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Journal of Alloys and Compounds 271–273 (1998) 620–624

Journal of ALLOYS AND COMPOUNDS

Investigation of thorium(IV) separation from cerium(IV) on a silica gel column coated with tri-octylphosphine oxide

Ümran Hiçsönmez*, Meral Eral

Ege University, Institute of Nuclear Sciences, 35100, Bornova, İzmir, Turkey

Abstract

The parameters effecting the efficiency of thorium extraction on silica gel coated with Tri-octylphosphine oxide(TOPO) such as; HNO_3 concentration, thorium concentration, TOPO concentration, flow rate and nature of diluent were studied and optimum conditions were determined. Various elution reagents were tried to elute thorium from the column. High recovery was obtained with 0.5 M H_2SO_4, 0.5 M HCl solutions. Extraction data have been used to separation thorium from iron(III) and Ce(IV). The solution that contains Fe(III), Ce(IV) and Th(IV) in nitric media was passed through the TOPO/silica gel column, whilst Th(IV) and Ce(IV) were extracted by TOPO, Fe(III) was not. Firstly Th(IV) was eluted with H_2SO_4 then Ce(IV) was eluted with HCl. As a result, optimum conditions are here reported for the separation of thorium from cerium(IV). © 1998 Elsevier Science S.A.

Keywords: Thorium (IV); Extraction chromatography; Trioctylphosphine oxide; Cerium (IV)

1. Introduction

Thorium, once used mainly in the Welsbach gas mantle [1], promises to become a nuclear fuel if is conjunction with enriched uranium [2]. For this reason, thorium-containing fuels may become important in the future. The recovery and separation of thorium from mineral acid media have been carried out by solvent extraction using various extractants [1]. However, the separation of thorium from rare earth is difficult and limited because their compounds show similar properties to thorium. Fundamentally, separation of thorium from rare earths is important in two aspects, firstly deposits of thorium and uranium are generally associated with rare earths such as monazit, bastnaesite etc. [3], and secondly to successfully separate it from radioactive rare earth elements during nuclear fuel reprocessing [2]. Therefore, it is of current interest compare the extraction behaviour of lanthanides and actinides so as to develop an efficient procedure for their separation and purification. In many applications, especially in radiochemistry, extraction chromatography techniques are preferable to other separation methods, since the equipment is simple and does not necessarily to contain moving parts. In principle, extraction chromatography is a liquid–liquid extraction where one of the organic phases is stationary and attached to a supporting material, and the other liquid phase is mobile [4]. This technique has been successfully employed in radiochemistry for separating individual lanthanides or actinides with various extractants [5–7]. Tri-*n*-octylphosphine oxide (TOPO) has been extensively used in solvent extraction for the separation of thorium from metal ion solutions. TOPO appears to be a good stationary phase [4,8,9]. Silica gel is the best among the various supporting materials used in extraction chromatography because it is colourless, porous with a large surface area and physically and chemically more stable. Its surface chemistry can be modified by silane derivatisation.

This paper presents systematic investigations on the extraction chromatographic separation of thorium on silica gel coated with TOPO as the stationary phase and nitric acid as the mobile phase. Different eluents were tried to elute thorium. This method was tested for solutions containing Fe(III) and Th(IV) and Ce(IV).

2. Experimental

2.1. Reagents

The following reagents were employed: Silica gel 60, 70–230 mesh (Merck, Germany); tri-*n*-octylphosphine oxide (TOPO), $[CH_3(CH_2)_7]_3$ P(O) (Merck, Germany);

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*Corresponding author. Fax: +90 232 3886757; e-mail: hicsonmu@egeuniv.ege.edu.tr

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PII: S0925-8388(98)00172-8

1,10-phenanthroline monohydrate, $C_{12}H_8N_2.H_2O$ (B.D.H., Great Britain); Alizarin Red S (B.D.H., Great Britain); thorium nitrate pentahydrate, cerium sulfate tetrahydrate and all the other reagents were of analytical grade (Merck, Germany). A stock solution, containing 10 g of thorium l^{-1}, was prepared by dissolving 2.457 g $Th(NO_3)_4.5H_2O$ in 1 M HNO_3. A 1000 mg l^{-1} thorium solution was prepared by appropriate dilution. A stock cerium solution of 1500 mg l^{-1} was prepared by dissolving 1.082 g of $Ce(SO_4)_2.4H_2O$ in 250 ml of 0.1 M H_2SO_4. 6.95 g of $FeSO_4.7H_2O$ was dissolved in 250 ml of 0.1 M H_2SO_4. The solution was standardized by titration with $KMnO_4$ [10]. A 1000 mg l^{-1} iron solution was prepared by appropriated dilution. A portion of cerium and iron stock solutions were evaporated to dryness. After dissolution of the residues with nitric acid, the solutions were again evaporated to dryness. Thus, cerium and iron (III) nitrate solutions were prepared from these solutions. Cerium was maintained in the tetravalent state by adding $KBrO_3$ before the experiments.

2.2. Preparation of the chromatographic column

Silica gel 60(70–230 mesh) was washed with methanol and dried at 105°C for 1 h. Then, 50 g silica gel was exposed in a desiccator to vapours of 10 ml dimethyldichlorosilane for one week. The resulting hydrophobic silica gel was dried at 105°C for 1 h, to remove the excess vapour. This hydrophobic silica gel (10 g) was mixed with 20 ml of 0.1 M TOPO/cyclohexane and 10 ml of acetone. The mixture was stirred by a mechanical stirrer to have a uniform coating for 1 h. The cyclohexane and acetone were evaporated under vacuum. Therefore, a dried sample of silica gel coated with TOPO was obtained. A known amount of the TOPO/silica gel was packed into the chromatographic column as a loose, dry powder and compacted lightly with cotton.

2.3. Apparatus and measurements

A digital pH meter (HANNA, model 8521, Italy) and recording spectrophotometer (Shimadzu, model UV–VIS 260, Japan) were used. The experiments with standard solutions were carried out in a 1×15 cm glass column and the experiments with synthetic mixture solutions, were carried out a 0.8×20 cm glass column. A separating funnel used at the column head as a reservoir of sample or eluting solutions. After the solvent extraction of thorium with 0.1 M TOPO in cyclohexane, the concentration of thorium in aqueous solution was determined spectrophotometrically at 545 nm as its complex with Thorin [9]. The cerium and iron concentration in solution was determined spectrophotometrically by the Alizarinsulfonate method at 550 nm and phenanthroline method at 510 nm [11,12]. The qualitative determinations of iron in each fraction was determined by the $K_4Fe(CN)_6$ [13].

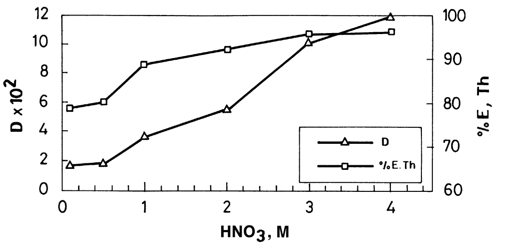

Fig. 1. Effect of HNO_3 concentration on thorium extraction (0.5320 g TOPO/silica gel, V=25 ml 200 ppm Th, flow rate 0.8 ml min^{-1}).

3. Results and discussion

3.1. Parameters effecting thorium extraction

One of the important parameters effecting on extraction ratio is the acidity of the aqueous phase [14]. Fig. 1 shows the influence of HNO_3 concentration. The extraction yield increases with increasing nitric acid concentration as extractable thorium nitrate complexes are formed.

The effect of thorium concentration was tested by using standard solutions of varying initial concentrations from 100–350 ppm. As is shown in Fig. 2 extraction falls down to 85% after the 250 ppm. A concentration of 200 ppm of the thorium has been chosen for the present investigation.

The effect of TOPO concentration on the thorium extraction is shown in Fig. 3. It was observed that extraction increases with the increase in the concentration of TOPO. The high extraction efficiencies were obtained at between 0.5–0.7 ml min^{-1} of flow rate.

The role of an organic diluent in the extraction process of Th^{4+} was investigated by employing diluents of varying dielectric constants like cyclohexane, benzene, toluene, chloroform, dichloromethane but no correlation was found between the degree of extraction and the dielectric constant of the solvent. The subsequent detailed studies were therefore carried out in cyclohexane only.

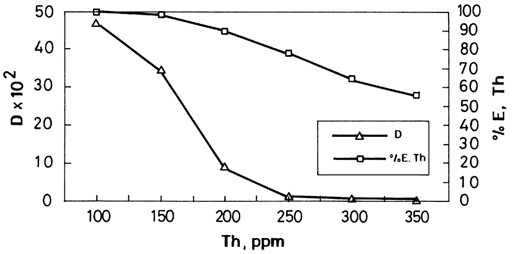

Fig. 2. Effect of thorium concentration on thorium extraction (0.5320 g TOPO/silica gel, 3 M HNO_3 V=25 ml, flow rate 0.8 ml min^{-1}).

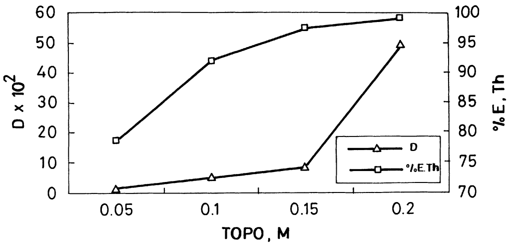

Fig. 3. Effect of TOPO concentration on thorium extraction (0.5000 g silica gel, 1 M HNO_3 $V=25$ ml 200 ppm Th, flow rate 0.8 ml min^{-1}).

As a result, following optimum conditions were found; $[HNO_3]=3$ M, $[Th]=200$ ppm 25 ml, $[TOPO]=2$ ml 0.1 M in cyclohexane for 1 g silica gel, flow rate$=0.6$ ml min^{-1}. At this determined optimum conditions, the yield of thorium extraction was found to be 91.5±3.6%.

3.2. Elution experiments of thorium

The thorium solution was passed through a column containing TOPO/silica gel under the conditions above. Then, the column was washed with 10 ml of water. The different elution reagents were passed through the column at a flow rate of 0.6 ml min^{-1} and eluent was collected in 4 ml fractions. The thorium concentration was determined in each fraction. The elution efficiencies of 0.1 M and 0.5 M HNO_3 were found to be 5.4 and 26.0%, respectively. The effect of different eluents is shown in Fig. 4. The thorium can be eluted by 0.5 M and 1 M HCl, 0.3 M and 0.5 M H_2SO_4, giving the percentage of total elution as 83, 77, 74, 92%, respectively. The thorium extraction by the TOPO decreases in the presence of the chlorine and sulphate ions [9].

Table 1
Extraction of Fe and Ce on TOPO/silica gel column from 3 M HNO_3 (column 1×15 cm, 0.5300±0.0020 g TOPO/silica gel, solution: 25 ml, flow rate: 0.7 ml min^{-1}, bed height: 1.6 cm)

Element, taken	Fe(III), 5 mg	Ce(IV), 5 mg
Extraction, %	32.0	91.0

3.3. Extraction of Fe(III) and Ce(IV)

Extraction behaviour of Fe(III) and Ce(IV) were investigated under optimum conditions determined for to thorium extraction. The Fe(III) and Ce(IV) feed solutions were passed through the chromatographic column. The results are shown in Table 1. Iron (III) extraction is low as seen by yellow colouration of iron (III) fraction. Also, partially extracted Fe(III) can be easily removed from the column by washing with deionized water. Cerium(IV) is extracted on column, due to the tetravalent state conferring similar chemical properties to thorium. Cerium(IV) exhibits a yellow band in the column.

3.4. Separation of Th(IV)–Ce(IV)–Fe(III)

Iron(III) is not complexed by TOPO in 3 M nitric acid solution where cerium(IV) and thorium were complexed. Furthermore, cerium(IV) was not eluted away by low molarity (0.5 M) sulfuric acid, therefore also the separation of thorium and cerium was possible.

25 ml of the feed solution were put at the top of the bed at a flow rate of 0.7 ml min^{-1}. Firstly, the column was washed with 0.05 M HNO_3. Elution of thorium from the column was carried out with 0.5 M H_2SO_4. Cerium which was extracted, was eluted with 1 M HCl. The results and

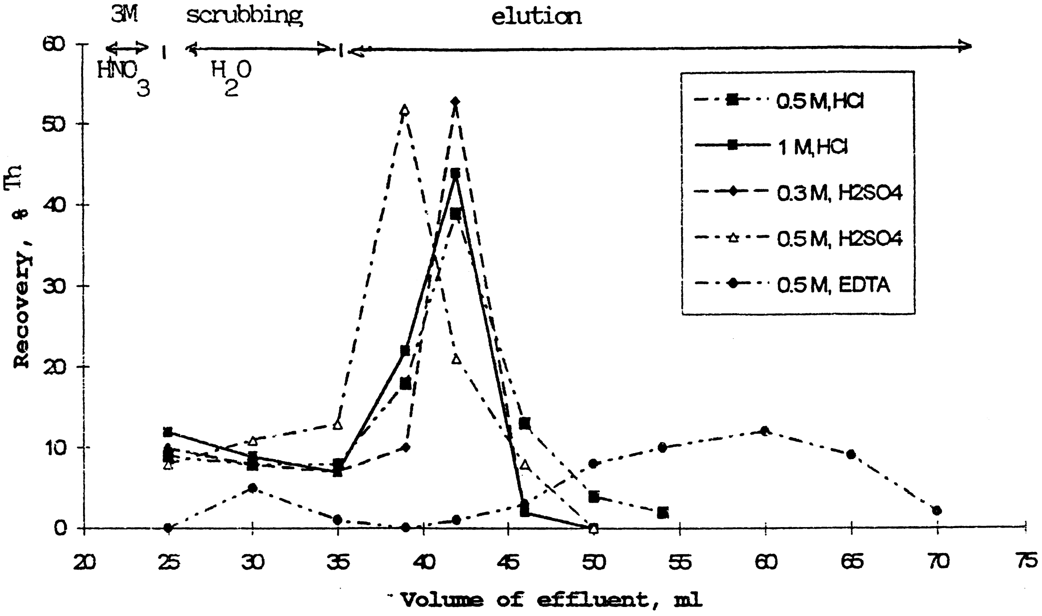

Fig. 4. Elution behaviour of thorium in nitric acid with various eluents.

Table 2
Separation of thorium from synthetic mixtures (aqueous phase: 3 M HNO_3, 25 ml; column: 0.8×20 cm and 1.0600±0.0030 g TOPO/silica gel, flow rate: 0.7 ml min^{-1}, bed height: 3.4 cm)

Extraction				Elution					
Mixture	Cations	Taken mg	E% Th	Eluent	Eluent Volume ml	Recovery			
						Th		Ce	
						Found mg	%	Found mg	%
I	Th	5.0	86	0.5 M H_2SO_4	16	2.2	44	–	–
	Fe	5.0		0.5 M HCl	12	–	–	0.5	19
	Ce	2.7							
II	Th	5.0	92	0.5 M H_2SO_4	12	3.7	74	–	–
	Fe	2.7		1.0 M HCl	8	–	–	1.8	67
	Ce	2.7							

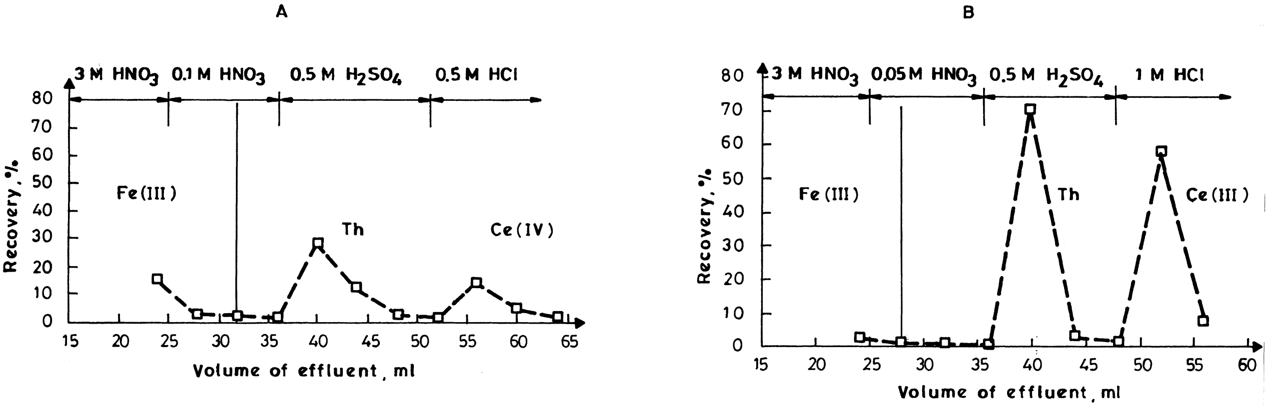

Fig. 5. Separation of Th(IV) from multicomponent mixtures A: Feed solution: 25 ml solution containing 5 mg Th, 5 mg Fe, 2.7 mg Ce in 3 M HNO_3. B:Feed solution: 25 ml solution containing 5 mg Th, 2.7 mg Fe, 2.7 mg Ce.

elution curves are reported in Table 2 and Fig. 5 respectively. The extraction and recovery of thorium increase with decreasing amount of iron(III). The collected fractions of cerium which produces a yellow band in the column is colourless. This is due to the reduction of Ce(IV) to Ce(III) in the presence of chloride ions [15]. The recovery of cerium up to 63% can be achieved if the molarity of hydrochloric acid is increased to 1 M.

4. Conclusions

The thorium extraction was found to be 91.5±3.6% on TOPO/silica gel under the optimum experimental conditions. Thorium from column can be eluted with solutions of 0.3, 0.5 M H_2SO_4 and 0.5, 1 M HCl. The iron(III) and Cerium(IV) extraction yields were determined as 32% and 91% under the optimum conditions. Iron(III) can be removed from column by washing with deionized water or diluted nitric acid solution. The thorium extraction yield was 92% in the solution containing Fe: Th: Ce (2.7: 5.0: 2.7 mg). After the column washed with 0.05 M HNO_3, thorium was eluted with 0.5 M H_2SO_4, then cerium with HCl solution.

This method should be improved for the separation and determination of thorium from leach or waste solutions, since it is simple and rapid.

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