Solvent Extraction, Preconcentration and Determination of Thorium with Monoaza 18-Crown-6 Derivative

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A solvent extraction separation, preconcentration and determination of thorium with a new crown, 2-ethyl-*N*-benzyl-4,7,10,13,16-pentaoxa-1-azacyclooctadecane (MACE), is described in the study. The amount of thorium in the aqueous phase and organic phase was determined by Inductively Coupled Plasma-Optical Emission Spectroscopy and Ultraviolet-Visible, respectively. Thorium loaded organic phase was quantitatively stripped in a stage by using 1.0 M HNO₃. Thorium was effectively extracted with MACE in the pH range of 6-7 to produce a 3:2 complex ratio in the chloroform. A highly sensitive and rapid spectrophotometric method was described for determination of trace amounts of thorium with MACE. The effective molar absorption coefficient at 281 nm is 1.98×10^3 mol⁻¹ cm⁻¹, and the system complies with Beer's law in the range from 0.464 to 2.32 μg mL⁻¹ of thorium. Thorium was also determined in standard and environmental samples.

Key Words : Thorium extraction, Determination, Preconcentration, Monoaza-18-Crown-6

Introduction

Thorium is the most abundant radioactive element in nature and has widespread applications in variable areas, such as optics, radio, aeronautics and aerospace, metallurgy and chemical industry, and material fields.[1] Thorium and rare-earth elements often coexist in their minerals and in waste water. Unfortunately, thorium not only has chemical toxicity as do other heavy metals, but also has radioactivity which can cause a large scale permanent damage in bone, kidney, and liver.[2,3]

Their recovery is essential to minimize their discharge into the environment in view of safety and economy. However, the separation of thorium from rare earth elements is difficult and limited since their compounds show similar properties to thorium.[4] The importance of intra- and inter-group separation of actinides and lanthanides is well known.[5,6] The determination of thorium by instrumental techniques, such as ICP-AES, ICP-MS and NAA, is still difficult because of insufficient sensitivity, lack of selectivity, presence of complex matrix, poor precision and accuracy.[7-10]

Preconcentration of trace elements holds an important place among the techniques used in modern analytical chemistry. Preconcentration has increased the possibilities of many analytical determinations by eliminating the matrix effect which often worsens significantly the detection limits and other metrological parameters of the procedure and which can sometimes prevent the determination of one more trace element. Solvent extraction is a frequently used method for preconcentration. It may be used for separation of trace elements in the extract or matrix in analysis of diverse industrial and natural materials.[11] In other words, a large increase in sensitivity is obtained in the analytical method, even when the analyte is analytically detectable in the original sample.[12]

Organophosphorus compounds have been frequently used for the separation of actinides and lanthanides.[13] The crown ethers are well known reagents used for separation and preconcentration of lanthanides and actinides as well as sorbents in chromatographic techniques.[14] The ion size of crown ethers plays an important role in complexation with metal ions. Hasegawa et al. studied over the extraction of lanthanide picrates with crown ethers into the chloroform.[15] They concluded that the extraction constants decreased through the lanthanide series and that these ions would not be trapped in the cavity of crown ether. Yaftian *et al.* reported the separation of thorium, lanthanium and europium ions by 2-nitrobenzo-18-crown-6 as a selective masking agent.[16] In addition, the solid state structures of lanthanide complexes of monoaza crown ether[17] and diaza crown ether[18] have also been documented. Umetani *et al*. reported an improved extraction-separation of lanthanides and alkali earth ions by acidic extractants, using 18-crown-6 and some sulfonated crown ethers in the aqueous phase.[19,20] They concluded that, by increasing the ionic radius in the series of lanthanides, the extraction of the ions moved to higher pH regions. However, limited information is available as regards separation of rare-earth element thorium by using crown ethers.

In the present study, a novel racemic monoaza-crown ether, (2-ethyl-*N*-benzyl-4,7,10,13,16-pentaoxa-1,-azacyclooctadecane MACE) containing a flexible benzyl and ethyl side arms was used for extraction, preconcentration and determination of thorium in the complex matrix. MACE was synthesized from precursor diol 1 by ring closure reaction with tetra ethylene glycol di(*p*-toluenesulfonate) in a high yield (Scheme 1). Thorium was determined by both ICP-OES and UV-vis spectrophotometrically. In addition, the method was extended to analyse thorium in geological bastnaesite ore sample and IAEA (Soil-7) as a standard
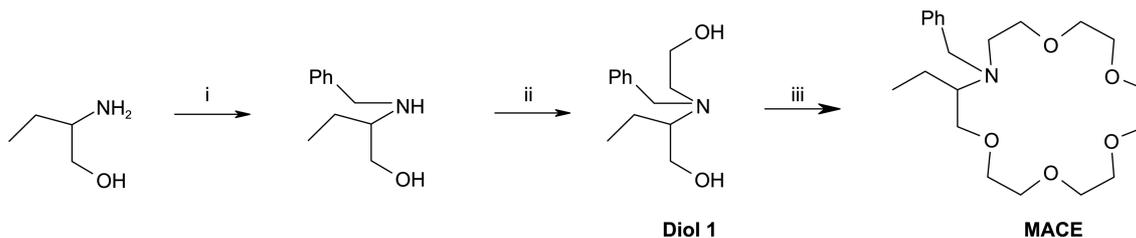
Scheme 1. Reagent and Conditions, i: BnCl, K$_2$CO$_3$, 110 °C, 24 h., ii: Ethylene oxide, −20 °C, 24h, iii: NaH/THF then tetra ethylene glycol di(*p*-toluenesulfonate), reflux, 50 h.

reference material.

Experimental

Reagents. All chemicals used in this work were of analytical grade of Merck unless otherwise stated. All aqueous solutions were prepared with quartz distilled deionized water by using a Millipore Milli-Q water purification system. Standard stock solution of thorium (1.0×10^{-3} mol·L^{-1}) was prepared by dissolving required amounts of Th(NO$_3$)$_4$ in quartz distilled deionized water. Adjustment of the pH of the aqueous phase was carried out with 1.0 mol·L^{-1} HNO$_3$ and 1.0 mol·L^{-1} NaOH. Ionic strength of aqueous phase was kept constant by adding 0.1 mol·L^{-1} KCl.

The Synthesis of MACE.

2-Ethyl-*N*-Benzyl-4,7,10,13,16-pentaoxa-1,-azacyclo-octadecane (MACE): Racemic mixture of **diol 1** was synthesized as described previously.[21] A suspension of (1.77 g 59.00 mmol, 80% in mineral oil) of NaH in 300 mL of the dry THF at 0 °C was added into a solution of **diol 1** (2.92 g, 13.10 mmol) in 500 mL of THF. The reaction mixture was refluxed for 2 h. After cooling it to 0 °C, a solution of tetra (ethylene glycol) di(*p*-toluenesulfonate) (6.58 g, 13.10 mmol) in 500 mL of THF was slowly added. The suspension was refluxed for 48 h. The solvent was evaporated after adding 100 mL of water to the residue. The mixture was extracted with CH$_2$Cl$_2$ (4 × 200 mL) and the combined organic layers were washed with 200 mL of water, dried over MgSO$_4$, and the solvent was evaporated. The crude product was purified by column chromatography (eluent: triethylamine/ethylacetate/petroleum ether 60-80: 3/17/80) to give it as a viscous oil (3.40 g, 68%). IR ν (cm^{-1}): 3095, 3063, 3031, 1503, 1458, 1355, 1297, 1252, 1124, 990, 951, 939, 707. ^{1}H NMR (CDCl$_3$) δ (ppm): 0.95(t, 7.4Hz, 3H), 1.39-1.51 (m, 2H), 2.76-2.84(m, 1H), 2.94-2.97(m, 2H), 3.45-3.77(m, 22H), 7.22-7.32 (m, 5H); ^{13}C NMR δ (ppm): 11.89, 21.84, 23.24, 50.37, 55.19, 61.50, 70.28, 70.57, 70.63, 70.67, 70.70, 70.84, 70.92, 70.96, 72.32, 126.50, 128.02, 128.50, 128.73 Anal. Calc. for C$_{21}$H$_{35}$NO$_5$: C, 66.48; H, 9.54; N, 3.42, found: C, 66.38; H, 9.56, N: 3.48%.

Apparatus. The amount of thorium in the aqueous phase was measured by using a Perkin Elmer Optima 2100 DV model ICP spectrometer (ICP-OES). Absorbance measurements were performed by using a Perkin Elmer Lambda 35 model UV-vis Spectrophotometer with 1.0 cm quartz cells. Infrared spectra were recorded on a Mattson 1000 Model

FTIR spectrophotometer. The Elemental analyses were obtained with Carlo-Erba Model 1108 apparatus. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AV-400 high performance digital FT-NMR spectrometer, with tetramethylsilane as internal standard solutions in deuterated chloroform. All extractions were performed by using a mechanical flask agitator in 50 mL glass flasks. The pH measurements were made by using a Mettler Toledo digital pH-meter equipped with a glass electrode.

Procedures

Extraction Procedure. Aqueous solutions containing 1.0×10^{-5} - 5.0×10^{-4} mol·L^{-1} thorium were contacted with various solutions of MACE in chloroform (1.0×10^{-4} - 1.0×10^{-3} mol·L^{-1}) by shaking it with a magnetic shaker at 25 °C. The ionic strength of aqueous phase was kept at 0.1 mol·L^{-1} by KCl. The correlation of contact time and distribution equilibrium experiments showed that the 60 minute is the best time to obtain maximum and reproducible results. After stirring the solutions, they were allowed to stand for 15 minutes, and then the aqueous and organic phases were separated. The pH of the aqueous phase was recorded as equilibrium pH. Thorium concentrations in the aqueous, and organic phase were measured by ICP-OES and UV-vis spectrophotometrically at 281 nm, respectively.

Preconcentration Procedure. An aqueous solution of thorium (2.314 μg in 100 mL water) was extracted into the solution of MACE in chloroform (30 mL, 1.0×10^{-4} mol·L^{-1}). Thorium was stripped from thorium loaded organic phase with 1.0 mol·L^{-1} HNO$_3$ (10 mL). After stripping, the amount of thorium was determined by ICP-OES. Recovery percentage (R %) and preconcentration factor were calculated.

Determination of Trace Amounts of Thorium in Bastnaesite Ore Samples Using Preconcentration Procedure by ICP-OES. Bastnaesite ore (1.0 g) was digested in 10 mL of concentrated HNO$_3$. The digested solution sample was extracted with 30 mL of 1.0×10^{-4} mol·L^{-1} of MACE in chloroform, and then thorium loaded organic phase was stripped into 10 mL 0.1-1.0 mol·L^{-1} solutions of HNO$_3$. The amounts of thorium in stripped solutions were determined by ICP-OES.

Determination of Thorium in IAEA Soil-7 (SRM) Samples with Spectrophotometric Method. The IAEA Soil-7 sample was digested with 10 mL of concentrated

HNO_3, and the digest solution was evaporated to dryness. The residue was dissolved in 100 mL of water. The concentration of thorium was determined spectrophotometrically at 281 nm by UV-vis.

Results and Discussion

The Effect of pH on the Extraction of Th(IV). The percentage of extraction and formation of complex is also influenced by the pH of the medium. Maximum extraction of thorium with MACE was obtained in the pH range of 6-7 (Fig. 1). The data given in Figure 1 show that the extraction is incomplete at lower and higher pH.

Absorption Spectra of the MACE and Thorium-MACE Complex and the Effect of pH on the Absorbance of the Complex. The absorption spectra of the MACE and thorium-MACE complex are shown in Figure 2. The spectra of thorium-MACE complex have two maxima: one overlaps with the maximum of the MACE at 219 nm., 281 nm higher than that of MACE, which means that maximum absorbance value increases due to complexation. This increase in absorbance shows us formation of thorium-MACE. Therefore, 281 nm was used in all subsequent measurements. The absorbance of thorium-MACE complex were measured between pH 2 and 10, as shown in Figure 3. One can see that the absorbance of thorium-MACE complex gradually

Figure 3. Effect of pH on absorbance of Th(IV)-MACE complex.

increased from pH 2 to 6; it increased slightly between pH 6 to 7. and after pH 7, the absorbance even decreased, meaning that complexation did not occur after this pH. In conclusion, it was determined that optimum pH was in the range of 6 to 7 for complexation.

Complexation ratio of MACE with Thorium. Job's plot method[22] was used to confirm the stoichiometry of thorium-MACE complex. In Job's method, the concentration of thorium in the aqueous phase and MACE in the organic phase are varied, so that their sum is equal to $0.1 \ mmol \cdot L^{-1}$. The pH was kept constant at 6.5; ionic strength was also kept constant at the addition of $0.1 \ mol \cdot L^{-1}$ KCl solution. The absorbance of the thorium complex in the organic phase was measured at 281 nm as shown in Figure 4. The maximum absorbance value corresponds to a molar ratio [Th(IV): MACE] of 3:2, which confirms the assumption of a Th_3MACE_2 stoichiometry.

Determination of Thorium. The applicability of the mono-aza-18-crown-6 (MACE) as a spectrophotometric determination method for Th(IV) was studied in the range of 0.464-2.32 $\mu g \ mL^{-1}$ Th(IV) solutions. The concentration of ligand in chloroform was $5.0 \times 10^{-4} \ mol \ L^{-1}$. The effective molar absorption was calculated from the data obtained by the measurements of organic phase absorbance at the conditions under which extraction was completed. The obtained calib-

Figure 1. Effect of pH on the extraction of Th(IV).
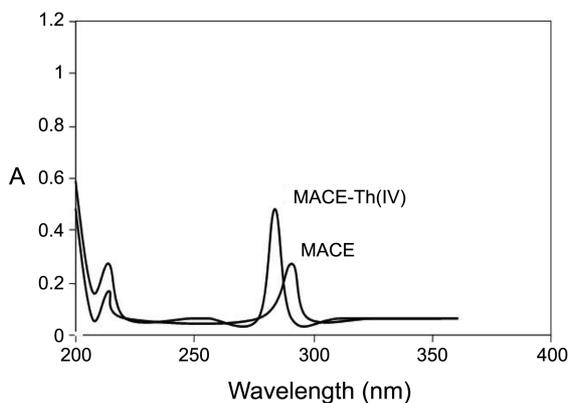
Figure 2. The Absorption spectra of the MACE and Th(IV)-MACE complex.
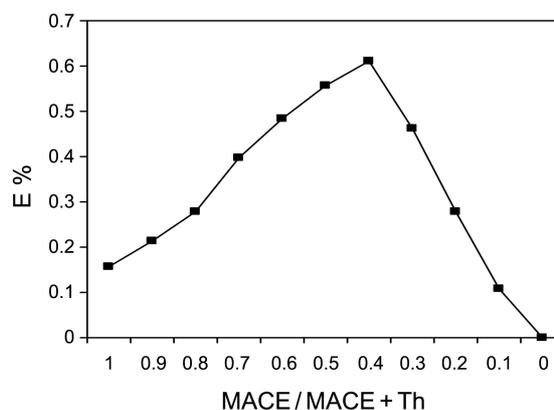
Figure 4. Thorium complex stoichiometry determination in the extraction with MACE by spectrophotometric measurements at 281 nm (Job's method).

y = 0.1188x + 0.2096
R^2 = 0.9855
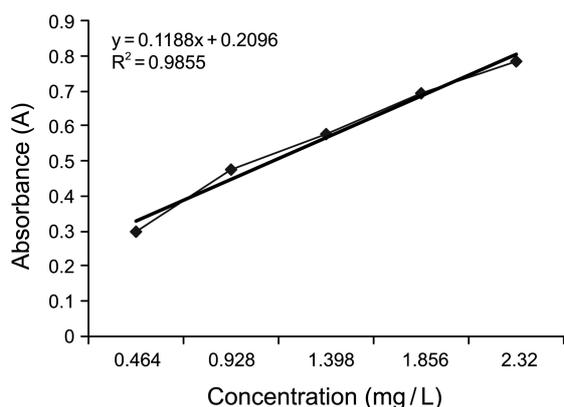
Figure 5. Calibration curve of Thorium-MACE complex (MACE: 5×10^{-4} mol L^{-1}).

ration graph was a straight line passing through the origin over the range mentioned above, as shown in Figure 5. The effective molar absorption coefficient at 281 nm was 1.98×10^3 mol^{-1} cm^{-1}. The complex was observed to be complied with Beer's law from 0.464 to 2.32 µg mL^{-1}. The developed procedure is highly sensitive and easy to apply for determining the concentration of Th(IV) in aqueous solutions.

Effect of Foreign Ions. A 25 mL solution containing

Table 1. Effect of Foreign Ions on the Determination 22.65 µg/mL Th(IV)

Foreign Ion	Amount Added (µg/mL)	Th(IV) Found (µg/mL)	Error (%)
K^+	1000	22.78	0.57
Na^+	1000	22.98	1.45
Zn^{2+}	1000	24.29	7.24
NH_4^+	1000	23.28	2.78
Mg^{2+}	1000	22.24	−1.81
Ca^{2+}	1000	23.04	1.72
Cd^{2+}	1000	23.62	4.28
Pb^{2+}	1000	24.97	10.24
Ni^{2+}	1000	23.44	3.48
Cu^{2+}	1000	24.08	6.31
Fe^{3+}	1000	23.74	4.81
Mn^{2+}	1000	22.90	1.10
F^-	1000	23.86	5.34
Cl^-	1000	23.13	2.12
SO_4^{2-}	1000	20.38	−10.02
CO_3^{2-}	1000	22.61	−0.17
NO_3^-	1000	23.48	3.66
None	-	22.65	0

Table 2. The Analysis of SRM (IAEA-Soil-7) Samples with the Proposed Spectrophotometric Determination Method

Sample	Elements	Proposed Spectrophotometric Determination Method	ICP-OES[a]	Certified valued (mg/kg)
IAEA (Soil-7)	Th(IV)	8.34 ± 0.41	7.61 ± 0.91	8.19

[a]Inductively Coupled Plasma-Optical Emission Spectroscopy

22.65 µg mL^{-1} Th(IV) and various amounts of foreign ions were treated as described in the procedure. The results are given in Table 1. One gram per liter concentration of Zn^{2+}, Pb^{2+}, Cu^{2+}, F^-, SO_4^{2-} interfered with the absorbance of the complexes as seen in the Table 1. The other ions listed in Table 1 did not interfere with an error below 5%.

Analysis of Standard Reference Materials (IAEA (Soil-7)). The spectrophotometric method was applied for determination of Th(IV) in pretreated IAEA (Soil-7) solutions. The results are given in Table 2. The results from the recommended method were compared with those from ICP-OES measurements and certified values. The results indicate that the recommended procedures provide both a fairly good accuracy and precision.

Preconcentration of Th(IV) and Determination by using ICP-OES. The effect of concentration of HNO$_3$ on the stripping of the aqueous solution containing 2.314 µg Th(IV)/100 mL is given in Table 3, for the preconcentration purpose. It was concluded that 0.1-0.4 M HNO$_3$ was not enough in concentration to decompose complex structure, and that HNO$_3$ at this concentration could not strip all Th(IV). The highest recovery values were obtained with 0.5-1.0 mol·L^{-1} HNO$_3$. The proposed procedure was also applied to the bastnaesite ore sample obtained with 2.314 µg Th(IV) into a sample of 100 mL. The solution containing 2.314 µg Th(IV) was extracted into organic phase with MACE ligand. Then, strpping was performed with 0.5 mol/L HNO$_3$, and Th(IV) was stripped with a recovery of 98.53 ± 3.02 % (n=3).Thus, Th(IV) in the ore was preconcentrated ten times, as shown in Table 4.

Table 4. Preconcentration factor and concentration limit of Th(IV) in Bastnaesite Ore Sample

Elements	Max. volume of solution (mL)	Concentration limit (µg L^{-1})	Preconcentration factor	Recovery (%)
Th(IV)	100 mL	23.14	10	98.53 ± 3.02

Table 3. The Effect of acid concentration on stripping

	HNO$_3$									
Acid (mol/L)	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
Found (µg)	1.564	1.887	1.954	2.019	2.301	2.295	2.313	2.322	2.319	2.325
R (%)	67.60	81.55	84.44	87.25	99.43	99.17	99.96	100.3	100.2	100.5

Analyical Figures of Merits.

Table 5. Analytical Figures of Merits

Linear Range	0.464-2.32 µg mL^{-1}
Calibration equations (y)	0.093X + 0.2376
Correlation Coefficient (R^2)	0.9855
LOD (Limit of Detection)	0.181 µg mL^{-1}
LOQ (Limit of Quantification)	0.603 µg mL^{-1}
RSD (0.928 µg mL^{-1} ; for n:10 times)	± 0.049 µg mL^{-1}

Conclusions

In this study, separation and preconcentration of thorium in bastnaesite ore, which is present in the Eskişehir province of Turkey and have a significant importance especially in view of thorium content, were investigated by the extraction with MACE ligand, and fairly good results were obtained. It was found that all thorium was extracted under optimum conditions obtained from experimental studies. Furthermore, it was observed that the formed thorium-MACE complex gave an absorbance at 281 nm on UV-vis. Thus, spectrophotometric determination method suggested for thorium was given. In order to investigate the extent of accuracy of the suggested spectrophtometric determination method, it was applied to standart reference material (IAEA Soil-7), and thus it was observed that the extent of accuracy of the method was quite high. When our results were compared to other studies, it was determined that the ligand we used provided us with more efficient results in thorium extraction.

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