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**SEPARATION OF LANTHANIDE ELEMENTS FROM ACIDIC MEDIA BY  
EXTRACTION CHROMATOGRAPHY USING MIXTURES OF  
 $\beta$ -DIKETONE (HTTA) AND RELATED CROWN ETHER SUPPORTED ON  
AMBERLITE XAD # 7 RESIN**

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**Abstract**

We have study the behavior of a new chromatographic material that uses a mixture of  $\beta$ -diketone, thenoyltrifluoroacetone (HTTA) and dicyclohexane-18-crown-6 (DCH18C6) sorbed on Amberlite XAD#7 in the extraction of Pr(III), Nd(III) and Eu(III) ions utilizing batch technique. The extraction parameters studied include the complex formation kinetics into the organic phase, media variations (acidic range and counter ion) and the influence of HTTA as a synergistic agent.

*Keywords:* Lanthanide ions; Crown ether; Extraction chromatography; Thenoyltrifluoroacetone; Synergistic extraction

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**1 INTRODUCTION**

The interest for rare earth elements has been growing in the last years due the development of the technology of extraction by solvents that formed an alliance with the extraction chromatography, which facilitated the attainment of enough amounts of those elements with high purity. This fact allowed the identification of its properties and made possible its use in several commercial applications like the aerospace, automotive, electronics and metallurgy industries, associated to advanced technologies as superconductors, ceramic materials, laser, special glasses, catalysts, alloys, magnetos and several other use.

Macrocyclic crown ethers have unique complexation properties for metals ions, that is, the size selectivity originated from the correct fit of metal ion into the cavity of crown ether[1-3]. This property of crown ethers renders them attractive as size-selectivity extractants for the extraction separation of a series of metal ions such as alkalis, alkaline earths and probably rare earths. It was found that formation of metal complexes is at maximum when the size of cavity of crown ether corresponds to the size of metal ion[1-4]. However only limited investigations have been reported on the extraction of lanthanides by crown compounds [5-10].

The high degree of selectivity of the " crown ether" favors them the capacity to enrich, to separate and to determine the concentrations of the metals that stay in them. These

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compositions have been showing plenty effective in the separation of alkaline, alkaline-earth metals and, when combined with  $\beta$ -diketones, rare earth and actinides.

For an other hand Extractant - chromatographic resins (CRs) have been shown to be effective media for the separation and recovery of species from diluted solutions, preconcentration of species in bioassay samples and environment samples. The CRs bridge the gap between solvent extraction and resin ion exchange processes[11]. They combine not only the advantages of resin ion - exchange for processing very diluted liquors with the specific properties of extractants, but also the high distribution ratio and selectivity characteristic of the extractants dissolved in a liquid organic phase with the simplicity of equipment and operation characteristic of solid ion - exchange technology.

A significant number of studies on the sorption and separation of metal ion with CRs have been carried out [12-22]. The impregnated extractants include acidic and neutral organophosphorus compounds like di (2- ethyl-hexyl) phosphoric acid, 2-ethylhexylphosphonic acid [12] bifunctional carbamoylmethylphosphonate [13] bifunctional carbamoylmethylphosphine oxide[14-15], etc. Also some extractants such as tri-n-octylamine [16], quaternary alkyl ammonium salts[17], hydroxyquinoline [19] and crown ethers[18] have often been adopted.

Among of these new classes of extractants the dicyclohexane 18crown 6 (DCH18C6) was selected as an extractor agent for the rare earth elements because its known affinity and selectivity together with HTTA for these elements.

The aim of this work is study the behavior of the new chromatography materials named Lanthanide Spec 1 (50% w/w 0.1MDCH18C6 in octhanol sorbed on Amberlite XAD#7) and Synergic Lanthanide Spec 1 (50% w/w 0.1 M DCH18C6 + 0.1M HTTA) sorbed on Amberlite XAD#7 ) in the extraction of lanthanide elements ( $\text{Pr}^{3+}$   $\text{Nd}^{3+}$  and  $\text{Eu}^{3+}$  )

## INSERT FIG 1

## 2 EXPERIMENTAL

### 2.1 Apparatus:

An UV- visible spectrophotometer CARY I with 10nm matched quartz cells were used for spectral measurements.

### 2.2 Reagents

Dicyclohexano 18-crown-6 and thenoyltrifluoroacetone were obtained from Aldrich. Amberlite XAD#7 support was Rohn and Haas. Nitric and hydrochloric acid solutions were prepared from Merck reagents. Water was deionized water and all other materials were ACS reagent grade and were used as received. The lanthanide solutions were obtained by dissolution of their oxides,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$ .

### 2.3 Procedures

2.3.1 *Preparation of extraction chromatographic resins.* The extraction chromatographic resins were prepared by impregnating Amberlite XAD#7 (5 grams) with the solutions described on table 1 The Amberlite XAD#7 requires treatment to remove traces of preservatives and unreacted monomer prior to impregnation, however [23].

#### INSERT TABLE 1

2.3.2 *Determination of the percent extraction (%E) and the weight distribution ratios of praseodymium neodymium and europium ( $D_{w_{Ln^{3+}}}$ ).* The sorption of lanthanide ions by resins from nitric and hydrochloric acid solutions was measured by contacting a know volume (usually 1mL) of a solution held the metal of appropriated concentration with a known weight of resin in a vial. The exact ratio of aqueous phase volume (mL) to resin weight (g) was varied as necessary to produce a measurable decrease in the concentration of metal ions in aqueous solution by a single contact with the resin. The mixing of the resin and each aqueous phase was performed using a Downer Mix. The stirring rate was chosen to produce a suspension of the resin in aqueous phase. The percent uptakes (%E) of  $Ln^{3+}$  by the resins were calculated from the following equation:

$$\%E = [(C_b - C_a) / C_b] \times 100 \quad (1)$$

where  $C_b$  and  $C_a$  are the concentration off metal ion in the bulk solution and after extraction, respectively.

Weight distribution ratios ( $D_w$ ) were calculated from the following equation:

$$D_w = [(C_b - C_a) / C_a] \times [W/V] \quad (2)$$

where  $C_b$  and  $C_a$  are the concentration of metal ion before and after extraction, respectively,  $W$  is the weight of resin (g) and  $V$  is the volume of aqueous phase (mL).

The separation factor is given by:

$$\alpha_{M1/M2} = D_{w_{MI}} / D_{w_{MII}} \quad (3)$$

where MI and MII are two different metals in the same extraction conditions.

The synergistic factor (S.F.) is defined as bellow:

$$S.F. = D_{w_{syn}} / (D_{w_{HTTA}} + D_{w_{CE}}) \quad (4)$$

where  $D_{w_{syn}}$  is the weight distribution ratio of the metal in the mixture resin,  $D_{w_{HTTA}}$  is the weight distribution ratio of the metal in the resin impregnated with HTTA and  $D_{w_{CE}}$  is the weight distribution ratio of the metal in the resin impregnated with crow ether only.

2.3.3 *Analysis* The  $Ln^{3+}$  concentrations in the aqueous phase were measured in spectrophotometer using an Alizarin red S method [24].

### 3 RESULTS AND DISCUSSION.

**3.1 Selection of a support material.** A wide variety of supports, both inorganic and organic, have been employed for extraction chromatography [25]. In a comparison of the absorption capacities of several types of support materials (eg: porous glass, polyethylene, styrene-DVB copolymers), Warshawsky and Patchornik [26] have demonstrated in their work that polymeric sorbents on Amberlite XAD series have excellent capacities for various extractants. In our previous work [27], we found that Amberlite XAD#7 holds three times more TBP than silica and alumina, yielding a more stable (to acid washing) impregnated resin. Amberlite XAD#7 appears to combine several essential features to a support in extraction chromatography: good capacity for extractant, acceptable kinetics and some resistance to extractant loss. For this reason, it was chosen for all the work described here.

### 3.2 Sorption capacity and weight distribution ratios ( $D_w$ ).

Figure 2a-d shows the extraction behavior of the lanthanides in two different acidic solutions. It was observed a similar behavior between the systems DCH18C6 and DCH18C6/HTTA in nitric acid solution, characterized by a maximum of extraction in  $[\text{HNO}_3] = 1\text{M}$ , followed by a decrease in the values of  $D_w$ . The decrease in the percent of retention that start at this point can be attributed to the increase of the ionic force of the acid solution. This fact is discussed by Gerow et al [3], and its attributed to the protonation of the crown ether, resulting in loss of availability of oxygen atoms as electrons donors, for the complexation (oxo-donors).

It becomes clear, for the other hand, that the use of a  $\beta$ -diketone in the system DCH18C6/HTTA is responsible for the formation of species ( $\text{Ln}^{3+}/\text{crown}/\text{quelante}$ ), species more extractable in the organic phase (synergism), evidenced by the increase in the values of  $D_w$  along the interval of acidity studied. This verification is reinforced by the results of Reddy et al[4], where demonstrated that neglected extraction of lanthanides with crown ether in chloroform are drastically reinforced by the addition of a  $\beta$ -diketone (3-fenil-4-benzoil-5-isoxazolona) in the system.

In relation to the stoichiometry of the obtained complexes, Shehata et al[5], studying the liquid-liquid extraction of lanthanides in nitric acid solution, using a mixture of HTTA with crown ether obtained, for the complex metal-HTTA, the following relationship  $\text{Ln}(\text{NO}_3)(\text{TTA})_2\text{HTTA}$  and, for the species metal-HTTA-crown ether the stoichiometry  $\text{Ln}(\text{NO}_3)(\text{TTA})_2\text{CE}$ . These results indicate that, for high ionic strength of the ion nitrate ( $\mu \geq 0,2$ ), this anion participates in the extraction process. El-Reefy et al [6], in parallel study, demonstrated that, in low concentrations of the nitrate ion ( $\mu \leq 0,1$ ), the extracted species do not present  $\text{NO}_3^-$  in its composition in the extraction of  $\text{Eu}^{3+}$  by HTTA alone or in mixture with soft donor ligand, as trifenilamine, trifenilarsine and trifenilfosfine. The lanthanide extraction in hydrochloric acid was shown quite difference in relation to the use of a  $\beta$ -diketone (HTTA) in presence of DCH18C6. The analysis of simple system crown ether / supports (Figure 2-c) indicates a growing tendency of the extraction in relation to the increase of acidity, being demonstrated a maximum of retention in  $[\text{HCl}] = 7\text{M}$ . It is noticed, for the interval of analytic concentration of 1 to 7 M, that the distribution ratios of extraction maintains the order  $D_{\text{Nd}} > D_{\text{Pr}} > D_{\text{Eu}}$ , for both studied systems.

In agreement with the figure 2c-d, a decreasing tendency in europium extraction is observed in relation to the chromatographic material DCH18C6/HTTA as function of the increase of the acidity. The behavior of the other lanthanides (Pr and Nd), however, converge for two isolated picks of extraction, in  $[HCl] = 1,5M$  (Nd) and  $[HCl] = 3M$  (Pr), followed by an abrupt decrease in its distribution ratios. The presence of maximums of extraction, in both systems, and independent of the against-ion ( $NO_3^-$  or  $Cl^-$ ), that is quite desirable of the point of view of the back extraction of the metal from the organic phase to aqueous phase.

The obtained results ( $D_w$ s 20 to 80 mL.g-1) in the tests here accomplished, however, they offer an alternative one quite promising in relation to the waste processing (of nitric composition) or industrial hazardous waste that contain those ions, without the needed to increase the complexity of the composition of the stationary phase of the chromatographic materials.

### 3.3 Time dependence of complexation rate.

To determine the rate of loading of lanthanide ions on the resin, batch experiments were carried out under the following conditions: 0.05g of resin beads was stirred with 1mL of feed solution containing lanthanide ions at room temperature ( $30^\circ C$ ). Aliquots of the solutions were taken out of analysis at predetermined intervals of time. The concentration of metal ions in the supernatant solution was determined and the amount of metal ions loaded on the resin phase was calculated by mass balance. The loading half time  $t_{1/2}$ , defined as the time needed to reach 50% of the resin's total lading capacity, was estimated by the experimental data to be less than 3 min. From the kinetics of lanthanide exchanger, it was observed that an equilibrium time less than 5 minutes was required for 90-100% sorption. The faster uptake of these metal ions on resin reflects a better accessibility of the metal ions to the crown ethers sites in the resin. The kinetics behavior was modeled according to a Michaelis-Menten hyperbola.

$$D_w = D_{w_{max}} (1/K+t) \quad (5)$$

where  $t$  is the time in minutes and  $D_w$  are the weight distribution ratios( L/g).

This fitting was done in origin 4.0 program that utilize the non-linear regression based on algorithm of Levenberg-Marquardt for minimize the total square error. The optimization of this parameter is made by a comparison of Chi-square distribution ( $\chi^2$ ), given an approach for random variable of the model in a confidence interval at about 95%. In table 2 there are the adjust parameters and the coefficient of correlation respectively.

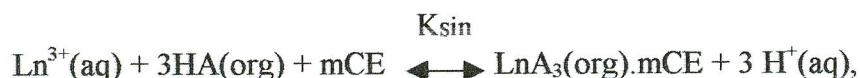
Figure 3 shows the behavior of the curves of europium ion. The other lanthanide ions follow the same comporment.

### INSERT FIGURE 3 AND TABLE 2

3.4 Separation factors. The table 3 illustrates the separation factors (SF) obtained for chromatographic material in relation to the selective extraction of lanthanides couple The separation factor is defined as mentioned above.

In agreement with these data a quite significant gain is observed in the selectivity of the system DCH18C6, expressed in terms of the separation factor, for the pair Pr/Eu in nitric acid solution. The same phenomenon repeats for equal Nd / Eu in presence of HCl for high values of acidity. The most expressive results are for Pr/Nd couple (in a low concentration of hydrochloric acid, by virtue of the proximity of its ionic rays), of difficult separation, in the interval of  $[HCl] = 0,05M$  the  $[HCl] = 3M$ , with potentials application in separation of an effluent contends a mixture of  $Nd^{3+}$  and  $Pr^{3+}$ .

3.5 *Synergism* According to Reddy et al [4], the balance of extraction of trivalent lantanídeos with a quelante agent and crown compound can be expressed for:



where  $m=0, 1$  or  $2$ .

The same author, working with liquid-liquid extraction technique in presence of HPBI (3-fenyl-4-benzoyl-5-isoxazolone) in mixtures with some crown ethers, demonstrated that  $m$  is equal to 1, confirming the results of Ensor[7], Dukov[8], Shehata[5] and Thakur[9], that proposed stoiquimetry  $Ln(HTTA)_3.CE$  for the extracted complexes. The use of nitric acid, as already discussed previously, is supplies, however, the attainment of the adult  $Ln(NO_3)(TTA)_2.CE$ , identified by Shehata[5]. The generic expression of the synergistic compositions in the organic phase is characterized by the reaction:



where: A = counter-ion ( $TTA^-$ ,  $NO_3^-$ ,  $Cl^-$  or their mix );

CE = crown ether;

$\beta_m$  = the complex constant formation in the organic phase =  $K_{sin}/\beta_m$ ;

$m = 1$ .

To the analyze of table 4 it was identified synergistic behavior ( $SC > 0$ ) for both Pr ( $HNO_3$ ) and Nd ( $HNO_3$ ), while the europium extraction in a low hydrochloric acid concentration on the system DCH18C6/HTTA/XAD#7 it was revealed predominantly antagonistic ( $SC < 0$ ). This table also allows observing synergism in the recovery of Pr in low hydrochloric acid concentration. The formation of the chemical species responsible for the synergism involves the substitution of a HTTA molecule for a crown ether molecule. This displacement is explained by virtue of the structure with two molecules of the  $\beta$ -diketone to be more compact than the structure with 3 molecules coordinated of the counter-ion.

In agreement with Ramakrishna & Patil [28], both effects observed can happen in agreement with the experimental conditions imposed to the studied system. This becomes quite evident to the analyze of the results in table, where the system Eu/crown/HTTA is antagonistic for  $[HNO_3] < 0,5M$  and synergic for  $[HCl] > 0,5M$ . The same phenomenology is repeated for the neodymium in a low hydrochloric acid concentration.

The synergism described here it was verified systematically by Reddy et al [4] and Thakur[9-10] in its solvent extraction studies utilizing crown ethers (DCH18C6, DB18C6 and B15C5) mixed with  $\beta$ -diketone (HTTA, HPBI, HPMTFP, etc) in lanthanide and actinide extraction. This last author, confirmed, the non-uniformity in the interactions of the present oxygen atoms in the ring of the crown ether on the sphere of coordination of the metal. The spectra in the infrared and RMN in their work demonstrated that just three of the six oxygen atoms of the crown inter link more strongly with the cation.

#### 4 CONCLUSIONS

The main conclusions that can be drawn from the experimental work described here and future perspectives are as follows:

- The extraction equilibrium of trivalent lanthanides with Lanthanide Spec 1, Lanthanide Spec 2 and Synergic Lanthanide Spec 1 has been investigated. Synergic Lanthanide Spec 1 was found to be a powerful extractant for Ln(III).
- Absorption kinetic of lanthanides in these chromatographic materials was found to be fast allowing its fitting as hyperbole of Michaelis-Menten model.
- In order to explain the absorption behavior of lanthanide ions, further experiments to determine the absorption mechanism are required.
- To demonstrate the feasibility of mutual separation between lanthanides (III) and other elements applying these material further experiments are clearly necessary.

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Table 1 Chromatographic Materials

Chromatographic Material	Solution impregnated
Lanthanide Spec 1	0.1M DCH18C6 in n-octanol( 50 %w/w)
Lanthanide Spec 2	0.1M HTTA in n-octanol( 50 %w/w)
Synergic Lanthanide Spec 1	0.1M DCH18C6 + 0.1M HTTA in n-octanol ( 50 %w/w)

Table 2 Michaelis-Menten parameters for the adjust of extraction kinetics of  $\text{Eu}^{3+}$ .

SYSTEM	$D_{w_{\max}}$	K	Correlation factor
Lanthanide Spec 1/ $\text{HNO}_3$	2.28	1.08	0.94
Synergic Lanthanide Spec 1/ $\text{HNO}_3$	5.18	0.05	0.97
Lanthanide Spec 1/ $\text{HCl}$	6.89	0.34	0.93
Synergic Lanthanide Spec 1/ $\text{HCl}$	7.88	0.02	0.90

Table 3 The separation factors between MI/MII.

MI/MII	Acid medium	Concentration	Resin	$\alpha$
$\text{Pr}^{3+}/\text{Nd}^{3+}$	$\text{HNO}_3$	0.1	Lanthanide Spec 1	1.33
		0.1	Synergic Lanthanide Spec 1	2.80
	$\text{HCl}$	all	Lanthanide Spec 1	>1
		all	Synergic Lanthanide Spec 1	>1
$\text{Pr}^{3+}/\text{Eu}^{3+}$	$\text{HNO}_3$	all	Lanthanide Spec 1	>1
		all	Synergic Lanthanide Spec 1	>1
	$\text{HCl}$	0.5	Lanthanide Spec 1	1.00
		0.5	Synergic Lanthanide Spec 1	9.66
$\text{Nd}^{3+}/\text{Eu}^{3+}$	$\text{HNO}_3$	all	Lanthanide Spec 1	>1
		all	Synergic Lanthanide Spec 1	>1
	$\text{HCl}$	1.45	Lanthanide Spec 1	2.25
		1.45	Synergic Lanthanide Spec 1	3.53

Table 4 The synergistic extraction parameters.