Sequential separation of actinides and lanthanides by extraction chromatography using a CMPO-TBP/XAD7 column

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CMPO/TBP sorbed on Amberlite XAD7 resin was used for the separation of actinides and lanthanides from nitric acid solutions by extraction chromatography. The distribution ratios of actinides and lanthanide fission products (Ce, Eu) as a function of acid concentration and some complexing agents were determined. In strong HNO_3 medium (>1 mol/l) the tri-, tetra- and hexavalent actinides as well as the lanthanides have shown great affinity for the CMPO/TBP/XAD7 sorbent. The same behavior was found in HCl medium except for trivalent actinides and lanthanides which show lower distribution values in the same acid range. The effect of some complexing agents as DTPA and ammonium oxalate were also investigated. In DTPA only hexavalent actinides showed higher distribution value. On the basis of these differences, an alternative procedure for actinide-lanthanide separation and actinides from each other is proposed.

Introduction

Bifunctional organophosphorous extractants, mainly of carbamoylmethylenephosphorous (CMP) and phosphine oxide type have been employed for the separation of actinides and lanthanides from high level waste streams.[1,2] These compounds show great affinity for lanthanides and tri-, tetra-, hexavalent actinides in strong HNO_3 solutions. The protonation of the CO-N group resulting CO-NH+ in strong acid medium, maintaining a partially free P=O group, is the property which distinguishes them from monofunctional organophosphorous extractants.[3] Among the phosphine oxides, specially the octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) is considered as one of the most promising extractants. Several studies on the use of CMPO for acid waste partitioning have been published.[4–9]

This paper describes the distribution studies of actinides (U, Pu, Am) and lanthanides fission products (Eu, Ce) in a CMPO-TBP/XAD7 system and an alternative procedure for sequential separation of these radionuclides by extraction chromatography.

Experimental

Reagents

Octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO), Atochem North America, U.S.A.

Tributyl phosphate (TBP), 99% purity, Merck, was contacted with 0.5% sodium carbonate solution and distilled water to remove its degradation products.

Amberlite XAD7 resin, 35–65 mesh, supplied by Rohm and Haas Co, U.S.A., washed with distilled water and methanol to remove preservatives and residual monomers.

^{233}U, ^{239}Pu and ^{241}Am tracer solutions in nitric acid medium were supplied by the Radiochemical Center, Amersham, England. ^{239}Pu tracer was used with any valence state adjustment as Pu_{total}. Eu(III) traced with ^{152}Eu and Ce(III) traced with ^{141}Ce solutions in nitric acid medium was supplied by the Radiochemistry and Radioisotope Production Department of IPEN/CNEN-SP, BR. Nitrate solution of U(VI) was prepared by dissoluting nuclear grade U_3O_8 (IPEN/CNEN-SP, BR). All other chemicals were of analytical grade.

Preparation of chromatographic CMPO-TBP/XAD7 sorbent

Four ml of 0.75 mol/l CMPO in TBP and 6 g XAD7 resin previously slurried in methanol were shaken during 15 minutes. The methanol was then removed by evaporation at room temperature. The CMPO-TBP loaded resin was washed with distilled water and dried at room temperature for several days. Under these conditions a 37 wt.% extractant loaded resin was obtained.

Determination of the distribution ratio

The distribution ratio measurements were performed by batch experiments from various acid and complexing solutions. Fifty µl of tracer solution of the desired element was added to 1 ml of aqueous phase and then shaken mechanically with 0.04 g of CMPO-TBP/XAD7 resin for 15 minutes at room temperature (23–26 °C). 0.5 ml and 50 µl of aqueous phase were taken for the measurement of γ-activity with a NaI(Tl) well-type scintillation detector and of α-activity with a surface barrier detector, respectively.

The distribution ratio (D) was determined as the ratio of nuclides in the CMPO-TBP/XAD7 sorbent to that in the aqueous phase:

$$D = [(C_0-C)/C] \; (V/M)$$

where C_0 is the initial metal concentration (μg/ml) or initial radioisotope concentration (cpm) in the aqueous phase, C is the equilibrium concentration in aqueous phase, V is the volume of the aqueous phase (ml) and M is the mass of the CMPO-TBP/XAD7 resin (g).

Preparation of the chromatographic column

Borosilicate glass chromatographic columns with 3.6 mm inside diameter and 30 cm length were used. The column was filled with ca. 2 ml of 37 wt.% CMPO-TBP/XAD7 (bed length = 17.8 cm) and then was rinsed with an excess of 1 mol/l HNO_3. The column was pre-conditioned with 5 ml of 4 mol/l HNO_3. The flow rate was maintained at 0.2–0.3 ml·min⁻¹ throughout. The column experiments were carried out at room temperature (23–26 °C).

Results and discussion

Distribution ratios of U, Pu, Am, Eu and Ce in nitric acid, hydrochloric acid, oxalic acid, diethylene-triaminepentaacetic acid (DTPA) and ammonium oxalate solutions were examined.

The effect of nitric and hydrochloric acids on the distribution ratio of actinides and lanthanides

Figure 1 shows the effect of nitric acid concentration on the distribution ratios of U(VI), Pu_{total}, Am(III), lanthanide fission products Eu(III) and Ce(III). The results indicate that all nuclides have great affinity for the CMPO-TBP/XAD7 sorbent and their distribution ratios increase with increasing the HNO_3 concentration.
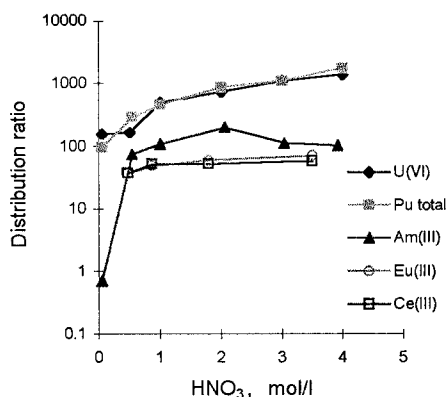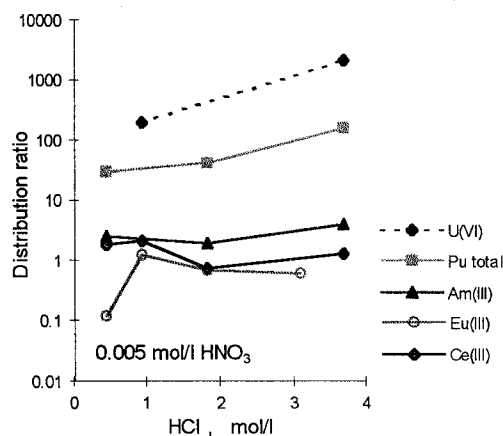
Fig. 2. Distribution ratios of nuclides on a 37 wt.% CMPO-TBP/XAD7 sorbent in HCl

The experiments performed in HCl solution at 0.005 mol/l HNO_3 (Fig. 2) have shown that the distribution ratios of U(VI) and Pu_{total} are higher at strong acid concentration (>2 mol/l) whereas the lanthanides Eu(III) and Ce(III) and the trivalent actinide Am(III) show lower extraction values at the same acidity.

Influence of DTPA on the distribution ratio of actinides and lanthanides

The effect of DTPA on actinide and lanthanide distribution ratios is shown in Fig. 3. The actinides Am(III) and Pu_{total} as well the lanthanides Eu(III) and Ce(III) are well complexed by DTPA unlike the hexavalent actinide U(VI) which is not complexed and shows a higher distribution ratio. The extraction data was obtained by maintaining a constant HNO_3 concentration (0.005 mol/l).
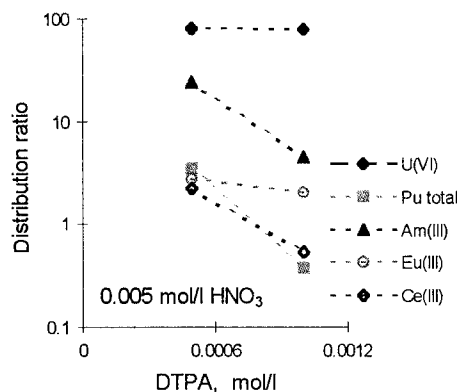
Fig. 1. Distribution ratios of nuclides on a 37 wt.% CMPO-TBP/XAD7 sorbent in HNO_3

Fig. 3. Distribution ratios of nuclides on a 37 wt.% CMPO-TBP/XAD7 sorbent in DTPA

Influence of oxalic acid on the distribution ratio of U and Pu

Figure 4 shows U(VI) the distribution ratio on a 37 wt.% CMPO-TBP/XAD7 sorbent. The low value observed is due to the great affinity of U(VI) for oxalate ions. But due to the competitive reaction between nitrate and oxalate ions, the U(VI) distribution ratio increases with increasing HNO_3 concentration, showing a higher distribution in 0.5 mol/l HNO_3. This competitive effect is lower for Pu $_{total}$ which shows a low distribution even in 0.5 mol/l HNO_3 (Fig. 5).

Influence of ammonium oxalate on the distribution ratio of U and Pu

Both U(VI) and Pu_{total} distribution ratios (Figs 6 and 7) in ammonium oxalate/nitric acid solution showed a similar behavior to that observed in oxalic acid/nitric acid solution.
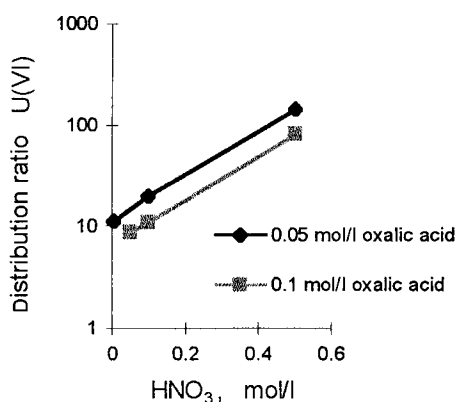

Fig. 6. U(VI) distribution ratio on a 37 wt.% CMPO-TBP/XAD7 sorbent in ammonium oxalate/nitric acid medium

Fig. 7. Pu_{total} distribution ratio on a 37 wt.% CMPO-TBP/XAD7 sorbent in ammonium oxalate/nitric acid medium
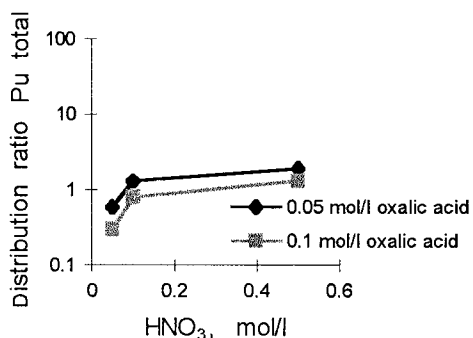

Fig. 4. Distribution ratio of U(VI) on a 37 wt.% CMPO-TBP/XAD7 sorbent in oxalic acid/nitric acid medium

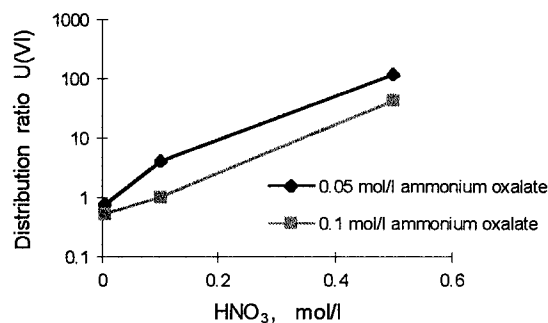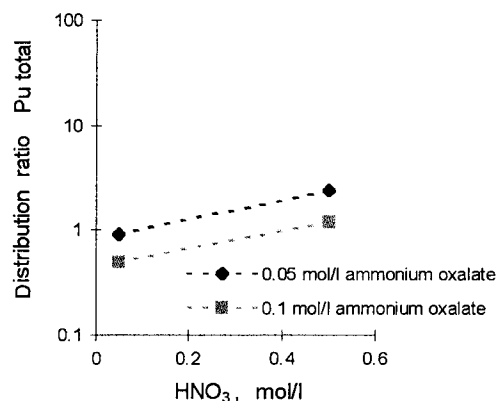Fig. 5. Distribution ratio of Pu_{total} on a 37 wt.% CMPO-TBP/XAD7 sorbent in oxalic acid/nitric acid medium

U and Pu separation from Am, Eu and Ce

On the basis of previously obtained distribution data an elution scheme for the isolation of actinides using a 37 wt.% CMPO-TBP/XAD7 sorbent was studied. In these experiments a nitrate solution containing $4.0 \cdot 10^{-3}$ mol/l U(VI) traced with ^{233}U, $2.6 \cdot 10^{-7}$ mol/l ^{239}Pu as Pu_{total}, $2.4 \cdot 10^{-9}$ mol/l ^{241}Am as Am(III), $1.9 \cdot 10^{-6}$ mol/l Eu(III) traced with ^{152}Eu and $1.3 \cdot 10^{-3}$ mol/l Ce(III) traced with ^{141}Ce in 4 mol/l HNO_3 was used as feed solution. A volume of 2.5 ml of this feed was passed through the column containing 0.62 g of 37 wt.% CMPO-TBP/XAD7 sorbent. After washing the column with 4 mol/l HNO_3, >99% of Am(III), Eu(III) and >98% of Ce(III) were removed by elution with 3.4 mol/l HCl. U and Pu were separated from the loaded resin by selective elution. Pu was first eluted with 8.5 ml of 0.1 mol/l oxalic acid/0.5 mol/l nitric acid and the remained uranium was recovered with 6.5 ml of 0.1 mol/l ammonium oxalate. An efficiency of 93% recovery for Pu with <0.2% U contamination and 98% recovery for U with 3.3% Pu contamination was achieved. Figure 8 shows the selective elution for actinide and lanthanide separation.
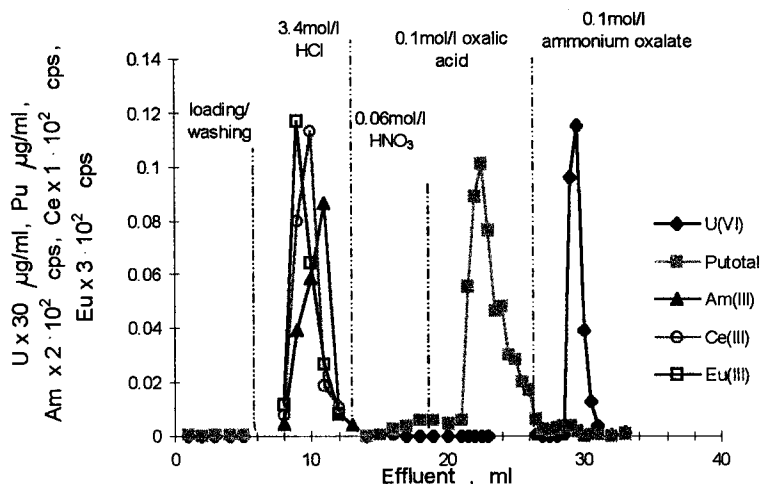
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Fig. 8. Sequential elution of actinides and lanthanides from a 37 wt.% CMPO-TBP/ column

Conclusions

The chromatographic extraction using 37 wt.% CMPO-TBP/XAD7 sorbent provides an effective method for the separation of actinides and lanthanides from nitric solutions. 98% U, Pu, Am, Eu and Ce were removed from 4 mol/l nitric solution by a CMPO-TBP/XAD7 column. The trivalent actinides and lanthanides are easily separated from tetra and hexavalent actinides by eluting the column with HCl. However, the Am(III)–Eu(III)–Ce(III) separation is more difficult and other complexing agents must be studied. U–Pu separation with oxalic acid/nitric acid solution is efficient but this separation would be carried out also with 0.001 mol/l DTPA.

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