

SOLVENT EXTRACTION OF THE LANTHANIDE ELEMENTS, SCANDIUM, URANIUM AND THORIUM USING TETRACYCLINE AS COMPLEXING AGENT*

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Hydrogen ion dependence and extractant dependence of the extraction of the lanthanide elements, scandium, uranium and thorium into a solution of tetracycline in benzyl alcohol have been determined. Possibility of using the tetracycline-benzyl alcohol system for separation of the lanthanide elements present in a mixture, as well as for the separation of uranium from those elements, was tested. In the first case discontinuous counter-current technique was used. In the second case a single step solvent extraction procedure was applied.

Introduction

Several analytical methods have been developed using tetracycline, aureomycin and terramycin as complexing agents for various cations.¹⁻⁴

One of the first applications of tetracycline for an analytical separation was a solvent extraction procedure presented by MASTERS⁵ for the determination of ⁹⁰Sr in environmental grass samples. MASTERS⁶ studied also the application of tetracycline for the extraction into benzyl alcohol of Ti, Sc, Fe, Ni, Y, Nb, Tl and Pb.

In a previous paper, NASTASI and LIMA⁷ have shown the formation of complexes between tetracycline and the lanthanide elements and scandium. In that paper they have presented the hydrogen ion dependence of the extraction of some of lanthanide elements, namely, La, Nd, Sm, Dy, Lu and Sc, as well as the extractant concentration dependence for La, Eu and Lu. The extraction system was a solution of tetracycline hydrochloride in benzyl alcohol. To show that the metal

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extracted into the benzyl alcohol phase was bonded to the tetracycline molecule, the radioactive lanthanide solution was contacted with pure benzyl alcohol at various pH values. No activity was detected in the organic phase showing that the extractable species was the lanthanide-tetracycline complex.

The scope of the present work was to extend the study of the solvent extraction behaviour to all the 15 lanthanide elements as well as to uranium and thorium and to study the application of the system tetracycline-benzyl alcohol for the separation of the mentioned elements.

The effect of the presence of a supporting electrolyte (NaCl) on the extraction as well as the effect of ageing of the extractant solution on its extractant properties were studied. The variation of distribution ratio with metal concentration was examined in order to verify whether or not polynuclear complexes were present in the conditions under which the work was performed.

Experimental

Preparation of solutions

Radioisotopes of the rare-earth elements, scandium and yttrium were obtained by thermal neutron irradiation of their respective oxides (BDH, 99.9% purity). 2–3 mg of each oxide were irradiated in a thermal neutron flux of about $5 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ for 30 min or for 8 hrs, depending on the half-life of the specific radioisotope considered. The oxides were dissolved in drops of hot HCl except in the case of CeO_2 in which it was necessary to use hot H_2SO_4 . The resulting sulfuric acid solution of cerium was passed through a bed of cation exchange resin and the cerium ions were eluted with 6N HCl solution. ^{147}Pm carrier free isotope was obtained from New England Nuclear (Boston, Mass.) and suitable aliquots of the original stock solution were diluted with 0.1N HCl solution.^{2,3,4} The tracer used was separated from a solution of uranyl nitrate using the procedure described by PALOMARES and TRAVESI.⁸ The uranyl chloride solution was obtained by dissolving nuclear grade ammonium diuranate with concentrated HCl. Tetracycline hydrochloride (TC) (Laborerápica-Bristol) was dissolved in slightly warm (60 °C) benzyl alcohol (Carlo Erba, p.a.). The solution was cooled to room temperature and benzyl alcohol was added up to the desired concentration value.

Distribution ratio determinations

The metal ions concentration of each solution was equal to 10^{-5} M, except in the cases of promethium and thorium in which carrier free isotopes ^{147}Pm and ^{234}Th were used.

Determination of the distribution ratio, D , was carried out as follows: a 5.0 ml portion of the aqueous phase containing the nuclide under study was added to 5.0 ml of a 5.3M sodium chloride solution, so that the final ionic strength, μ , of the aqueous phase was $\mu = 0.9M$.

To the aqueous phase a 5.0 ml portion of the tetracycline - benzyl alcohol solution was added. After the addition of the organic phase the pH of the aqueous phase was adjusted by adding small volumes of 0.1N solutions of hydrochloric acid or sodium hydroxide. A Metrohm Herisau E 350B pH meter coupled to a Metrohm combined electrode was used to measure the pH values. Both phases were brought into contact by shaking for 15 min at room temperature. Previous experiments⁷ had shown that equilibrium was reached before this time. The phases were then allowed to settle, separated and each of them was centrifuged for 5 min. Aliquots of one milliliter of both phases were taken for counting using a single channel gamma-ray spectrometer coupled to a 5.08 · 4.45 cm NaI(Tl) well-type scintillation detector. In the case of ^{147}Pm the activity was measured using a proportional gas flow counter. Uranium concentrations in the various extracted solutions were determined by epithermal neutron activation analysis, following the technique presented by ATALLA and LIMA.⁹

The dependence of the extraction on the hydrogen ion concentration was studied between pH 1.50 and 3.50 for the lanthanides and between 0.50 and 2.00 for Sc, Y and Th (Fig. 1). The initial tetracycline concentration in the organic phase was equal to $10^{-2}M$. The extractant dependence was studied for a tetracycline concentration range varying from $1.25 \cdot 10^{-3}M$ to $20.0 \cdot 10^{-3}M$. In this case the pH value which each set of experiments for a specific lanthanide was carried out was held constant, Table 1.

Table 1
pH values at which extractant dependence was studied

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
3.00	3.00	3.05	2.80	2.80	2.50	2.45	2.50	2.40	2.30	2.40	2.35	2.40	2.40	2.30

In order to verify the influence of addition of an electrolyte solution into the extraction system, the percentage of metal extracted was determined for systems with and without NaCl. The pH of the aqueous phase in both experiments was the same as well as the extractant concentration ($10^{-2}M$) (Table 2).

Aqueous solutions of tetracycline are not stable but its solutions in benzyl alcohol are effective as extractant for a rather long time, as shown in Table 3. The

Table 2
Percent europium extracted (%E)
In the presence or absence of sodium chloride

pH	%E	
	NaCl 0.9M	No NaCl
2.20	14.0	0.5
2.40	32.5	1.5
2.60	65.0	5.0
2.80	86.0	10.6

Concentration of tetracycline solution: 10^{-2} M.

Concentration of europium solution: 10^{-5} M.

Table 3
Effect of ageing of the tetracycline-benzyl
alcohol solution on its extracting properties, for a terbium solution

Time, days	1	3	9	11	18
%E	62.1	65.3	65.7	62.6	65.2

Concentration of tetracycline solution: 10^{-2} M.

Concentration of terbium solution: 10^{-5} M.

Ionic strength (NaCl): 0.9M.

partition experiments were carried out at a pH value equal to 2.50 using ^{160}Tb as tracer. The tetracycline solution concentration was equal to 10^{-2} M.

Eventual formation of polynuclear complexes was studied by determining the distribution ratio as a function of pH for three different initial lanthanum concentrations, namely $1 \cdot 10^{-5}$ M, $5 \cdot 10^{-5}$ M and $10 \cdot 10^{-5}$ M, and a constant TC concentration (10^{-2} M), Table 4.

Separation studies

Lanthanide elements separation. Multiple extraction procedures are, in general, required for separation of closely related substances such as the lanthanide elements. Two different mixtures of lanthanide elements were chosen to study the separation of the lanthanides using the system tetracycline – benzyl alcohol: a mixture of La and Tm and a mixture of Pr, Eu and Yb.

Table 4

Distribution ratio values as a function of metal concentration, for the case of La-TC complex

pH	lg D		
	$1 \cdot 10^{-5} \text{ M}^*$	$5 \cdot 10^{-5} \text{ M}^*$	$10 \cdot 10^{-5} \text{ M}^*$
2.001	-2.49051	-2.5259	-2.3643
2.15	-2.1260	-2.1389	-2.1008
2.30	-1.7474	-1.7709	-1.7238
2.40	-1.5346	-1.6105	-1.4547
2.50	-1.3380	-1.3321	-1.1671
2.65	-0.9842	-0.9927	-0.8301
2.80	-0.6700	-0.6702	-0.4047

*La concentration.

Tetracycline solution concentration: 10^{-2} M .

Ionic strength (NaCl): 0.9M.

For the La - Tm pair a 10-step extraction procedure was carried out, while for the Pr, Eu and Yb mixture a 23-step extraction was required. 50 ml of a $5 \cdot 10^{-5} \text{ M}$ aqueous metal ion solution (0.9M NaCl, pH 2.50), were shaken for 15 min with 50 ml of $1 \cdot 10^{-2} \text{ M}$ tetracycline - benzyl alcohol solution. The phases were allowed to settle, separated and the organic phase was transferred to the next separatory funnel. 50 ml of fresh organic solution of tetracycline were then added to funnel number zero and 50 ml of aqueous solution (0.9 NaCl, pH 2.50) to funnel number one and so on, until the final 10th or 23rd step was reached. In each funnel the phases were separated, centrifuged and aliquots of 2.0 ml of each phase were taken for determination of the radioactivities due to the radioisotopes ¹⁴⁰La, ¹⁷⁰Tm, ¹⁴²Pr, ¹⁵²Eu and ¹⁷⁵Yb. For these separation experiments as well as for the separation of uranium from fission products, to be described below, the counting-rates were determined using a 4096-channel Hewlett-Packard pulse height analyser coupled to a Ge(Li) detector (27 cm³).

Separation of irradiated uranium from some fission products. U₃O₈ was irradiated for 500 hrs in a thermal neutron flux of about $10^{12} \text{ n} \cdot \text{sec}^{-1} \cdot \text{cm}^{-2}$ and cooled for 10 months. The irradiated U₃O₈ was dissolved in concentrated hydrochloric acid and the uranium concentration was made equal to 10^{-5} M by dilution with a 0.9M NaCl solution. This solution was used to isolate uranium from the long-lived lanthanide fission products. The main gamma-ray emitters fission products, still present after a 10-month cooling time were ¹³⁷Cs, ⁹⁵Zr, ⁹⁵Nb, ¹⁰³Ru, ¹⁰⁶Ru.

^{141}Ce and ^{144}Ce . The pH of the aqueous phase was equal to 1.90 and the concentration of tetracycline in the organic phase 10^{-2}M . A single extraction step was used in this case. The uranium present in both phases was determined by using the epithermal neutron activation analysis method.⁹

Results and discussion

The presence of the supporting electrolyte, NaCl, at a concentration equal to 0.9M, greatly enhances the metal extraction at any given pH. This enhancement is shown in Table 2 for an experiment carried out using $^{152-154}\text{Eu}$ tracer.

The results of partition experiments carried out during 18 days, with the same 10^{-2}M stock solution of tetracycline hydrochloride in benzyl alcohol, have shown that this solution can be kept for this period of time without changing its extracting properties, Table 3.

Results of partition experiments carried out with three different concentrations of lanthanum tracer, namely $1 \cdot 10^{-5}\text{M}$, $5 \cdot 10^{-5}\text{M}$ and $10 \cdot 10^{-5}\text{M}$ are presented in Table 4. An "F" test applied to the data of Table 4 showed that the coefficients a and b for the three straight lines $\lg D = a \text{ pH} + b$ are the same, showing that no polynuclear complexes are formed for this metal concentration range.

Hydrogen ion dependence

Fig. 1 presents the extraction curves for thorium, uranium, scandium and the lanthanide elements, with the exception of gadolinium, erbium, holmium and lutetium, whose curves were too close apart to the curves for other lanthanides (Gd to Eu; Er and Ho to Dy; and Lu to Yb).

From the extraction curves it can be seen that separation of thorium, uranium and scandium from the lanthanide elements, can be achieved provided the extraction operation is carried out at a suitable pH value. Those curves show also that a single extraction operation is not enough to separate subsequent lanthanide elements one from the other, as is the general case for the lanthanide elements. In order to get this separation a multiple countercurrent extraction procedure has to be used.

Fig. 2 presents the variation of $\lg D$ as function of pH of the aqueous phase. From this figure it can be seen that it will be easier to get a separation between the members belonging to the group of the "light" lanthanides than between those of the "heavy" lanthanides group.

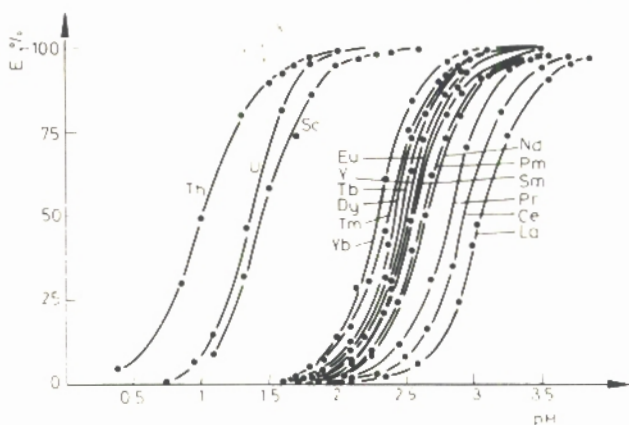


Fig. 1. Extraction curves for thorium, uranium, scandium and the lanthanide elements. Concentration of tetracycline solution: 10^{-2} M. Concentration of metal ions: 10^{-5} M. Ionic strength: 0.9M (NaCl)

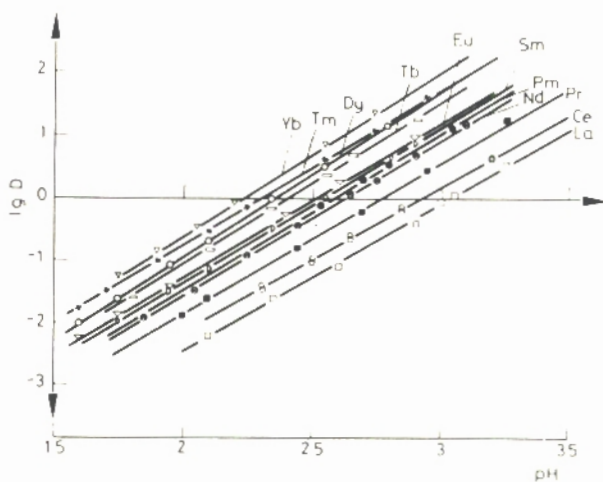


Fig. 2. pH dependence of the extraction of lanthanide ions into tetracycline-benzyl alcohol. Concentration of tetracycline solution: 10^{-2} M. Concentration of lanthanide ions: 10^{-5} M. Ionic strength: 0.9M (NaCl)

Extractant dependence

The least square method was used to determine the slopes of the plots $\lg D$ vs. tetracycline concentration for each of the lanthanides. The values obtained are shown in Table 5.

Table 5
Slopes of the lines: $\lg D = a' \lg(\text{TC}) + b'$ for the lanthanide elements

Elements	La	Ce	Pr	Nd	Pm	Sm	Fu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
a'	2.40	2.52	2.58	2.65	2.52	2.50	2.69	2.65	2.64	2.66	2.70	2.59	2.80	2.80	2.55
a'_a	0.06	0.10	0.05	0.07	0.08	0.06	0.08	0.05	0.04	0.06	0.07	0.02	0.04	0.04	0.03
c.c.	0.997	0.994	0.999	0.997	0.996	0.997	0.996	0.999	0.999	0.998	0.998	0.999	0.999	0.999	0.999

σ_a' : Standard deviation of a' as determined by the least squares method.

c.c.: Correlation coefficient.

Initial concentration of tetracycline in the organic phase varied from $1.25 \cdot 10^{-3}$ M to $20.0 \cdot 10^{-3}$ M.

Lanthanide concentration 10^{-5} M.

Ionic strength 0.9 M (NaCl).

Since no hydrolysis of the lanthanide elements is likely to occur in the pH range in which the partition experiments were carried out and since it has been shown⁷ that Cl^- is not coextracted with the complex formed, the lower than 3 slopes values found for $\lg D$ as a function of pH or as a function of tetracycline concentration in the organic phase, would indicate a stepwise formation of the complexes.

Separation of the lanthanides

From the $\lg D = f(\text{pH})$ lines presented in Fig. 2 the distribution ratios, D , of all the lanthanides, at any given pH value, can be evaluated. The separation factors, $\beta = D_{z+n}/D_z$, of any pair of lanthanide elements can thus be calculated, giving an indication of the feasibility of a separation between the two elements.

Separation factors, β , have been calculated for solutions of pH equal to 2.50. From the β values taken from Table 4 the following mixtures were studied as examples of separations: lanthanum and thulium; and praseodymium, europium and ytterbium.

A multiple extraction procedure was used in both cases. For the lanthanum-thulium pair, whose separation factor is 52.55, a 10-step extraction procedure was enough. For the praseodymium, europium and ytterbium mixture a 23-step extraction was required, since the values of the separation factors are 4.05, 5.38 and 21.77 for the Pr - Eu, Eu - Yb, and Pr - Yb pairs, respectively.

The distribution curves for the multiple extraction separations are presented in Figs 3 and 4. The ordinate values represent the fraction $T_{n,r}$ of element present in each tube (total amount in both phases) and the abscissa values are the corresponding serial number of the tubes. The theoretical value of the fraction $T_{n,r}$ of the solute present in the r^{th} tube after n transfers is given by CRAIG¹⁰

$$T_{n,r} = \frac{n!}{r!(n-r)!} \frac{1}{(D+1)^n} D^r$$

where D - the distribution ratio.

Fig. 3 shows that lanthanum and thulium are completely separated in a 10-step process. Fig. 4 shows that a 23-step process gave a complete separation of the Pr - Yb pair. However, a larger number of steps was necessary in order to obtain a complete separation of praseodymium, europium and ytterbium.

The recoveries found for praseodymium, europium and ytterbium were 66.8%, 74.9% and 81.6%, respectively. Although a complete coincidence of theoretical and

Table 6
Separation factors $\beta = D_{z+n} / D_z^*$ for the lanthanide elements

Elements	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	1.82													
Pr	4.00	2.20												
Nd	8.36	4.60	2.09											
Pm	10.00	5.50	2.50	1.20										
Sm	13.45	7.40	3.36	1.61	1.35									
Eu	16.18	8.90	4.05	1.93	1.62	1.20								
Gd	16.18	8.90	4.05	1.93	1.62	1.20	1.00							
Tb	35.45	19.50	8.86	4.24	3.55	2.64	2.19	2.19						
Dy	40.73	22.40	10.18	4.87	4.07	3.03	2.52	2.52	1.15					
Ho	44.73	24.60	11.18	5.35	4.47	3.32	2.76	2.76	1.26	1.10				
Er	45.64	25.10	11.41	5.46	4.56	3.39	2.82	2.82	1.28	1.12	1.02			
Tm	52.55	28.90	13.14	6.28	5.25	3.91	3.25	3.25	1.48	1.29	1.17	1.15		
Yb	87.09	47.90	21.77	10.41	8.71	6.47	5.38	5.38	2.46	2.14	1.95	1.91	1.66	
Lu	58.91	32.40	14.73	7.04	5.89	4.38	3.64	3.64	1.66	1.45	1.32	1.29	1.12	1.48

* D_{z+n} : Distribution ratio for the lanthanide of atomic number $z + n$ ($n = 0, 1, 2, \dots, 15$).

Tetracycline solution concentration 10^{-2} M.

Aqueous phase pH 2.50.

Ionic strength (NaCl): 0.9M.

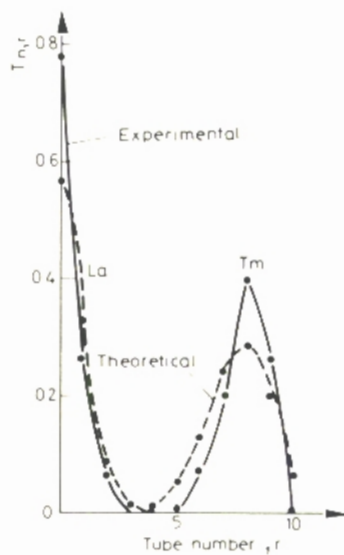


Fig. 3. Distribution curves for lanthanum and thulium for a 10-step countercurrent extraction process

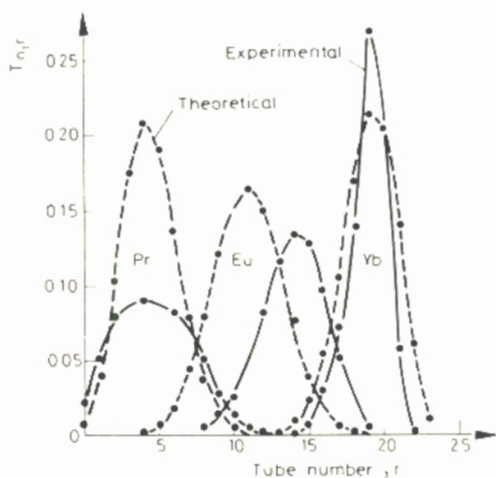


Fig. 4. Distribution curves for praseodymium, europium and ytterbium for a 23-step countercurrent extraction process

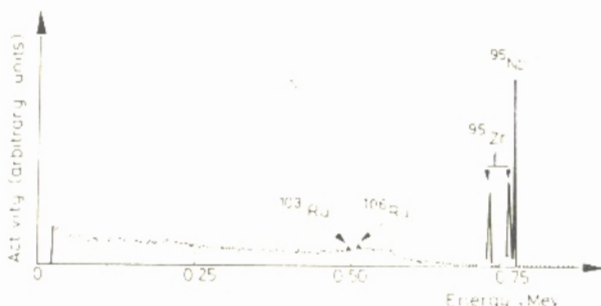


Fig. 5. Separation of uranium and fission products: gamma-ray spectrum of the radioisotopes present in the organic phase

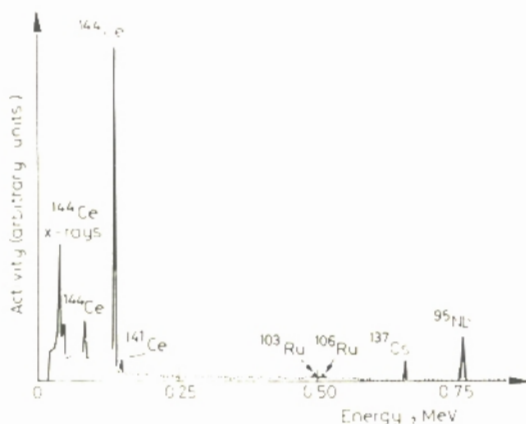


Fig. 6. Separation of uranium and fission products: gamma-ray spectrum of the radioisotopes present in the aqueous phase

experimental curves was not found, their general pattern is in fair agreement. The experimental distribution curve for europium shows a shift to the right and the maximum that should be located in tube 11 is displaced towards tube 14.

BROWN et al.¹¹ have also found a shifting of the experimental curves relative to the theoretical ones when studying the countercurrent extraction of the rare-earth acetylacetonates.

Separation of uranium from some fission products

The total recovery found for uranium was equal to 88.0%. From this amount 92% were in the organic phase and 8% in the aqueous phase, what is in good

agreement with the uranium distribution curve presented in Fig. 1, for a pH value equal to 1.90.

Figs 5 and 6 present the gamma-ray spectra of aliquots of both phases. It can be seen that no radioactivity due to cerium or cesium was found in the organic phase and that no zirconium was found in the aqueous phase, although niobium and ruthenium distributed between both phases.

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