

SEPARATION OF RARE EARTH BY COLUMN CHROMATOGRAPHY USING ORGANIC RESINS XAD / DEPHA

J.Zini¹, J.C.Ferreira^{*1}, V.S.Bergamaschi¹, I.Santos¹, F.M.S.Carvalho¹

Instituto de Pesquisas Energéticas e Nucleares,

Av. Professor Lineu Prestes 2242, Cidade Universitária, São Paulo-SP, CEP 05508-900. Brasil.

1 - Centro de Células a Combustível e Hidrogênio CCCH – IPEN/CNEN

** E-mail: jcferrei@ipen.br*

ABSTRACT

The designation of light and heavy rare earth was used the fractionation used in separation processes. In this study the process of separation of rare earth, in groups, by chromatographic column consisting in fixing of cations these elements in an organic resin Amberlite XAD16 functionalized with the extracting agent DEPHA and another portion functionalized with a mixture of extractors DEPHA / TOP . The preparation of these resins was performed in two forms, one directly as the extracting agent to the resin and the other to be used in ethyl alcohol. Conditioned resins were introduced in chromatographic columns in separation of groups, light and heavy, using a standard solution of cerium nitrate and standard solution of holmium nitrate groups to represent light and heavy respectively. The characterization technique used to identify the rare earth elements was Spectrometry X-Ray Fluorescence (XRF). The results using the technique of chromatography were satisfactory, obtaining 100% separation of the elements.

1. INTRODUCTION

In recent years the extraction chromatography technique has been widely used, due to the arising of a large number of new resins, thus providing several extractions techniques with high purity, even if in the case of trace elements present in the samples.

Extraction chromatography works basically the same way as the solvent extraction. Such methods are employed when the elements to be separated have much similarity in their chemical properties and a simple precipitation, or crystallization, do not provide the sufficient degree of separation required [1.2].

The great advantage of extraction chromatography is in the choice of the stationary phase, each of which has characteristic properties, in order to allow for the resolution of a large number of problems.

Rare earth elements are currently of great interest, due to the rapid technological development, especially when it comes to cutting edge technology, where these elements are widely used. With a brief literature review are over two thousand and four hundred works, in the last ten years, fractionation of rare earths, with the most diverse techniques and media [3].

The di (2-ethylhexyl) phosphoric acid, known as D2HEPA or DEHPA, dialkylphosphoric acid extractor is an agent used in the field of liquid-liquid extraction, for separation of rare earth, due to potential availability in large quantities, low cost and ability to extract.

Amberlite XAD16 resins are polymeric adsorbents in the form of insoluble white balls, reticular, non-ionic polymers and hydrophobic, which has its adsorptivas properties derived from the patented reticular macro structure (containing both the polymer phase and the solid porous phase), with high surface area and aromatic in nature.

Amberlite XAD resins have been physically or chemically modified with various binders, to prepare new chelating resins, and so extensively exploited for the pre-merger and/or separation of metals [4]. Its main attractive features are: easy multiple regeneration sorption-desorption cycles; chemical stability; reproducible sorption characteristics; selectivity; mechanical stability and good pre-merger factor [4.5].

Matsunga et al [6] impregnated different amounts of reagent 2-ethylhexyl 2-ethylhexyl phosphonate hydrogen (PC88A) Amberlite XAD resins in several (XAD2, XAD4, XAD7 and XAD16), and studied the extraction of rare earth elements on these systems. Between the amounts of reactants impregnated in resins, which featured best result was 50% of impregnation.

Choi et al [7] used XAD16 resins impregnated with phosphonic acid, 2-ethylhexyl mono-2-ethylhexyl ester (PC88A) to eliminate impurities (Ag, B, Cd, Dy, I and Sm) in array of Gd, Gd and Sm are eluted with HNO_3 0, 3 mol.L⁻¹, separating them from other impurities which are eluted with HNO_3 0,1 mol.L⁻¹. The recovery reached to Ag, B and Cd was 90-104%, while for me, Gd and Sm was 100-102%.

Sun et al [8], Amberlite resin XAD7 functionalize with Cyanex 923 and then impregnated with an ionic liquid in order to improve the extraction of rare earths. Observed that the addition of this Ionic Liquid (1-Octyl-3-metilimidazolhexafluorofosfato ([C8mim] [AF6])) there is the contribution to the efficiency of mass transfer, i.e. decreases the equilibrium time 40 to 20 minutes, increasing the efficiency of extraction of 29 to 80%. This resin still separated Y (III) of Sc (III), Ho (III) (III), Er and Yb (III), by adding a complexing agent in water soluble elution procedure.

Shibata et al [9], have thinned out the extractor agent PC-88A in chloroform and Amberlite resin mixed with XAD7 in a evaporator route to 100° c. The resins were later treated with sodium lauryl ether sulphonate 0.1% for the present material hydrophilic character. Studied so the separation of Dy, Y, Tm and Yb of a residue containing Tb, Dy, Ho, Er, Tm, Y and Yb in hydrochloric medium. The sorption of rare earths occurs at pH 0 to 2, where they observed that the sorption curves vs. pH are very closed, hampered the separation, which was made gradually changing the concentration of hydrochloric acid that was used as the eluent. In a single cycle were obtained the following values: Dy-94.3%; Y – 82.4%; Tm-99.7%, and Yb-99.9%.

El-Sofany [10] XAD4 Amberlite resin was impregnated with Aliquat 336-to remove La (III) and Gd (III) 0, nitric acid 1mol solution.L⁻¹. With all the optimized conditions, resin's ability for La (III) and Gd (III) was 4.73 and 4.44 mg. g⁻¹ resin, respectively.

Must et al [11] studied the complexing properties (capacity, effect of pH, breaking curve) Amberlite resin XAD4 up with bicina (N-N-bis (2-hydroxyethyl) glycine), to La (III) ions, Nd (III), Tb (III), (IV) and U (VI). Trace amounts of these metals were quantitatively retained in the resin and recovered by Elution with 1mol. L⁻¹ hydrochloric acid achieving separation of U (VI) and Th (IV) Ni (II), Zn (II), (II) and Cu (II) synthetic solutions. The capacity of functionalized resins were, to La (III), Nd (III), Tb (III), (IV) and (VI) of 0.35, 0.40, 0.42, and 0.38 0.25 mmol g⁻¹ resin, respectively.

Benamor et al [12] have studied the extraction of cadmium ions in Amberlite XAD7 supported with DEHPA. Studies have shown that the impregnation of the extractor agent varies significantly with the hydrophobicity of the solvent used in this procedure. The extraction experiments were started by varying the initial pH of 2.5 to 4, the cadmium ion concentration of 10 to 150 ppm and the amount of resin supported on DEHPA 0.84 to 1.55 mmol g⁻¹. The authors found that the best pH value for extraction was equal to 4. Up to the maximum concentration of 150 ppm extraction continues with the same behavior than when using dilute solutions, regardless of the amount of resin supported extractor agent.

Masi and Olsina [13] pré-concentraram lanthanum and cerium, praseodymium in two different solvent impregnated resins: Amberlite XAD4 with 8-Quinolinol (oxine) and Amberlite XAD7 with 2-(2-(5cloroperidilazo)-5-dimethylamino)-phenol. After the retention of rare earths, the resins were directly analyzed by x-ray fluorescence. The pH values from which the elements are best retained are 8, 9 and 7.5 for lanthanum and cerium, praseodymium respectively. Found that under these conditions, 10 mg of resin (both) absorb 50 ppm of each element.

Kaur and Agrawal [14] synthesized a new chelating agent, bis [2-(O-carbometoxi) phenoxy] ethylamine and Amberlite XAD4 resins and advorveram in these studied sorption and chromatographic separation of pairs (III), Nd (III) and Nd (III), Sm (III). The authors observed that Sorption is heavily dependent on the pH of the solution being the best value of 5.5. Elution was performed with 2 mol HCl solution.L⁻¹. The total capacity of sorption of metal ions by functionalized, studied in *bach's* method was 1, 84 mmol g⁻¹. Have a good separation of the factor pairs studied, using different electrolytes and keeping the flow of columns in 0, 25 mL.min⁻¹.

2. METHODOLOGY

The materials and reagents used in this work were: chromatographic columns of glass, 25 cm tall and 1 cm in diameter. Polymer resin Amberlite XAD16; di (2-ethylhexyl) phosphoric acid (DEHPA), Sigma Chemical Company, USA; Cerium nitrate standard solution, obtained by dissolution of salt CeNO₃.6 H₂O of Acros Organics, New Jersey, USA, with distilled water. Holmium nitrate standard solution obtained by dissolving of the Ho₂O₃, assigned by the center of chemistry and environment/IPEN; Other reagents used were of analytical grade of Merck, Sigma, Carlo Erba, J.T. Backer, Synth, Nuclear, chemical kinetics, Vetec, CAAL and Reactif.

In this work we used the organic DEHPA extractors/TOPO. These were functionalized in resin XAD-16. These resins were prepared in two different ways, by contacting directly the extracting agent in resin and another the extractor agent was mixed with ethyl alcohol and then there was the contactation with the resin. These two different techniques were performed to study the adsorption efficiency Extractor agent in resins and its influence on extraction. After contactation and manual agitation, the resins were dried at room temperature. The containing ethanol, this was evaporated in its entirety, and should result in a more uniform coating of polymer resin.

The amount of resin impregnated extractor agent was calculated by the difference in weight of resins, before and after functionalization. The characterization was made by infrared spectrometry.

Were used in each experiment 10 ml of Amberlite XAD16 resin functionalized with DEHPA.

The solutions used were the same as those for the three chromatographic columns: cerium nitrate standard solution and holmium $0,1 \text{ mol.L}^{-1}$ at pH 3.5 (load); in the procedure of washing of columns after percolating bi-distilled water was used; Elution was used in nitric acid solutions with different pH values.

The volume of effluent charge in all experiments was 5 ml, 5 ml were used in the washing of bi-distilled water and cerium Elution procedure, necessary volumes were used for Elution was complete, making the control with oxalic acid test.

The solutions obtained from all the experiments focused on rare earths, had their pH adjusted to 1 and were precipitated with oxalic acid 15% under slow agitation and heating. After cooling the precipitate was kept in ice bath, to better training of the crystals [15]. The precipitate was separated into filter paper and then calcined in muffle furnace at temperatures $\geq 800^\circ \text{ C}$ for 3:0, thus obtaining the analysis of oxide x-ray fluorescence.

3. RESULTS AND DISCUSSION

During percolation, columns with functionalized resins with DEHPA extracted all the load solution cerium; percolate more solution to saturate the columns for the determination of cerium retention in these columns.

In the procedure of washing of columns, it was observed the presence of a very small amount of cerium, thus demonstrating that the element has not been eluted by water, but only removes the amount that was impregnated in the chromatographic bed.

To elute the cerium compounds extracted by the columns chosen initially, a nitric acid solution of pH 1.5, because in liquid-liquid extraction this is the pH used for reversal of cerium, being that the Group of heavy lanthanides elements is eluted in pH. However not managed to the elution of cerium in this pH.

It was used, then nitric acid solutions at lower pH. At pH 0.77 some cerium was eluted, the same happening with 0.3 pH solutions. Even in nitric acid solutions with pH 0.15 cerium continued, yet, being eluted from the column. In table 10 presents the ratio of amount of cerium recovered by resins prepared differently, keeping all other conditions the same.

Table 1: Cerium extracted by chromatographic systems Amberlite XAD16 / (1) DEHPA, (2) prepared in ethanol DEHPA

chromatographic system	Ce mg / g functionalized resin
XAD16 functionalized directly com	
DEHPA	8,26
XAD16 functionalized with DEHPA	
through ethanol	8,79

The amount of cycle's studies operated by columns, during the percolation detected-if the output of the cerium, with tests performed with oxalic acid, as the first drops of effluent in both columns, demonstrating that reuse the same chromatographic column for a new procedure no longer shows.

After the end of the second cycle, the resins of the columns were removed, dried and weighed in order to verify that there was loss of the extractor agent. The weights remained virtually the same, with no significant loss of mass. A likely scenario was that the nitric acid, in the first cycle, has caused some degradation in DEHPA Extractor agent.

To elucidate this question, a sample of this resin was analyzed via infrared spectrometry, before and after its use. The spectra are shown in Figure 1.

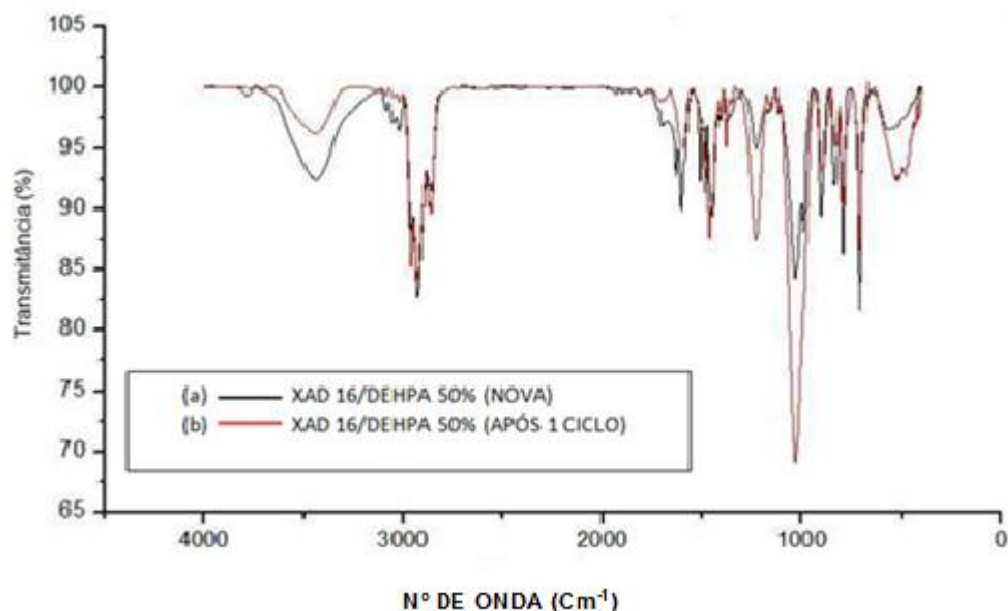


Figure 1: Spectrum obtained by infrared spectrometry XAD16/DEHPA50% Amberlite resins (a) before use (b) be used after

By spectra obtained via infrared it is seen that the bands of the functional groups are the same, showing that there was no change in the chromatographic material.

There was also the desorption of the extractor, agent in an aliquot of resin, with ethyl alcohol. The solution was then analyzed by gas chromatography and mass spectrometry (GC-MS), the mass spectra and chromatograms are shown in Figure 2.

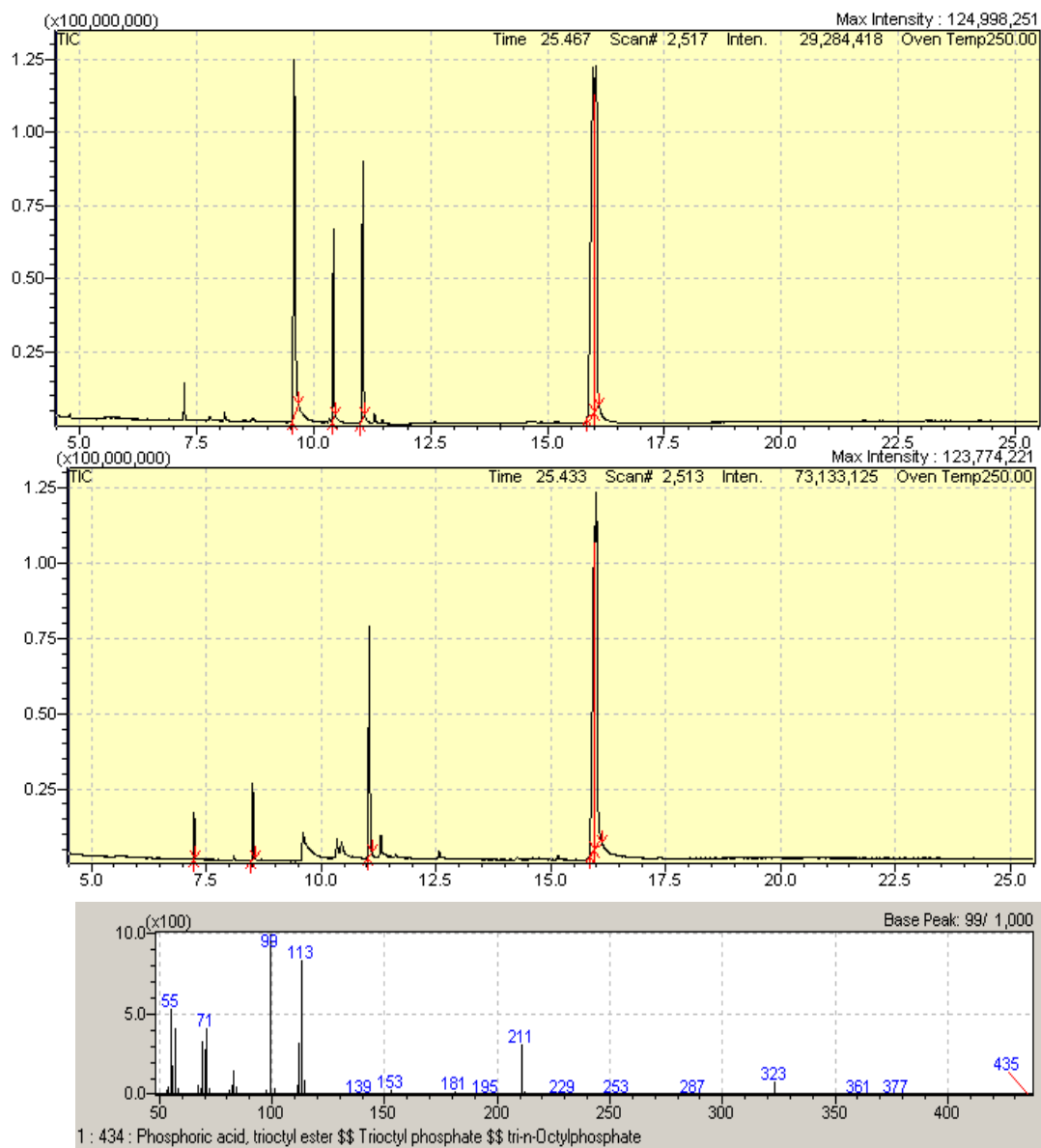


Figure 2 - Analysis by GC-MS DEHPA extractor agent (a) new extractor agent chromatogram; (b) the chromatogram of the same extractor agent once used in a cycle in the extraction chromatography; (c) mass spectrum of the eluted with more intense peak with retention time of 16 min

In the chromatograms note that DEHPA compound is eluted with retention time of 16 minutes. This molecular identity is confirmed by mass spectrometry, using the technique of electron impact ionization with 70 eV energy, getting the molecule ion fragmentation that compared with the NIST mass spectra library (National Institute for Standards and Technology) identifies as the di (2-ethylhexyl) phosphoric acid (DEHPA).

It is observed that the compound is present in the analysis entirely DEHPA of extractor agent after its use. The difference between the two spectra obtained is the presence of impurities in the extractor when new agent. However, who commands the extraction is the DEHPA and not the impurities do not justify the loss of system extraction from the second cycle. In this way it is necessary a deeper study to find the explanation for this behavior.

3.2 Standard Holmium

Prepared a solution of holmium, representing the heavy rare earths, in the midst of nitric acid at pH 3.5. All experimental parameters were identical to those used for cerium. Low extraction was observed of this element in the XAD16/50% DEHPA resins with and without contactation with ethanol, chosen because they were the best retained the cerium, by testing with oxalic acid. During washing with bi-distilled water no Elution of holmium. In the intervals of pH studied for Elution, this starts to be efficient in nitric acid below pH 0.5. The amount of holmium eluted was not enough to determine it by the gravimetric method.

Also in these experiments was obtained only in the first cycle retention percolation on resins.

4. CONCLUSION

The extraction system studied, Amberlite XAD16/DEHPA, proved attractive for extraction of rare earths and the possible separation of light fractions of heavy, since the system was not attractive to the retention of heavy rare earths. It was observed that the behavior of rare earth elements in liquid-liquid extraction with DEHPA is quite different than when the same Extractor agent is adsorbed on polymeric support. Further studies are needed to evaluate the behavior of this chromatographic system in the fractionation of rare earth elements and compare it with other methods already studied at IPEN.

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