
Cu^{2+}	1200	Al^{3+}	1800
Cr^{3+}	1500	Zn^{2+}	1200
Mn^{2+}	1500	La^{3+}	1800
Ce^{4+}	900	Ti^{4+}	1200
Pb^{2+}	1200	Fe^{3+}	1500
Zr^{4+}	900	UO_2^{2+}	900
Hf^{4+}	900	Sm^{3+}	1500

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: 30, 60 and 90 μg/25 mL, respectively. The results showed on Table-2. It was found that the recovery of thorium is 100 ± 9 at 95 % confidence level, respectively. In conclusion, the precision of the method is very good and the recovery of the analyzed is quantitative.

TABLE-2
CONCENTRATION OF THORIUM IN
SOME SYNTHETIC SAMPLES

Content of forigen ions in 25 mL	Th added (μg/25 mL)	Th found (μg/25 mL)*	RSD (%)
Cu^{2+}, Zn^{2+}, Ni^{2+}, Ti^{4+}, 0.9 (mg); Fe^{3+}, Mn^{2+}, Cr^{3+} 1.2 mg; Hf^{4+}, Zr^{4+}, UO_2^{2+}, Ce^{4+} 0.8 (mg); La^{3+}, Sm^{3+} 0.9 (mg); PO_4^{3-} 4.0 (mg), SO_4^{2-}, NO_3^-, 4(mg)	30 60 90	29.2 ± 2.6 61.7 ± 5.8 88.1 ± 8.2	8.9 7.9 8.2

*Average of five determinations.

Linearity: Under the optimum conditions, Beer's law was obeyed in the range 15-120 μg/25 mL of Th(IV), the linear regression equation was determined to be: $A = 0.00378 \times C(μg/25\ mL) + 0.0804$ ($R^2 = 0.9977$, n = 6).

Proposed procedure: Weigh accurately 0.500 g of monazite sand samples into a platinum crucible and add 15-20 mL of conc. $HF + H_2SO_4$, evaporating the resulting solution to almost dryness and then dissolving the residue with dilute 0.1 N HNO_3. Add 0.2 mL La^{3+} solution 1 mg/mL as a carrier and use NH_4OH dilute to adjust pH = 2 and add 2 mL 10 %, oxalic acid, filtrate the precipitate and wash by 1 % $H_2C_2O_4$. After that, this precipitate is dissolved by conc. HNO_3. Transfer the solution into a 25 mL volumetric flask, wash the beaker and dilute with water to mark.

Transfer 2 mL 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_2O and mix well. Measure the absorbance at 520 nm against water as blank.

The neutron activation analysis method was also used to evaluate the content of thorium in these samples. The results were shown on the Table-3. The concentration of Th in monazite ore which were collected in some provinces of Viet Nam such as Ha Tinh, Binh Dinh, Phu Yen found a good agreement with previous literature[13]. However, these values were lower than in monazite of China and Greenland. The present results provided that the recommended method in this work were reliable and have good accuracy and precision.

TABLE-3
COMPARISON OF RESULTS FROM THE PROPOSED METHOD
AND NEUTRON ACTIVATION ANALYSIS (mg/kg)

Samples	Proposed method*	NAA Method
HT-1	2278.7 ± 160.2	2249.6 ± 156.7
HT-2	956.1 ± 89.1	942.6 ± 97.9
HT-3	1699.7 ± 124.2	1781.5 ± 145.6
BT-1	587.4 ± 68.1	596.7 ± 55.2
BT-2	687.4 ± 65.1	687.9 ± 63.4
BT-3	517.9 ± 45.7	527.2 ± 51.2
PY-1	892.2 ± 79.8	852.1 ± 71.9
PY-2	987.6 ± 67.3	967.5 ± 94.2
PY-3	751.2 ± 66.1	741.3 ± 69.1

*Average of five determinations.

Conclusion

Combining data from H NMR, IR, Raman and UV-vis spectra we could provide the existent of complex and based on the optimum of complex formation, we have proposed the method for the determination of Th(IV) with TEAC and used this method to investigate the content of this element in monazite sand samples.

REFERENCES

1. S. Shinkai, *Tetrahedron*, **49**, 8933 (1993).
2. F. Karci, I. Sener and H. Deligoz, *Dyes Pigm.*, **59**, 53 (2003).
3. Y. Dong, T.H. Kim, H.J. Kim, M.H. Lee, S.Y. Lee, R.K. Mahajan, H. Kim and J.S. Kim, *J. Electroanal. Chem.*, **628**, 119 (2009).
4. L. Lu, S. Zhu, X. Liu, Z. Xie and X. Yan, *Anal. Chim. Acta*, **535**, 183 (2005).
5. Q. Ma, H. Ma, M. Su, Z. Wang, L. Nie and S. Liang, *Anal. Chim. Acta*, **439**, 73 (2001).
6. T.H. Kim, S.H. Kim, L.V. Tan, Y.J. Seo, S.Y. Park, H. Kim and J.S. Kim, *Talanta*, **7**, 1294 (2007).
7. L.V. Tan, D.T. Quang, M.H. Lee, T.H. Kim, H. Kim and J.S. Kim, *Bull. Korean Chem. Soc.*, **28**, 791 (2007).
8. J. Lu, R. Chen and X. He, *J. Electroanal. Chem.*, **528**, 33 (2002).
9. T.H. Kim, S.H. Kim, L.V. Tan, Y. Dong, H. Kim and J.S. Kim, *Talanta*, **74**, 1654 (2008).
10. P. Kumar, *Talanta*, **77**, 1057 (2009).
11. A. Kumar, P. Sharma, L.K. Chandel and B.L. Kalal, *J. Incl. Phenom. Macrocycl. Chem.*, **61**, 335 (2008).
12. A.M. Hassan, *Appl. Radiat. Isot.*, **48**, 149 (1997).
13. N.V. Suc, *J. Radioanal. Nucl. Chem.*, **1**, 51 (1995).
14. M.S. Chaudhary, *J. Radioanal. Nucl. Chem.*, **57**, 137 (1980).
15. R. Saran and N.K. Baishy, *Atom. Spectrosc.*, **18**, 60 (1997).
16. M. Rozmaric, A.G. Ivsic and Z. Grahek, *Talanta*, **80**, 352 (2009).
17. K. Shinotsuka, *Anal. Sci.*, **12**, 917 (1996).
18. N. Nashine, M.K. Deb and R.K. Mishra, *Fresenius. J. Anal. Chem.*, **355**, 34 (1996).
19. T.Q. Hieu, N.N. Tuan and L.V. Tan, Proceeding on International Conference Chemistry Engineering and Application, Singapore, World Academic Press, pp. 25-29 (2010).