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

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ABSTRACT

Acid and extractant concentrations dependence for the extraction of the 15 lanthanide elements with benzyl alcohol tetracycline are reported

The behaviour towards solvent extraction of uranium thorium and scandium as well as the study of the possibility of using the system tetracycline benzyl alcohol for the separation of the lanthanide elements and for the separation of uranium from those elements are presented

INTRODUCTION

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

Ishidate and Sakaguchi[1] have shown that aureomycin can be used for the colorimetric analysis of Th(IV) ions

Oxford[2] presented a method for the detection of aureomycin in the presence of aminoacids and proteins, which depends on the formation of complexes between aureomycin and Ca(II) ions

Kohn[3] used the property of tetracycline to form mixed complexes with calcium and barbiturates, to develop a procedure that combines the use of fluorometry and complexometry extraction, to analyse the tetracycline antibiotics

Ashton[4] investigated the possibility of using tetracycline as a fluorescent indicator in the microdetermination of group II cations The method proposed by Ashton[4] was shown to be highly sensitive in ultraviolet light for complexometric titrations of calcium, strontium and magnesium with EDTA

One of the first applications of tetracycline for an analytical separation was a solvent extraction procedure presented by Masters[5] for the determination of Sr 90 in environmental grass samples. A further study was then undertaken by Masters[6] to determine the feasibility of application of tetracycline to the extraction of other metallic elements.

The scope of the present work was to verify if tetracycline would form complexes with the lanthanide elements and to study their solvent extraction behaviour with benzyl alcohol. Separation of the lanthanide elements as well as of uranium, thorium and scandium was also investigated

EXPERIMENTAL

I Formation of the Ln TC[*], Y TC, U TC and Th TC Complexes

The spectrophotometric technique was used to examine whether the formation of complexes between the tetracycline molecule and the lanthanide elements, yttrium, uranium and thorium did occur

1 Preparation of the Solutions

Aqueous solutions of the lanthanide elements and yttrium were prepared by dissolving their respective oxides (BDH 99 9% purity) in hot concentrated hydrochloric acid and diluting with water in order to obtain 10^{-1} M metal ion Solutions

The solution containing UO_2(II) ions was obtained by dissolving ammonium diuranate (ADU) with concentrated hydrochloric acid After dissolution of the ADU the solution was diluted to give a concentration of UO_2(II) ions corresponding to 10^{-2} molar

A 10^{-1} M Th(IV) ions solution was prepared by dissolving $Th(NO_3)_4$ in water and diluting to the desired concentration

Tetracycline hydrochloride (Laborterápica Bristol) was dissolved in water and dilutions were made to obtain a 10^{-4} M solution

All the aqueous solutions were prepared by using deionized water which was further distilled over quartz

2 Absorption Measurements

The absorption spectra of pure aqueous solutions of tetracycline hydrochloride at different pH values, of pure metal ions solutions and of the solutions of tetracycline hydrochloride plus lanthanide ions, were recorded

The pH of the solutions varied from 3 0 to 8 0 and the solutions were prepared as follows: 2 0 ml of a 10^{-1} M aqueous solution of the metal ion were added to 2 0 ml of a 10^{-4} M aqueous tetracycline hydrochloride solution The value of the pH was adjusted with diluted HCl and/or NaOH solutions and the final volume made up to 5 0 ml

Aliquots of the solutions were transferred to 5 mm silica cells and the absorption spectra were recorded The apparatus used for this purpose was a Beckman DB spectrophotometer coupled to a Beckman 10" Linear log recorder

II. Solvent Extraction Studies

1 Preliminary Experiments

(*) Ln will be used as an abbreviation for the lanthanide elements and TC for the tetracycline molecule

In order to determine if benzyl alcohol would extract the lanthanide ions by itself, partition experiments were carried out by agitating benzyl alcohol with aqueous solutions of lanthanum and europium radioactive tracers

For the lanthanum experiment the pH of the radioactive aqueous phases varied from 2 90 to 6 80, and for europium it varied from 1 50 to 8 00 After separation of organic and aqueous phases no radioactivity was detected in the organic phase for both experiments, indicating that benzyl alcohol alone did not extract the lanthanide ions

For the systems where the aqueous phases were made up of solutions of the europium tracer and the organic phase of tetracycline benzil alcohol solution, partition experiments were carried out in the presence and in the absence of sodium chloride as salting-out agent. The results of these two series of experiments have shown that the addition of the electrolyte greatly enhances the metal extraction at any given pH Table I presents the results of such distribution experiments

TABLE I

Percent europium extracted (E) as function of presence and absence of sodium chloride

pH	2 20		2 40		2 60		2 80	
NaCl	Yes	No	Yes	No	Yes	No	Yes	No
(E) (%)	14 0	0 5	32 5	1 5	65 0	5 0	86 0	10 6

Concentration of the Tetracycline Solution 10⁻³ M
Concentration of the Sodium Chloride Solution 0 9 M
Concentration of the Europium Chloride Solution 10⁻⁵ M

The results of Table I show that the addition of sodium chloride to the aqueous phase allows the extraction of the metals to occur at lower pH values than that needed for the extraction when sodium chloride is absent The presence of sodium chloride provides also a constant ionic strength medium

It was verified that for the system considered, the equilibrium between the phases is attained in 3 minutes However, in all partition experiments the two phases were shaked for 15 minutes, with the aid of a mechanical apparatus

The results of partition experiments carried out daily, with the same tetracycline solution, during 18 days, have shown that a 10⁻³ M solution of tetracycline hydrochloride in benzyl alcohol can be kept for this period without losing its properties as an extracting agent.

2 Determination of Distribution Ratio

In order to obtain the radioactive tracer solutions of the lanthanide ions, their respective oxides were irradiated in a 10^{12} n cm^{-2} s^{-1} thermal neutron flux in the research reactor IEA R1 After irradiation they were dissolved with concentrated hydrochloric acid and diluted to the desired concentration Promethium 147 was furnished by New England Nuclear

Analytical grade benzyl alcohol was used and the tetracycline hydrochloride was supplied by Laborterápica Bristol, São Paulo

The concentration of the solution of each of the metal ions studied was 10^{-5} M and the concentration of the tetracycline hydrochloride solution in benzyl alcohol was 10^{-2} M

The determination of the distribution ratio was carried out as follows: a 5 0 ml portion of the aqueous phase containing the nuclide under study was added to 1 0 ml of a 5 3 M sodium chloride solution, so that the final ionic strength of the aqueous phase was $\mu = 0 9$ To this aqueous phase a 5 0 ml portion of the tetracycline benzylalcohol solution was added. After the addition of the organic phase the pH of the aqueous phases was adjusted by adding small volumes of dilute solution of hydrochloric acid and/or sodium hydroxide A Metrohm Herisau E 350B pH meter coupled to a Metrohm combined electrode was used to measure the pH values

After shaking both phases during 15 minutes, at room temperature, they were allowed to settle and each of them was centrifuged for 5 minutes

One milliliter aliquots of both phases were then taken for gamma counting using a gamma spectrometer coupled to a 5 00 x 4 38 cm NaI(Tl), well type scintillation detector In the case of Pm 147 the activity was measured using a proportional gas flow counter

In the case of uranium, concentrations of the element in the various extracted solutions were determined by epithermal neutron activation analysis following the technique presented by Atalla and Lima [7]

RESULTS

I. Formation of the Complexes

Figure I shows the wavelengths of maximum absorbance of pure tetracycline solutions and those of the lanthanide tetracycline mixtures as well as of the mixtures containing uranium or thorium, at several pH values

The change observed in the wavelength of maximum absorbance of pure solutions of tetracycline (360 nm) relative to that of the mixtures, shows complex formation between the various ions and tetracycline
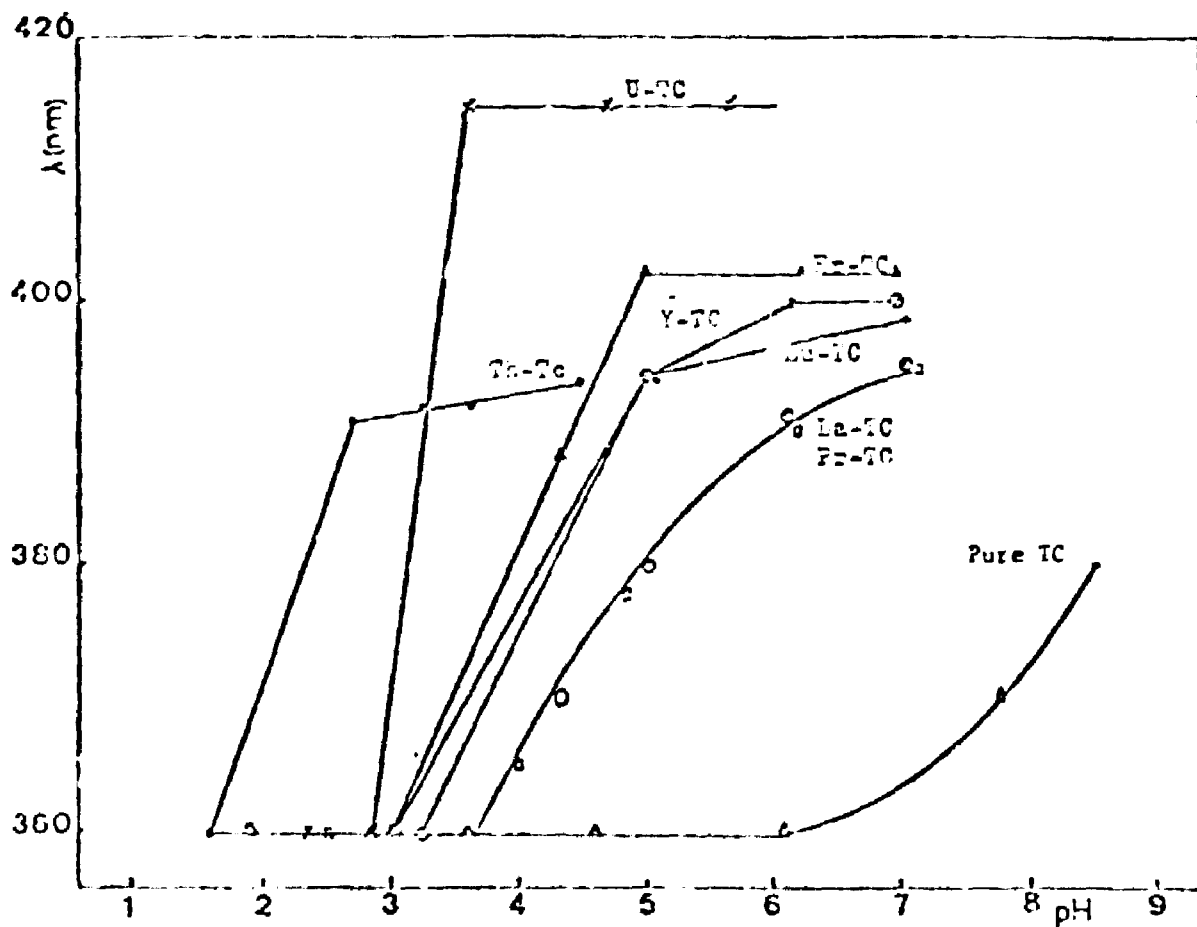
FIGURE I

Wavelengths of the absorption peaks of pure TC-solutions
and of TC metal ions solutions at various pH values.

II. Solvent Extraction Behaviour.

II 1 Acid Dependence

Figure II presents the extraction curves of thorium, uranium, scandium and the lanthanide elements, exception made to gadolinium, erbium and lutetium. Although the extraction curves for these three elements have been experimentally obtained, they are not presented in Figure II, since the curve for gadolinium coincides with the one for europium and the curves of erbium and holmium coincide with the one for dysprosium This occurs also with the curves for lutetium and ytterbium
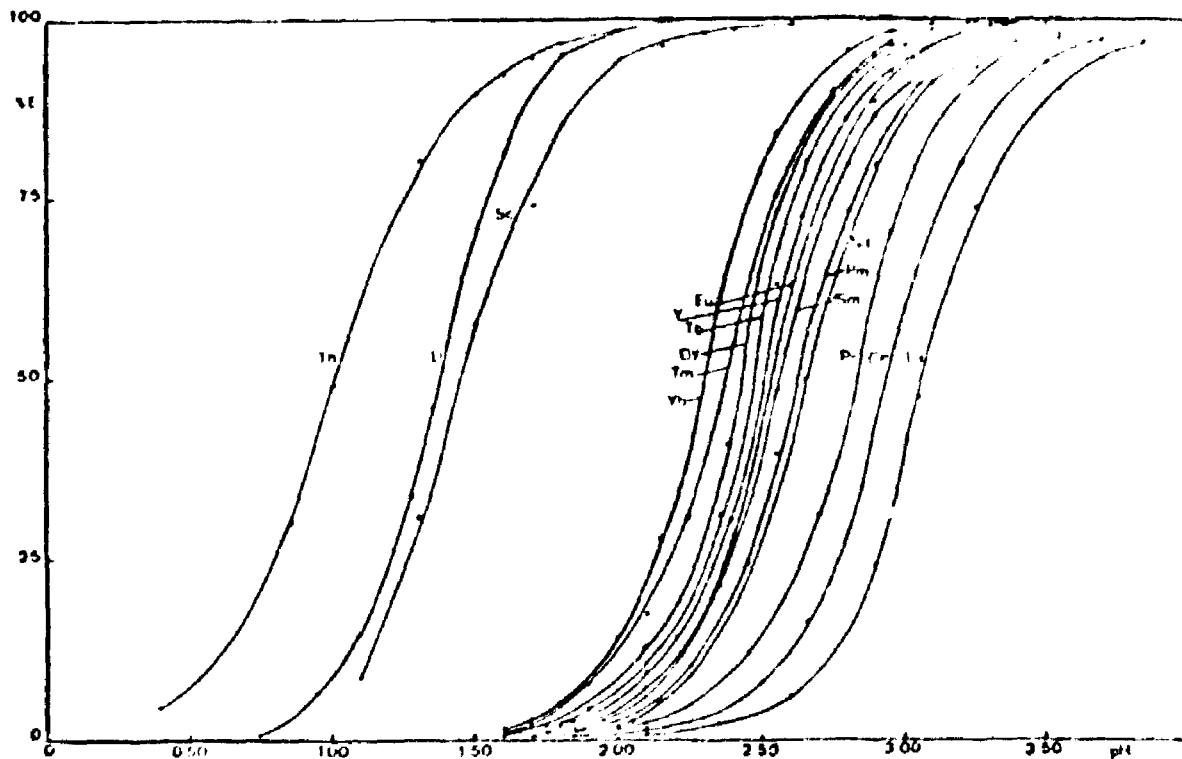

FIGURE II

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

From the extraction curves it can be seen that separation between 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, in general, is the case for the lanthanide elements. In order to get this separation a multiple countercurrent extraction procedure has to be used

Figure III is the graphical presentation of the logarithm of the distribution ratio q as function of pH of the aqueous phase. The slopes of the lines for each one of the lanthanide elements are shown in Table II

From Figure III it may 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
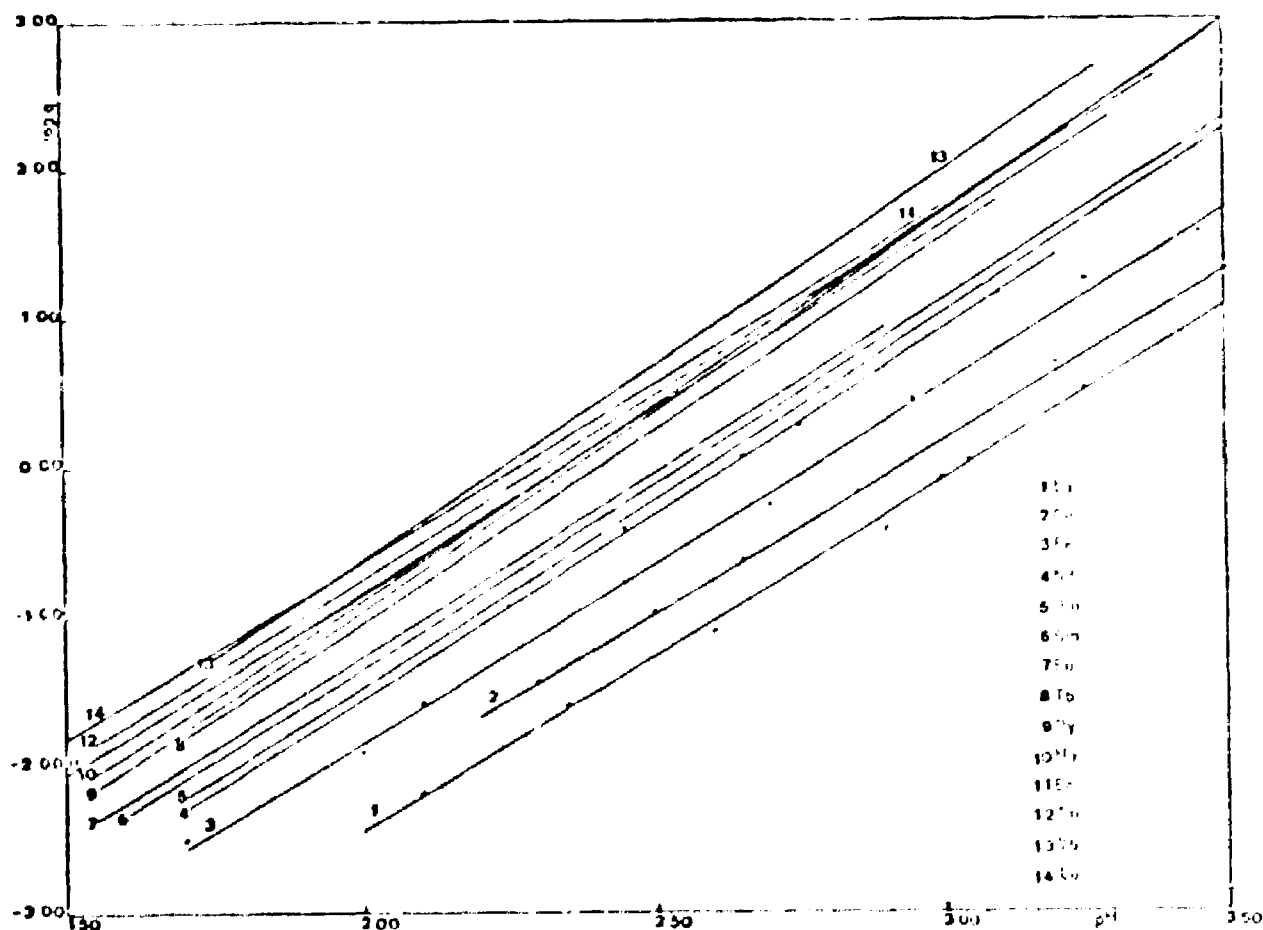

FIGURE III

pH dependence of the extraction of lanthanide ions into tetracycline-benzylalcohol.
Concentration of tetracycline solution 10^{-2} M,
of lanthanide ions 10^{-4} M, ionic strength: 0.9

TABLE II

Parameters of the line $\log q = a\,pH + b$ for the lanthanide elements

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
a	2.36	2.31	2.39	2.47	2.50	2.46	2.46	2.48	2.57	2.66	2.59	2.45	2.45	2.61	2.37
σ_a	0.06	0.03	0.04	0.04	0.03	0.02	0.02	0.03	0.05	0.02	0.03	0.02	0.03	0.04	0.05
b	-7.17	-6.77	6.63	6.50	6.51	6.28	6.20	6.24	6.19	6.30	6.08	5.77	5.67	5.86	5.39
σ_b	0.16	0.08	0.10	0.10	0.08	0.06	0.05	0.07	0.12	0.06	0.09	0.04	0.07	0.09	0.12
c.c.	0.998	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999

σ_a : Standard Deviation of a.

σ_b : Standard Deviation of b.

c.c. : Correlation Coefficient.

II 2 Extractant Dependence

The variation of the distribution ratios as a function of the concentration of the tetracycline in the organic solvent was determined for the 15 lanthanide elements, the pH and ionic strength of the aqueous phase being held constant. The least square method was used for determination of the slopes of both lines log q=f (pH) and log q=f(TC) for each one of the lanthanides.

The concentration of the tetracycline solutions used varied in the range from 1.25×10^{-3}M to $20.00 \times 10^{-}$M.

The slopes of the lines log q as function the logarithm of tetracycline concentration are shown in Table III

The equilibrium or extraction constant K for the extraction equation:

$$M_a^{N+} + N(HA)_o \rightleftharpoons (MA_N)_o + N H_a^+$$

is

$$K = \frac{(MA_N)_o \ [H^+]_a^N}{[M^{N+}]_a \ [HA]_o^N} = q \ \frac{[H^+]_a^N}{[HA]_o^N}$$

(sub-index a: aqueous phase; o: organic phase).

By taking the logarithms and rearranging, one has

$$\log q = \log K + N \ pH + N \log [HA]_o$$

For a fixed value of $[HA]_o$ the extraction constant K can be calculated from the intercept at the origin for the above equation

$$\log K = \log q_{pH=0} - N \log [HA]_o$$

The calculated values of the extraction constants for the 15 lanthanide elements are presented in Table IV.

TABLE III

Slopes of the lines: log q' = a' log (TC) + b' for the lanthanide elements

	La	Ce	Pr	Nd	Pm	Sm	Eu	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
σ_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'.

c.c. : Correlation Coefficient.

TABLE IV

Extraction constants, K, for the systems lanthanide elements tetracycline

Ln	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
(log K)	2.37	1 73	1 47	1 20	1 47	1 28	0 82	0 94	0 96	0 98	0 68	0 59	0 07	0 26	0 29

APPLICATIONS

1 Separation of Some of the Lanthanides Using Tetracycline as the
Extracting Agent.

From the log $q=f(pH)$ lines presented in Figure III the distribution ratios of all the lanthanides, at any given pH value, can be evaluated. Therefore the separation factors of any pair of lanthanide elements can be calculated, giving an indication of the feasibility of a separation between the two elements.

Such separation factors, β, have been calculated for solutions of pH equal to 2 50. Taking into account the found β values the following separations have been carried out: lanthanum and thulium; praseodymium, europium and ytterbium.

A multiple extraction procedure has been used in both cases. For the lanthanum thulium pair, whose separation factor is 52 55, a 10 stage extraction procedure was enough, while for the praseodymium, europium and ytterbium mixture a 23 stage 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 are presented in Figures IV and V. The ordinates values are the fraction Tn.r of element present in each tube (both phases) and the abscissae values are the corresponding serial number of the tubes.
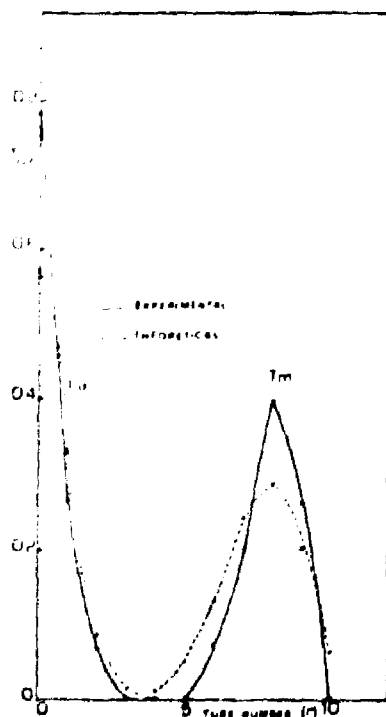

FIGURE IV

Distribution curves for lanthanium and thulium after a 10 stage
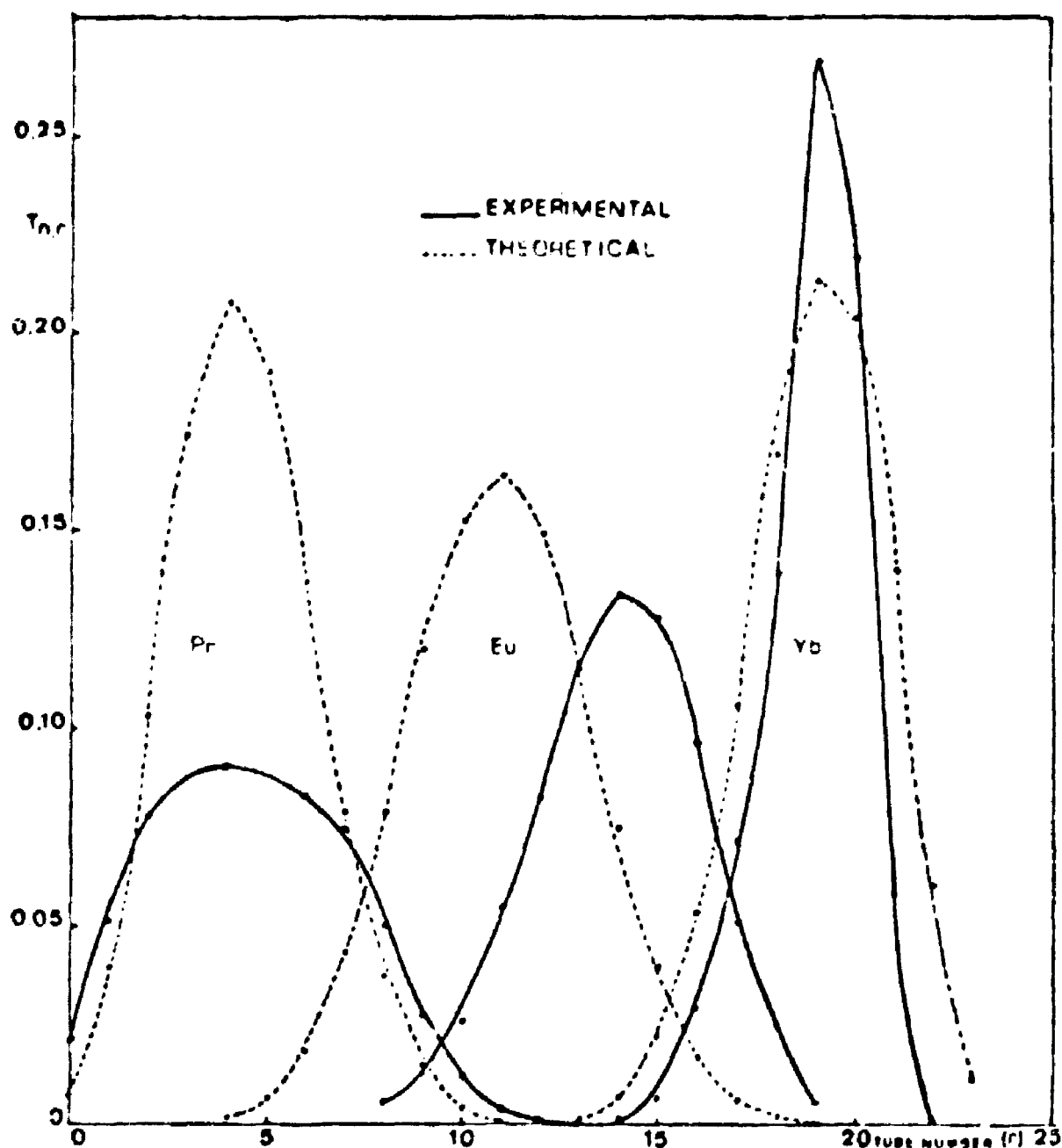countercurrent extraction process

FIGURE V

Distribution curves for praseodymium, europium and ytterbium after a 23 stage countercurrent extraction process

The determination of such fractions have been made by counting the radioisotopes in the aliquots of both phases namely: La 140 and Tm 170 in one case and Pr 142, Eu 152 and Yb-175 in the other. For this purpose a Ge Li detector, coupled to a 4096 channels Hewlett-Packard analyser, was used.

Figure IV shows that lanthanum and thulium are completely separated in a 10 stage process. Figure V shows that a 23-stage process gives a complete separation of the Pr Yb pair. However, a higher number of stages is necessary in order to obtain the complete separation between the three components, that is, praseodymium, europium and ytterbium.

2 Separation of Irradiated Uranium from Some Fission Products

U_3O_8 was irradiated for 500 hours in a thermal neutron flux of about $10^{1\cdot2}$ n/s cm^2 and cooled for 10 months The irradiated U_3O_8 was dissolved with concentrated hydrochloric acid and the resulting solution was used to isolate uranium from fission products, special attention being given to the lanthanide elements present in the mixture Practically, the only gamma-rays emitting lanthanide radioisotopes present in the mixture, after 10 months cooling time, were Ce 141 and Ce 144

The uranium in both phases was determined using the epithermal neutron activation analysis method[7], showing that uranium remained in the organic phase The pH of the aqueous phase was equal to 1 9 and the concentration of tetracycline in the organic solvent was equal to 10^{-2} M.

Figures VI and VII 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 No zirconium was found in the aqueous phase, although niobium and ruthenium distributed between both phases.
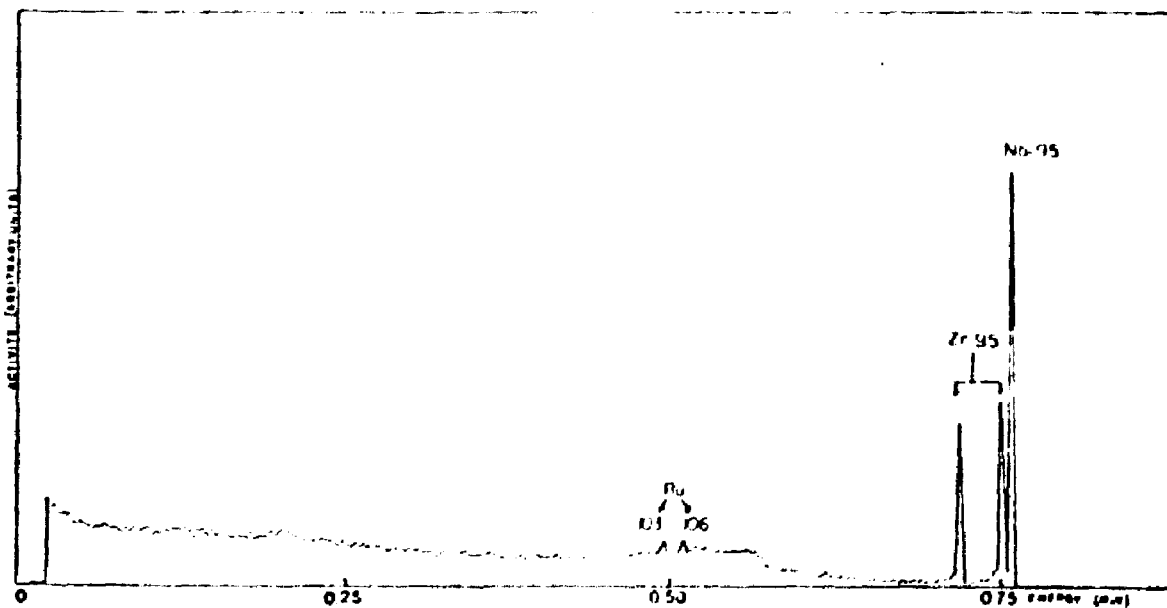

FIGURE VI

Separation of uranium and fission products: gamma ray spectra
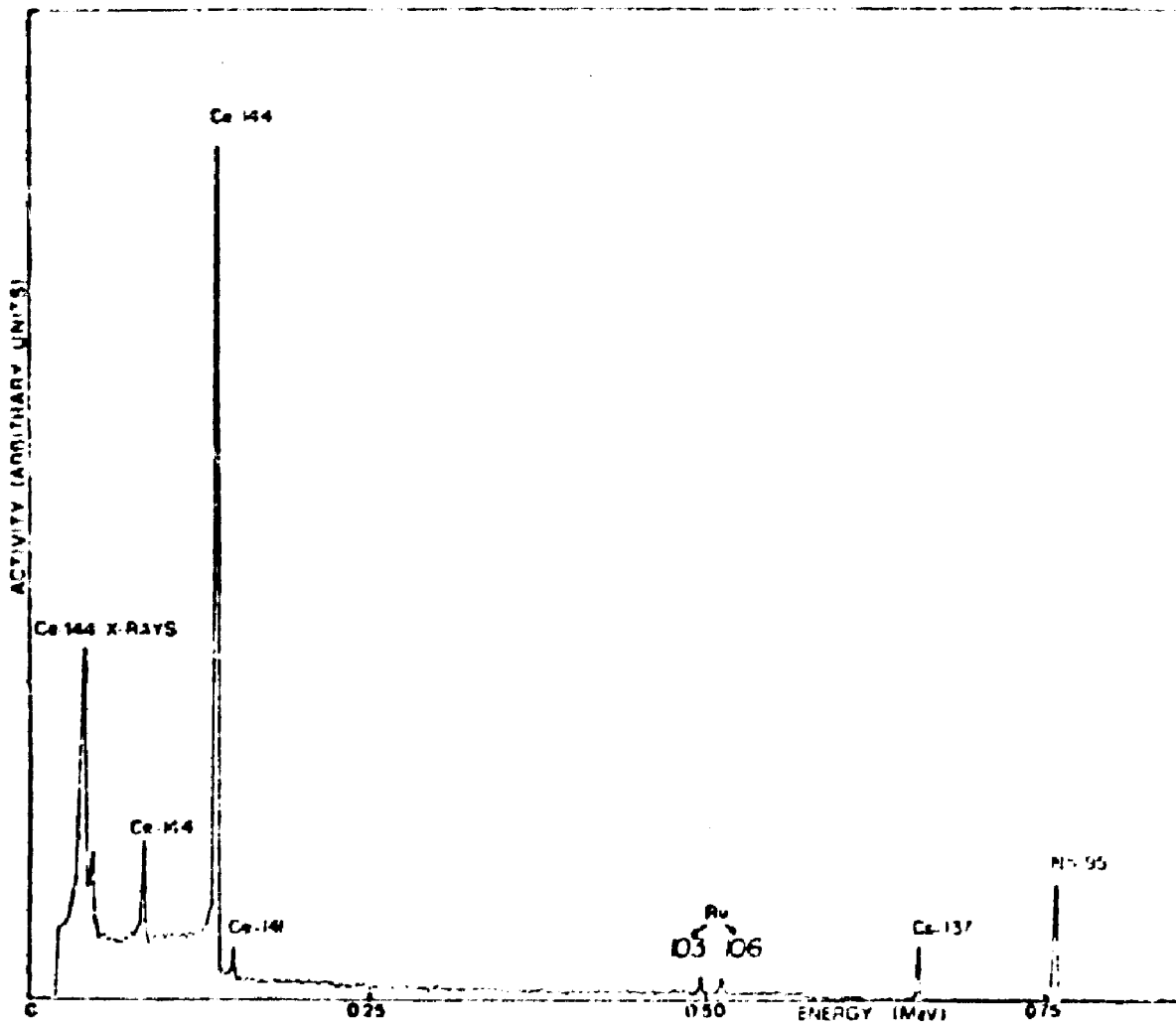of the radioisotopes present in the organic phase.

FIGURE VII

Separation of ur nium and fission products: gamma ray spectra
of the rauioisotopes present in the aqueous phase.

DISCUSSION and CONCLUSIONS

Formation of complexes is shown by the shift of the absorption peak of the pure aqueous tetracycline solutions which is displaced from 360 nm to about 400 nm for the tetracycline metal ions mixtures

The extraction curves presented in Figure II show that the separation of thorium and uranium from the rare earth elements is feasible provided the extraction operation is carried out at a convenient pH value The same curves show that in the case of the separation of scandium from the lanthanide elements more than one extraction operation will be necessary to obtain a complete separation

Figure III indicates that it will be easier to obtain a separation between the "light" lanthanides than between the heavy' lanthanides

Since no hydrolysis of the lanthanide elements, in the pH range in which the partition experiments have been carried out, is likely to occur, and since it has been shown elsewhere by Nastasi and Lima[8] that the ion Cl is not coextracted with the complex formed, the lower than 3 slopes found for the log $q=f(pH)$ and log $q=f(TC)_o$ lines can be explained by taking into account the step wise formation of the complexes Thus it is likely that besides the Ln^{3+} ions present in the aqueous phase, the species $(Ln\ TC)^{++}$ and $(Ln\ TC_2)^+$ should also be found in the same phase.

Figure IV shows that the experimental data for the multi stage separation of lanthanum and thulium are in good agreement with the theoretically calculated values

The distribution curves presented in Figure V show that although the recoveries for praseodymium europium and ytterbium were quite low, namely 66.8%, 74 0% and 81.6%, respectively the distribution of these elements followed the theoretical pattern, except in the case of europium where a shift of the practical curve was observed, relatively to the theoretical one.

ACKNOWLEDGEMENTS.

RESUMO

É apresentado o estudo da variação da extração dos 15 elementos lantanídios em função da variação do pH da fase aquosa e também em função da concentração da solução de tetraciclina.

É examinada, também a possibilidade do emprego do sistema tetraciclina álcool benzílico para a separação dos elementos lantanídios entre si, bem como para a separação do urânio destes elementos.

RÉSUMÉ

On a étudié l'extraction des 15 lanthanides en présence de la tetracycline et de l'alcool benzylique en fonction du pH de la phase aqueuse bien que de la concentration de la solution de tetracycline.

On a aussi étudié l'emploi du système tetracycline-alcool benzylique pour séparer les lanthanides entre eux bien que pour séparer l'uranium de ces elements.

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