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Removal of rare earth elements from fission products

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Abstract

Studies of extraction of Eu(III) and Ce(III) ions in CMPO-TBP/XAD7 resin has been carried out. Distribution ratios of lanthanides as a function of nitric and hydrochloric acids and some complexing agents were investigated. The lanthanides have shown great affinity for CMPO-TBP/XAD7 resin in >0.5 mol/L nitric acid medium. Sorption studies of Eu and Ce from nitric medium by CMPO-TBP/XAD7 chromatographic column and elution with hydrochloric acid are presented.

Keywords: extraction chromatography, lanthanides, rare earths, CMPO

1. Introduction

The extraction chromatographic technique has been widely used for analytical or technological separation purposes [1, 2]. The stationary phase is generally composed by an inert support impregnated with water insoluble organic extractant. The ability of bifunctional organophosphorus compounds, mainly octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) to form stable chelates with several metal ions has been shown great interest as an extractant for actinides and lanthanides separation from environmental and biological samples and from nuclear waste streams [3,4].

In this work, the extraction behavior of Ce and Eu lanthanides, as the fission products, onto extraction chromatography method has been investigated. Bifunctional organophosphorus (CMPO) mixed with monofunctional organophosphorus (TBP) extractants sorbed on Amberlite XAD7 nonionic polymer was used as stationary phase.

2. Experimental

2.1. Reagents and Materials

Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, extraction grade; tri-n-butyl phosphate (TBP), Merck, 99% purity, previously treated with 0.5% sodium carbonate and distilled water to remove the degradation products; Amberlite XAD7 resin, 35-65 mesh, supplied by Aldrich Chemical Company, Inc., USA, washed with distilled water and methanol to remove preservative and residual monomers; Eu(III) traced with $^{152/154}\text{Eu}$ and Ce(III) traced

with ^{141}Ce in nitric acid medium supplied by Radiochemistry and Radioisotope Production Department of IPEN-CNEN/SP-BR; all other chemicals were of analytical grade.

2.2. Preparation of CMPO-TBP/XAD7 resin

The supporting material loaded with CMPO-TBP extractants was prepared by solvent evaporation technique [5].

4 mL of 0.75 mol/L CMPO in TBP and 6 g of 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 37% extractant loaded resin was obtained.

2.3. Procedure for column operation

0.62 g of 37 wt.% CMPO-TBP/XAD7 solid extractant were packed in a column glass (30 cm height and 3.6 mm internal diameter). The column was conditioned with 4 mL 0.01 mol/L HNO_3 , followed with 3 mL 1 mol/L HNO_3 and finally with 4 mL 4 mol/L HNO_3 . The column experiment was carried out at room temperature, using 1.5×10^{-4} mol/L $\text{Ce}(\text{NO}_3)_3$ in 4 mol/L HNO_3 solution and 2×10^{-6} mol/L $\text{Eu}(\text{NO}_3)_3$ in 4 mol/L HNO_3 solution as feed solution. The flow rate was maintained at $0.3\text{--}0.4$ mL min^{-1} throughout.

2.4. Determination of distribution ratio

Batchwise uptake of Ce(III) and Eu(III) by CMPO-TBP/XAD7 resin from different HNO_3 and HCl

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concentrations and complexing agents, as diethylenetriamine pentaacetic acid (DTPA), ethylenediaminetetraacetic acid, disodium salt (EDTA) and oxalic acid, was performed to determine the distribution ratio. The sample containing traced solution and CMPO-TBP/XAD7 resin was equilibrated by mechanical shaking for 15 min at room temperature. $^{152/154}\text{Eu}$ and ^{141}Ce contents in the aqueous phase were controlled using NaI(Tl) scintillation detector and the distribution ratios were calculated, according to:

$$D = [(C_0 - C)/C] \cdot V/m \quad (\text{mL/g})$$

where C_0 and C are the initial and final radioisotope concentration, respectively, V is the volume of the aqueous phase (mL) and m is the weight of chromatographic material (g).

3. Results and discussion

3.1. Distribution ratio of Eu(III) and Ce(III) ions

Distribution ratios of Eu(III) and Ce(III) in nitric acid, hydrochloric acid and DTPA medium were verified. Fig. 1 and 2 show the dependency of HNO_3 and HCl concentration on the distribution ratios of Eu(III) and Ce(III), respectively. The results indicate that the lanthanides present great affinity for CMPO-TBP/XAD7 resin in HNO_3 medium and lower extraction values in HCl medium. On the other hand, in the same HNO_3 concentration range ($> 0.5 \text{ mol/L}$), the addition of complexant as DTPA shows no significant influence on the lanthanide distribution ratio, as observed in Fig. 3 and 4. However, in lower concentration HNO_3 solution (0.005 mol/L) and in presence of 0.001 mol/L DTPA, Ce(III) and Eu(III) are well complexed by DTPA, thus they are not extracted by CMPO-TBP/XAD7 solid extractant. These results are given in Fig. 5, 6, 7, 8 for Eu and Ce, respectively.

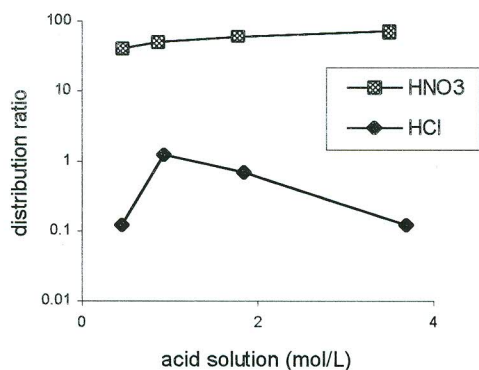


Fig. 1. Eu(III) distribution on CMPO-TBP/XAD7 in HNO_3 and HCl .

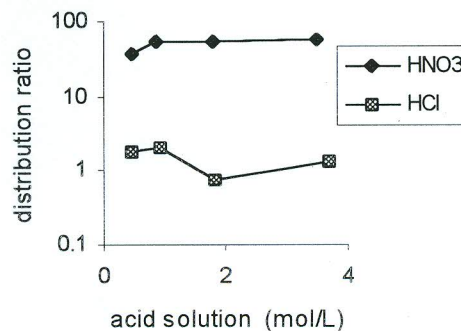


Fig. 2. Ce(III) distribution on CMPO-TBP/XAD7 in HNO_3 and HCl .

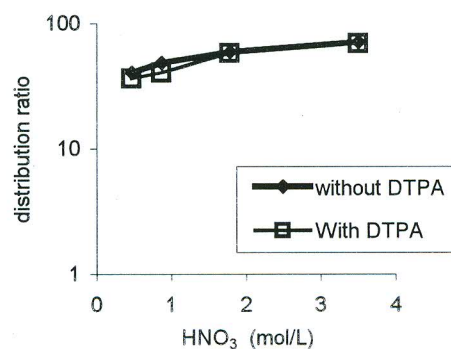


Fig. 3. The influence of DTPA on Eu(III) distribution in CMPO-TBP/XAD7- HNO_3 system. DTPA=0.001 mol/L.

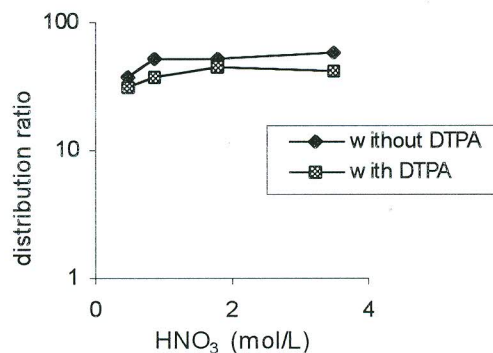


Fig. 4. The influence of DTPA on Ce(III) distribution in CMPO-TBP/XAD7- HNO_3 system. DTPA=0.001 mol/L.

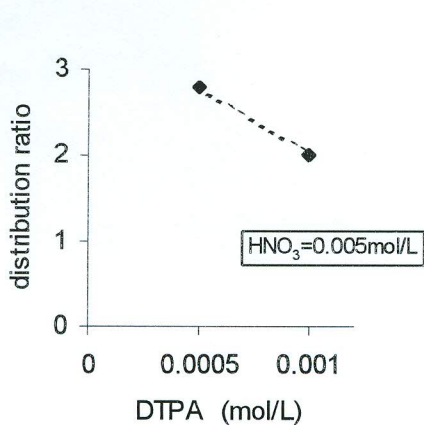


Fig. 5. Eu(III) distribution on CMPO-TBP/XAD7 in DTPA solution.

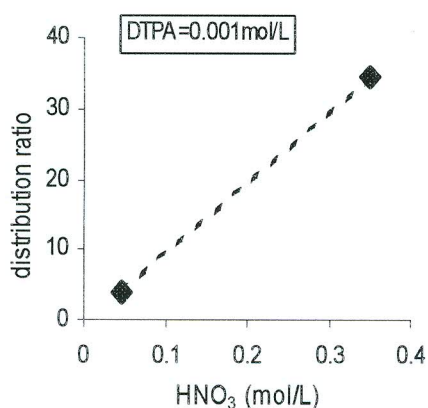


Fig. 6. Eu(III) distribution on CMPO-TBP/XAD7 in HNO₃/DTPA solution.

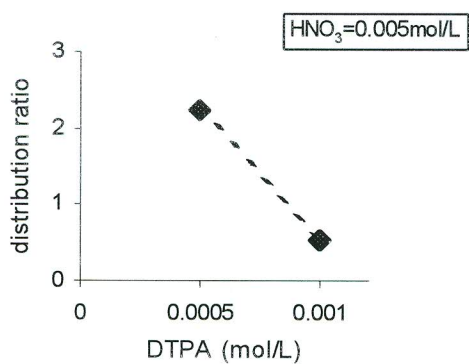


Fig. 7. Ce(III) distribution on CMPO-TBP/XAD7 in DTPA solution.

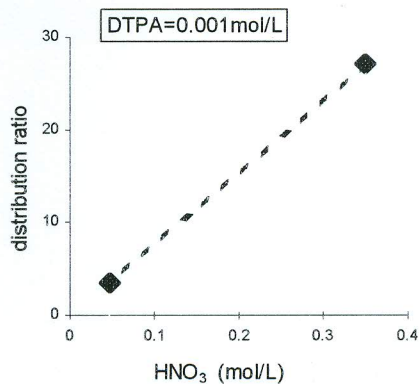


Fig. 8. Ce(III) distribution on CMPO-TBP/XAD7 in HNO₃/DTPA solution.

The same studies were done for more two complexants, oxalic acid and EDTA. In 0.01 mol/L HNO₃ medium, Eu(III) is well complexed by both complexants and presents lower distribution ratio as given in Fig. 9.

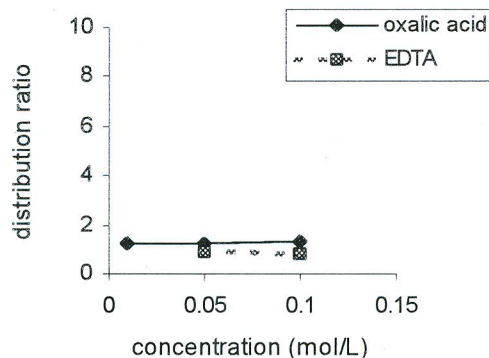


Fig. 9. Distribution of Eu(III) in oxalic acid/HNO₃ and EDTA/HNO₃ solutions. HNO₃=0.01 mol/L.

3.2. Retention and elution behavior of Eu(III) and Ce(III) ions

In this experiment, 4 mL of 1.5×10^{-4} mol/L Ce(NO₃)₃ in 4 mol/L HNO₃ solution was passed through the 37 wt.% CMPO-TBP/XAD7 column. The loaded resin was washed with 3 mL of 4 mol/L HNO₃ and then eluted with 3 mol/L HCl. The same experiment was carried out with 2.0×10^{-6} mol/L Eu(NO₃)₃ in 4 mol/L HNO₃ solution and loaded Eu was eluted with 3.7 mol/L HCl solution. The results are reported in Fig. 10. More than 99% retention with 0.9% lost during column washing step and 94.5% recovery of sorbed cerium(III) were obtained. Concerning to europium behavior, 100% retention and 98.6% recovery of sorbed Eu(III) was achieved.

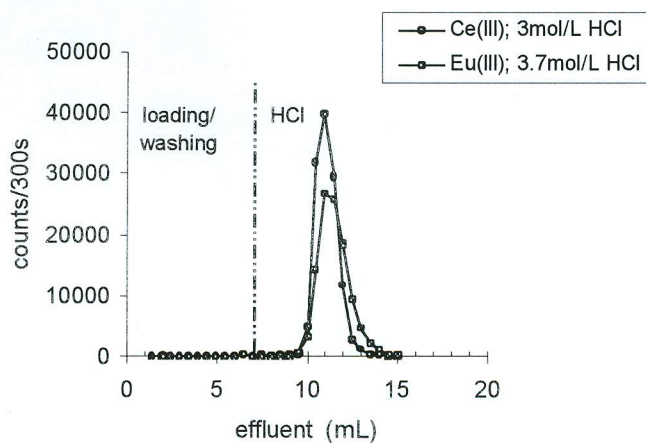


Fig. 10. Ce(III) and Eu(III) elution from CMPO-TBP/XAD7 column with HCl.

4. Conclusion

Extraction chromatography system composed with CMPO-TBP mixture impregnated in Amberlite XAD7 resin as stationary phase can be used to separate lanthanides from nitric acid solutions and to recovery by eluting the column with HCl. The lanthanides, here represented by Eu and Ce, as fission products can be isolated from liquid radioactive waste and separated from tetra and hexavalent actinides, normally present in trace level in this type of nuclear effluent.

Acknowledgement

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References

- [1] M. Yamaura, H. T. Matsuda, *J. Radioanal. Nucl. Chem.*, 224 (1997) 83.
- [2] M. C. F. C. Felinto, H. T. Matsuda, M. Yamaura, *Proc. of Reunião Anual da Sociedade Brasileira de Química*, 18, Caxambú, BR, May 30-Jun. 2 (1995).
- [3] E.P. Horwitz, R. Chiarizia, M.L. Dietz, H. Diamond, *Analytica Chimica Acta*, 281 (1993) 361.
- [4] M. Yamaura, H. T. Matsuda, *J. Radioanal. Nucl. Chem.*, 241 (1999) 277.
- [5] T. Braun, G. Ghersini, *Journal of Chromatography Library*, v.2 (1975).