

Research Article

Solvent Extraction of Thorium Using 5,11,17,23-Tetra[(2-ethyl acetoethoxyphenyl)(azo)phenyl]calix[4]arene

Quang Hieu Tran,¹ Van Tan Le,² and Van Cuong Nguyen²

¹Saigon Technology University, 180 Cao Lo, Ho Chi Minh City 70000, Vietnam

²Department of Chemical Engineering, Industrial University of Ho Chi Minh City, 12 Nguyen Van Bao Road, Ho Chi Minh City 70000, Vietnam

Correspondence should be addressed to Van Tan Le; tanlvdhcn@yahoo.com.vn and Van Cuong Nguyen; nvc@iuh.edu.vn

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A rapid, sensitive, and selective method for determination of thorium based on the complex with *ortho*-ester tetraazophenylcalix[4]arene (TEAC) was described. In the presence of pH of 4–6, TEAC-Th(IV) complex is extracted from an acidic aqueous solution into chloroform layer. The absorbance intensity of complex was measured by UV-Vis spectrometer at 525 nm and the molar absorptivity was found to be 2.4×10^4 . Beer's law was obeyed in the range of 1.0 to 25×10^{-5} M thorium(IV). The effects of pH, TEAC concentration, and shaking time were also studied. The tolerance limits for several metal ions were calculated. The proposed method was applied to the determination of thorium in synthetic solution and in the monazite sand samples with good results.

1. Introduction

Thorium is a natural radioactive element which has been paid more attention for energy demands and environment concerns. The main source of thorium is monazite sand mainly associated with a small amount of uranium and other rare earth metals, which are undesirable because of their radioactivity [1, 2]. Therefore, it is important to separate thorium to avoid the environment pollution before monazite processing. Separation of toxic Th(IV) ions is of intense current interest in research and environmental cleanup [3, 4]. The traditional preconcentration and separation methods for Th(IV) are liquid-liquid extraction, coprecipitation, liquid membrane and ion-exchange resins, and so forth [5–8]. These methods often require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems. In this case, the solvent extraction processes were the most interesting technique for separation and recovery of thorium [9]. Various extractants have been employed for the extraction of thorium and rare earths, such as organophosphorus reagents [10, 11], amines [12–14],

isoxazolones, crown ethers [15], fatty acid [16], and ionic liquids [17, 18].

Calixarenes have attracted much attention due to their distinctive structures. Calixarene was extensively used for solvent extraction of transition metals, lanthanides and actinides [19–22]. The most prominent research belonged to Delemez team who investigated the ability extraction of azocalix[4]arenes for solvent extraction of various transition metals from the aqueous phase to the organic phase [23–25]. Oueslati and coworkers have synthesized four azocalixarene derivatives bearing bipyridyl units with functional groups such as amide, ester, and pyridine at the phenolic oxygen atoms [26]. The extraction properties towards different metals of these azocalixarenes derivatives using liquid-liquid extraction by atomic absorption spectrometry have been studied and exhibited high selectivity for Ag^+ . Calix[4]arene semicarbazone derivatives of resin showed the good separating ability with maximum sorption pH between 2.5 and 4.5 for thorium(IV) which was reported recently. The procedure was applied for determination of thorium in monazite sand and some standard geological materials

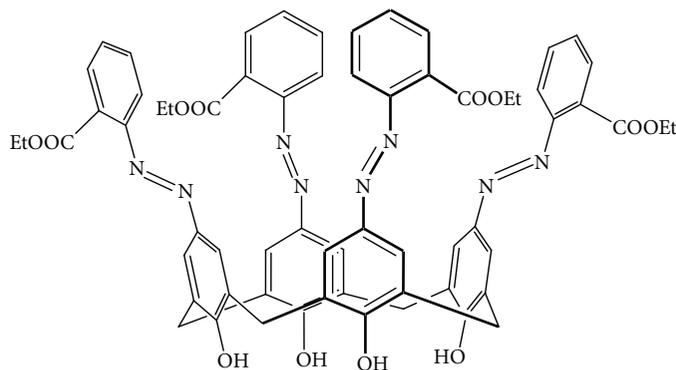


FIGURE 1: Structure of 5,11,17,23-tetra[(2-ethyl acetoethoxyphenyl)(azo)phenyl]calix[4]arene.

[27]. To the best of our knowledge, however, the TEAC has not been reported as an extractant for extraction of thorium. In this study, we reported the novel method for solvent extraction of thorium using 5,11,17,23-tetra[(2-ethyl acetoethoxyphenyl)(azo)phenyl]calix[4]arene (TEAC) as an extractant. The effects of various experimental parameters such as pH, contact time, and extractant concentration were investigated.

2. Experimental Section

2.1. Reagents and Instruments. All chemicals and solvents were of analytical grade and used without further purification unless otherwise mentioned. Double distilled water was degasified before experiment. The preparation and characterization of 5,11,17,23-tetra[(2-ethyl acetoethoxyphenyl)(azo)phenyl]calix[4]arene (TEAC) was reported elsewhere [28, 29]. The structure of TEAC is shown in Figure 1. Certified reference materials (soil: IAEA-SOIL-7, sediment IAEA-SL-1) have been used for the standardization of this study.

Standard solutions of TEAC 10^{-3} M and Th(IV) 10^{-3} M were prepared by dissolving TEAC in CH_3OH and $\text{Th}(\text{NO}_3)_4$ in double distilled water. All work solutions were obtained by appropriate dilution of the standardized stock solutions. pH values of the solutions were adjusted by the addition of HNO_3 and NaOH solutions. Perkin Elmer's Lambda 25 UV/Vis Scanning Spectrophotometer was used to record the absorbance spectra with 1.0 cm path length quartz cell.

Real samples (monazite) were collected from Ha Tinh, Binh Dinh, and Phu Yen Provinces, Vietnam. The monazite samples were dried at 105°C until the weight reached a constant value; they were ground in blender and kept in the clean polyethylene containers for elemental analysis. 0.5 g of monazite and 20 mL of concentrated HF and H_2SO_4 solution were placed in a platinum crucible and then evaporated. The residue was dissolved with 0.1N HNO_3 and diluted with double distilled water to 25 mL by using volumetric flask. The concentration of thorium in sample was determined as below.

2.2. General Procedure. To a solution of 2 mL Th(IV) 10^{-4} M in aqueous solution and 5 mL 5×10^{-4} M TEAC in MeOH

was added 5 mL acetate buffer solution. The pH of the resulting solution was adjusted to pH 4/5 by HNO_3 and NaOH solutions. The complex solution was diluted by adding $\text{CH}_3\text{OH} + \text{H}_2\text{O}$ (7:3 v/v) to a final volume of 25 mL and mixed with 5 mL organic solution and then shaken for 5 min at 25°C . After splitting of organic and aqueous phases, the red-coloured organic phase was separated and 1g of anhydrous Na_2SO_4 was added to remove contaminated water. The content of Th(IV) was determined spectrophotometrically at 525 nm using TEAC as the reference. The extraction percentage (E) and distribution ratios (D) were calculated as follows:

$$E\% = \frac{C^0 - C}{C^0} \times 100\%, \quad (1)$$

$$D = \frac{C^0 - C}{C} \times \frac{V_a}{V_0},$$

where C^0 is the initial metal ion concentration in the aqueous phase before extraction and C is the equilibrium concentration of metal ion in the aqueous phase after extraction, V_a is volume of the aqueous phase, V_0 is volume of the solvent extraction, and C^0 is determined by INAA method.

3. Results and Discussion

3.1. Extraction of Th(IV) with TEAC. The preparation and characterization of 5,11,17,23-tetra[(2-ethyl acetoethoxyphenyl)(azo)phenyl]calix[4]arene (TEAC) was reported elsewhere. In the previous works, the complex of TEAC with Th(IV) and its property were also investigated [30]. The FT-IR of TEAC and complex of TEAC with thorium exhibited 1512 cm^{-1} and 1639 cm^{-1} for $\text{N}=\text{N}$ groups and $-\text{C}=\text{N}$, respectively. The new bands at 1639 cm^{-1} ($-\text{C}=\text{N}$) and 576 cm^{-1} (Th-N) provided the evidence for the bonding of nitrogen to the metal ion at the azo region. The ^1H NMR spectrum of TEAC-Th(IV) showed a small downfield shift in the δ values of the peaks that occurred in the aromatic region and the signal of protons in $-\text{OH}$ groups disappeared. Additionally, a new peak which appeared at 405 cm^{-1} was attributed to the bonds of Th(IV) with nitrogen atoms of TEAC in the Raman spectra of TEAC-Th(IV). The ESI-MS of TEAC-Th(IV) was

TABLE 1: Influence of solvents on extraction (%) of Th(IV).

Solvents	λ_{\max} (nm)	Extraction (%)	Distribution ratio
Toluene	523	50	5.42
Isoamyl alcohol	495	30	2.14
Benzene	535	70	12.85
Carbon tetrachloride	515	80	28.33
Chloroform	525	98	328.33

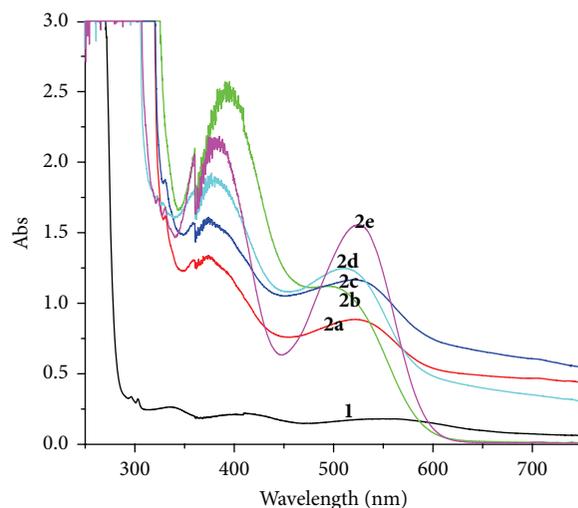
recorded in solution and showed the fragment ion TEAC-Th ($m/z = 1357$) in the MS spectra.

The complexation ratio between the TEAC reagent and metal ions was carried out by varying the concentration of both host and metal ions by Job's plot experiment. The maximum absorbance was observed at a mole fraction of $[\text{TEAC}]/([\text{TEAC}]+[\text{Th(IV)}])$ of about 0.5 corresponding to a TEAC-Th(IV) complex ratio of 1:1. The stability constant was estimated by monitoring the decrease in the intensity of the absorbance at the peak with the data reduction being effected using Benesi-Hildebrand plots and the stability constant (K) was calculated to be $6.2 \times 10^4 \text{ mol}^{-1}\cdot\text{L}$ by this method.

Different types of solvents were examined (toluene, isoamyl alcohol, benzene, carbon tetrachloride, and chloroform). Absorption spectra and the extraction efficiency were demonstrated in Figure 2 and Table 1. The absorption peak of TEAC is at 385 nm, corresponding to $\pi \rightarrow \pi^*$ transition of the $-\text{N}=\text{N}-$ bond, whereas the absorption peak of the TEAC-Th(IV) complex is located at 525 nm for chloroform, which is in accordance with typical diazo spectra [28]. However, for methanol and a mixture of methanol: water, the maximum absorption peak appeared at 520 nm; the difference in maximum absorption may be explained by effect of the polar solvent. Additionally, the extracted species was stable for several hours. Results showed that the optimal solvent for the extraction of thorium is chloroform. Therefore, chloroform was selected for further studies. In this work, the extraction of TEAC-Th(IV) complex was examined and the spectrophotometric determination procedure of thorium after extraction process was proposed.

3.2. Effect of pH on Extraction. The optimum pH for extraction of Th(IV) was determined by carrying out the extraction with pH in the range of 1 to 10. As can be seen in Figures 3 and 4, the extraction (%) and the distribution ratio of Th(IV) reached maxima at the pH of 4–6. The lower extraction at higher pH values may be attributed to the hydrolysis of the Th(IV) ions which indirectly promotes competing equilibrium with the formation of complex. The pH range of 4–6 is recommended to control pH, as the use of sodium acetate and acetic acid buffer solution was found to give a maximum and constant absorbance.

3.3. Effect of Contact Time and Stability. To determine the equilibrium time, effect of contact time on the distribution ratios was evaluated from extraction of TEAC-Th(IV) with chloroform. The shaking time for the extraction was varied from 30 to 350 s. The highest distribution ratios for extraction



1: TEAC-Th(IV) 2c: benzene
2a: toluene 2d: carbon tetrachloride
2b: isoamyl alcohol 2e: chloroform

FIGURE 2: Absorption spectra of TEAC-Th(IV) before and after extraction with various solvents: (1) TEAC-Th(IV) in MeOH, 8×10^{-6} M, and (2a to 2e) TEAC-Th(IV) complexes after extraction from 25 mL of complex solution into 5 mL solvent.

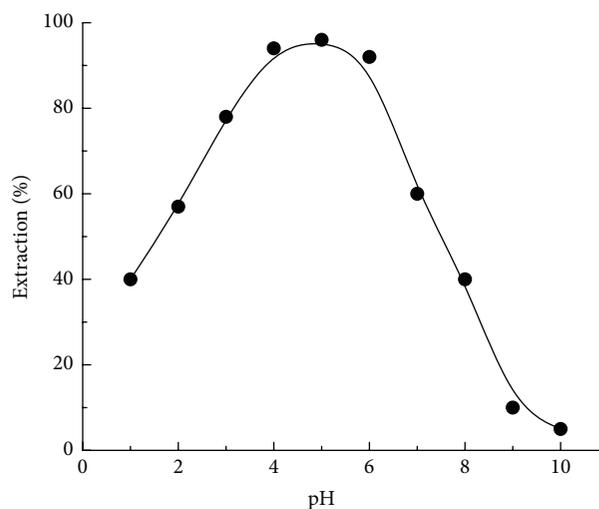


FIGURE 3: Effect of pH on the extraction of TEAC-Th(IV) complexes at 525 nm with chloroform solvent.

of TEAC-Th(IV) with chloroform were observed within 60 s at $25 \pm 5^\circ\text{C}$. Therefore, to ensure the complete equilibrium, the contact time was chosen as 60 s in all further extraction experiments. Additionally the results also indicated that the absorbance of TEAC-Th(IV) complex in chloroform is stable for at least 5 h at wavelength of 525 nm.

3.4. Effect of Extractant Concentration. The effects of extractant concentration on the extraction of Th^{4+} were investigated with varying the concentration of TEAC within $0.1\text{--}20 \times 10^{-5}$ M. As shown in Figure 5, the extraction (%) of thorium ions increased with rising TEAC concentration from

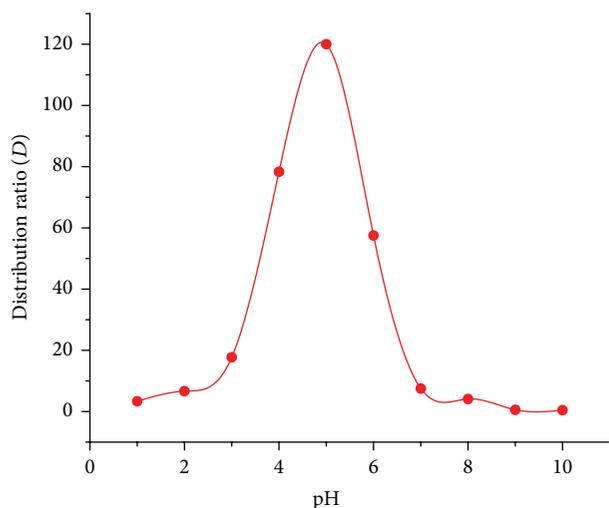


FIGURE 4: Effect of pH on the distribution ratio (D).

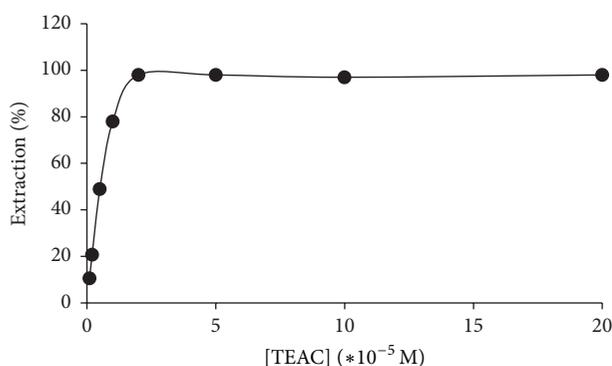


FIGURE 5: Effect of TEAC concentration on the extraction of Th(IV): chloroform as solvent, at 525 nm and Th(IV) 1×10^{-4} M.

0.1 to 2.5×10^{-5} M. However the extraction was constant when the TEAC concentration was higher than 2.5×10^{-5} M. The maximum extraction efficiency of thorium ions occurred at extractant concentration of 2.5×10^{-5} M and reached 98%.

3.5. Calibration Curve. A calibration curve for the determination of thorium was prepared under optimum conditions. A good linear relationship was obtained over the concentration range of 1×10^{-6} to 2.5×10^{-5} M of Th(IV) ions per 5 mL of chloroform. The molar absorption coefficients of the extracted species were approximately 2.8×10^4 at 525 nm. This value is about 1.2 times as high as that obtained by direct reaction in aqueous solution [30].

3.6. Effect of Foreign Ions. In order to study the effect of various ions on the determination of the TEAC-Th(IV) complex, a fixed amount 2×10^{-5} M of Th(IV) was taken with different amounts of foreign ions and the recommended procedure was above. The tolerance limits are summarized in Table 2. The results showed that most common ions do not interfere with the determination suggesting the high selectivity of the proposed method. Only some elements

TABLE 2: Effect of diverse ions on the determination of Th(IV) (relative error $\pm 5.0\%$).

Ion	Added	Tolerance limit (molar ratio)
Na ⁺	NaNO ₃	150
K ⁺	KNO ₃	100
Ca ²⁺	Ca(NO ₃) ₂	100
Mg ²⁺	Mg(NO ₃) ₂	100
Cu ²⁺	CuSO ₄	10
Ni ²⁺	NiCl ₂	20
Zn ²⁺	ZnCl ₂	15
Fe ³⁺	Fe(NO ₃) ₃	20
Cr ³⁺	Cr(NO ₃) ₃	10
Pb ²⁺	Pb(NO ₃) ₂	10
Hf ⁴⁺	Hf(NO ₃) ₄	10
Zr ⁴⁺	Hf(NO ₃) ₄	20
Sm ³⁺	Sm(NO ₃) ₃	20

TABLE 3: Determination of Th(IV) in the synthetic mixtures.

Samples	Th (mg/L) added	Th found (mg/L) (*)
1	2	2.4 ± 0.1
2	3	3.5 ± 0.2
3	4	3.7 ± 0.2
4	5	5.6 ± 0.4

(*) Average of five measurements.

interfered which can be eliminated by masking with 1,10-phenanthroline and EDTA solutions.

3.7. Application of Synthetic Mixtures. The proposed method has been successfully applied to the determination of Th(IV) in the synthetic mixture. The analytical results for the synthetic mixture are given in Table 3. Results indicated a clear separation of Th(IV) ions from Al³⁺, Ni²⁺, Hf⁴⁺, Zr⁴⁺, UO₂²⁺, Ce⁴⁺, and Fe³⁺ ions and left these metal ions in the aqueous phase. After extraction of Th(IV) ions, the concentrations of Al³⁺, Ni²⁺, Hf⁴⁺, Zr⁴⁺, UO₂²⁺, Ce⁴⁺, and Fe³⁺ ions were determined by INAA.

3.8. Application of the Method to Standard Samples and Real Samples

3.8.1. Standard Samples. Two standard samples SOIL-7 and SL-1 were also analyzed by this proposed method. To prepare a solution of these samples, 0.5 g of the sample was weighed and dissolved in concentrated HNO₃ and HClO₄. The solution was evaporated nearly to dryness, extracted with 10 mL of 0.05 M HCl, filtered, and diluted to 100 mL with distilled water. An aliquot of this solution was analyzed for Th(IV) ions by the proposed method. The result was shown in Table 4. The results showed that certificated values and found values had good agreement. The difference of the proposed method and INAA method is not significant (Fisher standard). Therefore,

TABLE 4: Determination of Th(IV) in the standard samples.

Samples	Certificated values (mg/kg)	Found (mg/kg)	Recovery (%)	RSD (%)
SOIL-7	8.2	7.8 ± 0.8	95.1%	4%
SL-1	14.0	14.9 ± 1.3	106.4%	6.4%

TABLE 5: The content of thorium in monazite samples (mg/kg).

Samples	This work	Previous work [30]	INAA method
HT-1	2385.8 ± 202.8	2278.7 ± 160.2	2249.6 ± 156.7
HT-2	930.7 ± 98.2	956.1 ± 128.2	942.6 ± 97.9
HT-3	1729.5 ± 183.2	1699.7 ± 124.2	1781.5 ± 145.6

the proposed method presents the potential application for determination of thorium ions in real samples.

3.8.2. Real Samples. The results of Th(IV) ions estimated by this proposed method were compared with that found by previous method [30]. Additionally, as shown in Table 5, the results were in agreement with those determined by neutron activation analysis method (INAA). Therefore, the proposed method provides a simple, rapid, and selective determination for thorium ions in real samples.

4. Conclusion

The extraction of Th(IV) ions using 5,11,17,23-tetra[(2-ethyl acetoethoxyphenyl)(azo)phenyl]calix[4]arene at pH of 4–6 was studied. The results showed that the extraction efficiency was 98% and the complex of TEAC-Th(IV) was stable. The foreign ions had no significant effect on the extraction of thorium ions. The results of this study clearly showed the potential and versatility of calixarene derivative for separation of Th(IV) from rare earths. This method also increased the sensitivity of the analysis and can be applied to the analysis of thorium ions in real samples.

Conflict of Interests

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

Authors' Contribution

The authors have contributed equally to this work.

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