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CENTRO DE OPERAÇÃO E UTILIZAÇÃO DO REATOR DE PESQUISAS – COURP
ÁREA DE RADIOQUÍMICA

## ERRATUM

On the back of the front page, "INIS Categories and Descriptors" should be as follow:

B12
TETRACYCLINES : Complexometry
RARE EARTHS : Solvent extraction
ZINC : Solvent extraction
SCANDIUM : Solvent extraction
URANIUM : Solvent extraction
THORIUM : Solvent extraction
NEPTUNIUM : Solvent extraction
PROTACTINIUM : Solvent extraction

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# USE OF TETRACYCLINE AS COMPLEXING AGENT IN RADIOCHEMICAL SEPARATIONS

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## ABSTRACT

A comprehensive review of the work carried out in the "Instituto de Pesquisas Energéticas e Nucleares" up to June 1981 on the use of tetracycline for analytical purposes in solvent extraction procedu es is presented.

Individual extraction curves for the lanthanides, zinc, scandium, uranium, thorium, neptunium and protactinium were obtained. Separations of those elements one from another, and of uranium from selenium, bromine, antimony, barium, tantalum and tungstem were carried out. In all cases benzyl alcohol was the diluent used to dissolve tetracycline hydrochloride. Sodium chloride was used as supporting electrolyte for the lanthanides separations and sodium perchlorate for the other mentioned elements.

Stability or formation constants for the lanthanides complexes as well as for thorium complex with tetracycline were determined by using the methods of average number of ligands, the limiting value (for thorium), the two parameters and the weighted least squares. For the lanthanides, the logarithms of stability constants of the complexes $Ln(TC)_3$ go from $9.35 \pm 0.22$ for lanthanum up to $10.84 \pm 0.11$ for lutetium. For the $Th(TC)_4$ complex the logarithm of the formation constant is equal to $24.6 \pm 0.3$.

Radioisotopes of the respective elements were used for the determinations. When more than one radioelement was present in an experiment, multichannel analyser coupled to Ge (Li) or NaI(Tl) detectors were used for counting the activities. When only one radioisotope was used, counting of the radioisotopes was made with a single-channel analyser (integral mode counting) coupled to a NaI(Tl) detector. Uranium was determided by activation analysis (epithermal neutrons). Radioisotopes of the elements were obtained by irradiation in the IPEN swimming-pool reactor. The natural radioisotope $^{234}$Th was used as label in the thorium experiments.

In some separations procedures such as in the case of the pair uranium-neptunium, and of the pair scandium-zinc, the separation was obtained by properly adjusting the pH value of the aqueous phases, before the extraction operation. In other cases, addition of masking agents to the extraction system was required in order to perform the separation between the elements under study. In this way ethylenediaminetetraacetic acid (EDTA) was used as masking agent for scandium and the lanthanides in order to allow separation of uranium from those elements.

Diethylenetriaminepentaacetic acid (DTPA) was used as masking agent for thorium in order to extract uranium into the organic phase.

Separations of protactinium from thorium, and of uranium from protactinium and thorium, were accomplished by using sodium fluoride as masking agent for protactinium and DTPA as masking agent for thorium and protactinium at the same time.

In the case of the separation of the lanthanides one from another it is necessary to resort to a multi-stage extraction procedure since the stability constants for those elements are too close apart.

## INTRODUCTION

Several analytical methods have been developed using tetracycline, aureomycin (chlorotetracycline) and terramycin (oxytetracycline) as complexing agents for various cations. Ishidate and Sakaguchi[10] have shown that aureomycin can be used for the colorimetric analysis of Th(IV) ions.

Ashton[4] investigated the possibility of using tetracycline as a fluorescent indicator in the microdetermination of group II cations. The method proposed by Ashton 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[12] for the determination of $^{90}Sr$ in environmental grass samples. A further study was then undertaken by Masters[13] to determine the feasibility of application of tetracycline to the extraction of other metalic elements.

Albert[2] and Albert and Rees[3] have determined, by means of potentiometric titrations, the stability constants of the complexes formed by chlorotetracycline, oxytetracycline and and tetracycline with several bivalent cations, namely: Cu(II), Fe(II), Co(II), Zn(II) Mn(II) and Ni(II) as well as with Fe(III) and Al(III).

The stability constants of some alkaline-earth chelates of tetracycline have been determined by Maxwell et al.[14] using potentiometric titrations.

Our investigations concerning the analytical uses of tetracycline (TC) were started by showing that the lanthanide elements, uranium and thorium form complexes with the tetracycline molecule. Spectrophotometry was the technique used to show the formation of the complexes[17].

Extraction curves for the 15 lanthanides, for scandium, thorium, uranium[17], neptunium[16], zinc[23] and protactinium were determined for the extraction system made up by TC-benzyl alcohol as the organic phase.

A 10-stage extraction procedure applied to the mixture of lanthanum and thulium was enough for isolating both elements one from another. In the case of the mixture of praseodymium, europium and ytterbium, a 23-stage extraction procedure was used since the separation factors of the elements present in the second case were smaller than the separation factor for the pair lanthanum-thulium.

Following the sequence of our investigations, stability constants of the complexes formed between the lanthanides and TC molecule were determined[21], as well as the one of the thorium-TC complex[24].

The rather high values found for the stability constants of the complexes under study led to the conclusion that these compounds would be of interest to be used for analytical purposes.

The behavior of protactinium in connection with this extraction system was also investigated.

The studies in connection with the separation of uranium from selenium, bromine, antimony, barium, tantalum and tungsten[22] are of practical interest since these elements may cause interferences in the determinations of uranium by epithermal neutron activation analysis. The radioisotopes $^{79m}Se$, $^{81m}Se$, $^{80m}Br$, $^{122m}Sb$, $^{131}Ba$, $^{182m}Ta$, $^{182}Ta$ and $^{187}W$ have gamma-rays whose energies are too close to 74.6 keV photopeak of $^{239}U$.

Both uranium and thorium are extracted into the TC-benzyl alcohol solution but the extraction curves for these two elements are too close one to the other to allow the separation of both elements in a single extraction operation.

Nevertheless, TC-benzyl alcohol system can successfully be used for separating uranium from thorium, provided the thorium reaction with TC is masked by means of thorium complexation with DTPA[19]. The non-extractable Th-DTPA complex has a stability constant higher than that of the Th-TC complex and the presence of DTPA does not interfere with the extracting capacity of TC relatively to uranium.

Similarly, separation of uranium from scandium and from the lanthanides[20] is easily performed when both scandium and the lanthanides are held on the aqueous phase by masking the reaction with EDTA, since the non-extractable Sc-EDTA and lanthanide-EDTA complexes have stability constants higher than the ones of Sc-TC or lanthanide-TC complexes.

The use of TC-benzyl alcohol extraction system was also studied for isolating scandium from zinc[23]. Separation of these two elements is important in activation analysis when both elements are present in the same sample since the radioisotopes $^{65}Zn$ and $^{46}Sc$ have gamma-rays with energies too close one to the other. $^{46}Sc$ can be determined in a mixture of the two radioisotopes by means of the photopeak of 889.3 keV; however, the main photopeak of $^{65}Zn$, with energy correponding to 1115.52 keV, suffers interference from the 1120.5 keV photopeak of $^{46}Sc$. The annihilation peak of $^{65}Zn$ suffers interference from many other radioisotopes. Half-lives of both radioisotopes are too long (83.9 days for $^{46}Sc$ and 245 days for $^{65}Zn$) to wait one of the isotopes to decay in order that the other might be counted free from interferences.

## EXPERIMENTAL

### 1 – Preparation of Solutions

The radioisotopes of the lanthanide elements were obtained by irradiation of their respective oxides (Johnson Matthey Chemicals Limited, London) in a thermal neutron flux of about $5 \times 10^{12} n.cm^{-2}.s^{-1}$ from 0.5 to 8 hours, according to the nuclear properties of each particular radioisotope. After irradiation the oxides were dissolved with hot hydrochloric acid or perchloric acid, depending on the salting-out agent i.e., NaCl or NaClO$_4$, to be added to the aqueous phase. The solutions were then diluted to the desired concentrations that ranged from $10^{-4}$ to $10^{-5}$ M in metal ion.

Radioactive tracers for the elements selenium, bromine, antimony, barium, tantalum and tungsten were obtained by irradiation of compounds of the elements, (Table I).

Carrier-free $^{147}Pm$ was purchased from New England Nuclear (Boston, Mass.) and suitable aliquots of the original stock solution were diluted with 0.1N HCl solution.

Carrier-free $^{239}Np$ was separated from irradiated $U_3O_8$. Irradiation of $U_3O_8$ was carried out using cadmium containers in order to practically eliminate the thermal neutron fission of $^{235}U$. $^{239}Np$ was isolated from the uranium solutions by coprecipitating neptunium, in the trivalent oxidation state, with lanthanum fluoride[9].

## TABLE I

Radioactive Tracer Solutions

| Element | Irradiated Compound | Dissolution With | Radioisotope |
|---------|---------------------|------------------|--------------|
| Se | Se (metal) | HNO$_3$ | $^{75}Se$ |
| Br | KBrO$_3$ | H$_2$O | $^{82}Br$ |
| Br | KBr | H$_2$O | $^{82}Br$ |
| Sb | Sb (metal) | Acqua Regia | $^{124}Sb$ |
| Ba | BaCO$_3$ | HCl 0.2M | $^{131}Ba$, $^{133}Ba$ |
| Ta | Ta (metal) | HF 28M | $^{182}Ta$ |
| W | $(NH_4)_{10}W_{12}O_{41}5H_2O$ | H$_2$O | $^{187}W$ |

Irradiation time = 8 min up to 24 hours.

Thermal neutron flux ≈ $5 \times 10^{12} n.cm^{-2}.s^{-1}$.

Container for irradiation: aluminium sheets and quartz ampoules for bromine (bromide).

[234]Th tracer was obtained by passing an uranyl nitrate HF solution through a column of alumina and removing the retained [234]Th with hot HCl[11]

Carrier-free [233]Pa was obtained by irradiation of thorium hydroxide with thermal neutrons during 8 hours. After a cooling time of about 20 hours, thorium hydroxide was dissolved with hydrochloric acid and [233]Pa was isolated from thorium by means of an ion exchange operation[11]. After its isolation [233]Pa was kept in 8M HCl solution, in polyethylene vials.

Uranium and thorium solutions used for the extractions were prepared by dissolving $U_3O_8$ and $ThO_2$ with nitric acid solution.

Tetracycline hydrochloride(TC) was dissolved with benzyl alcohol (p.a., Carlo Erba) previously washed with distilled water. The concentration of TC in the organic solution was in the range from $10^{-3}$ to $10^{-2}$ M. The solution was used within six hours after its preparation in order to avoid its decomposition.

## 2 – Operation Procedure

The extraction system was made up of 5.0 ml of TC-benzyl alcohol solution and 5.0 ml of the aqueous solutions of each of the radioactive tracers of the elements under study

For the determination of the extraction curves of the lanthanides and of [239]Np, NaCl, at a concentration equal to 1.0M, was used as salting-out agent in the aqueous phases. In the other cases the salting-out agent was $NaClO_4$ at a concentration of 0.1M.

Masking agents EDTA or DTPA were added to the aqueous phases so that their final concentration was equal to $2.5 \times 10^{-3}$ M.

For the separation between thorium and protactinium NaF was used to mask the reaction between protactinium and TC. The final concentration of the masking agent NaF was $4.9 \times 10^{-3}$ M.

For separation of uranium from both protactinium and thorium, DTPA ($2.5 \times 10^{-3}$ M) was used as masking agent.

Measurements of pH values were performed using a Metrohm pH meter Model E-350B, allowing a scale reading of 0.05. The pH values of the aqueous phases were adjusted by adding dilute acid solutions (HCl or $HClO_4$) and dilute NaOH solution. The phases were then equilibrated by shaking mechanically, for 30 minutes, at a temperature of $25.0 \pm 0.5^\circ$ C.

The phases were separated, centrifuged, the pH of the aqueous phases were measured and aliquots of one milliliter of both phases were then withdrawn for counting. Whenever there was only one radioelements present in the samples, a well type NaI(Tl) scintillation counter, coupled to a single channel analyser was used for integral gamma-ray counting. In the case of samples containing more than one radioelement, a Ge-Li detector coupled to a 4096 channel analyser was used. In the case of [147]Pm samples a proportional gas flow counter was used to measure the activities.

Concentration of uranium in both phases was determined by epithermal neutron activation analysis[15] measuring the activity corresponding to the 74.6 keV photopeak of [239]U

## RESULTS AND DISCUSSION

I — Stability Constants for the Complexes of the Lanthanide Elements and of Thorium with Tetracycline

In order to calculate the stability constants of the complexes under study, several preliminary determinations were carried out.

### I.1 — Complex Formation and Extraction

To show that the metal extracted into the organic phase is bonded to the tetracycline molecule, the radioactive lanthanide or thorium tracer solutions were contacted with benzyl alcohol at various pH values. No activity was detected in the organic phase (benzyl alcohol only) showing that the extractable species were the lanthanide-tetracycline complex or thorium-tetracycline complex.

### I.1.1 — Type of Complex Formed

In order to check if polynuclear complexes would be formed, distribution ratios, D, were determined for several concentrations of terbium and of thorium, maintaining the TC concentration constant at $1.0 \times 10^{-2}$M and $2.0 \times 10^{-3}$M, respectively, and varying the pH values of the aqueous phases. Results are presented in Figure 1.
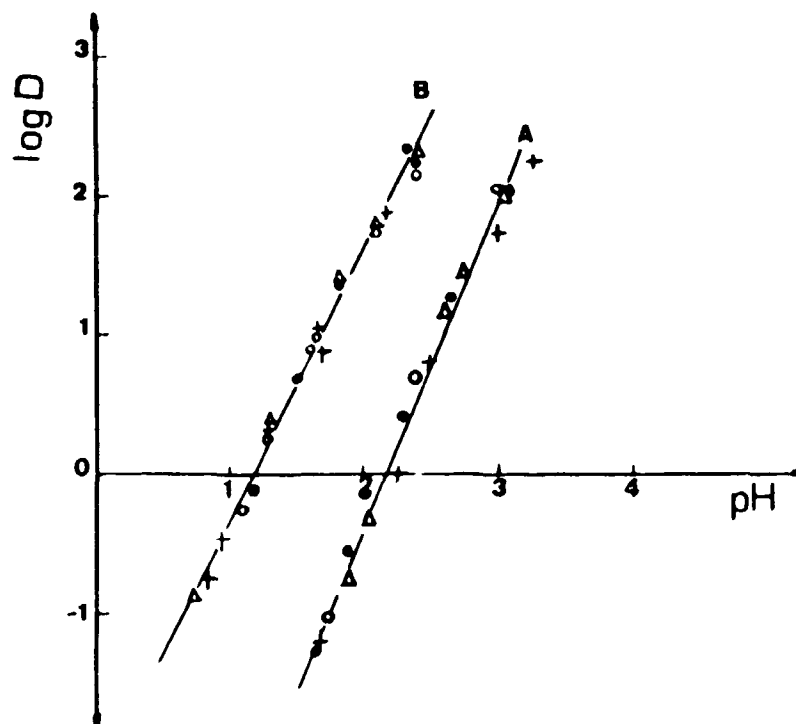


Figure 1 — Distribution Ratio of Metal Versus pH.
Curve A — [TC] = $C_0$ = 0.01M; [Tb] : (Δ) — $1.0 \times 10^{-5}$M; (+) — $2.0 \times 10^{-5}$M; (0) — $4.0 \times 10^{-5}$M; (●) — $1.0 \times 10^{-4}$M.
Curve B — [TC] = $C_0$ = $2.0 \times 10^{-3}$M; [Th] : (○) — $4.0 \times 10^{-6}$M; (+) — $1.0 \times 10^{-5}$M; (Δ) — $8.3 \times 10^{-5}$M; (●) — $1.0 \times 10^{-4}$M.

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Statistical "F" test and Students's "t" test[15] applied to the data obtained showed that the straight lines corresponding to four metal concentrations, within the ranges $1.0 \times 10^{-5} M$ to $1.0 \times 10^{-4} M$ for terbium, and $4.0 \times 10^{-6} M$ to $1.0 \times 10^{-4} M$ for thorium are coincident at a confidence level of 95%. This means that the distribution ratio is not dependent on the metal concentration in the ranges of concentration investigated, showing the formation of mononuclear complexes for the lanthanide elements and thorium[26].

To check if the complexes formed in the extraction system under study are of the general formula $MA_n(OH)_p(HA)_r$, $MA_n(OH)_p$ or $MA_n$, the distribution ratios, log D, were determined as a function of the cologarithm of the concentration of free ligand (pA) for various initial concentrations of TC[21].

In the case of lanthanides and of thorium it was shown that the distribution ratio (log D) is function only of pA, for various concentrations of TC, indicating the formation of complexes of the type $MA_n$[26], Figure 2.
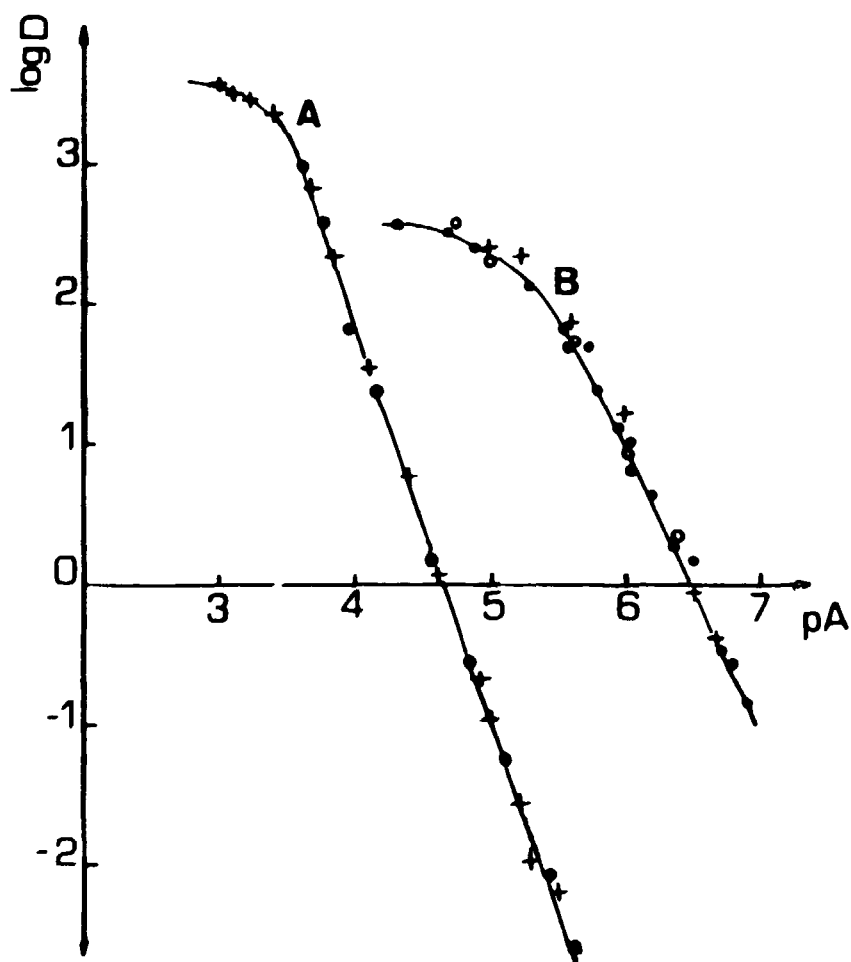


Figure 2 — Distribution Ratio of Metal Versus pA, as a function of TC concentration.
Curve A: [Tb] = $2.0 \times 10^{-5} M$; concentration of TC: (+) — 0.010M; (●) — 0.004M.
Curve B: [Th] = $10^{-4}$ — $10^{-5} M$; Concentration of TC: (○) — $5.0 \times 10^{-3} M$;
(●) — $2.0 \times 10^{-3} M$; (+) — $7.5 \times 10^{-4} M$.

The formation of negatively charged complexes for lanthanide elements and thorium was ruled out in the pH intervals at which D values were obtained. If such complexes existed, the curves of Figure 2, log D versus pA, would show a maximum value for log D or a plateau followed by a decrease of log D for decreasing pA values[18]. In order to calculate the stability constants it was assumed that only uncharged complexes $Ln(TC)_3$ (Ln = lanthanide elements) and $Th(TC)_4$ are extracted into the organic phase, what is to be expected to be true for organic solvents of low dielectric constants[26,18].

### 1.1.2 - Complexation Position in the Tetracycline Molecule

TC has three ionizable hydrogen atoms corresponding to the tricarbonylmethane, phenolic diketone and dimethylamino groups. The dissociation constants are $pK_1 = 3.39$, $pK_2 = 7.44$ and $pK_3 = 8.85$, respectively[21].

Complexation position for the lanthanide ions and for thorium was determined by potentiometric titrations as well as by as by infrared absorption spectrophotome..y. Conductimetric titrations were also used in the case of the lanthanide elements.

Results for TC potentiometric titrations with sodium hydroxide solution in presence and in absence of lanthanum and of thorium ions are shown in Figures 3 and 4, respectively. It can be seen that the increase of pH on titrating La–TC and Th–TC solutions is less pronounced than when titration is carried out in absence of the metal ions. This indicates that in the case of lanthanum and of thorium, formation of the complexes occurs by means of the tricarbonylmethane group, since this group is the one that dissociates at pH values smaller than 5.50.
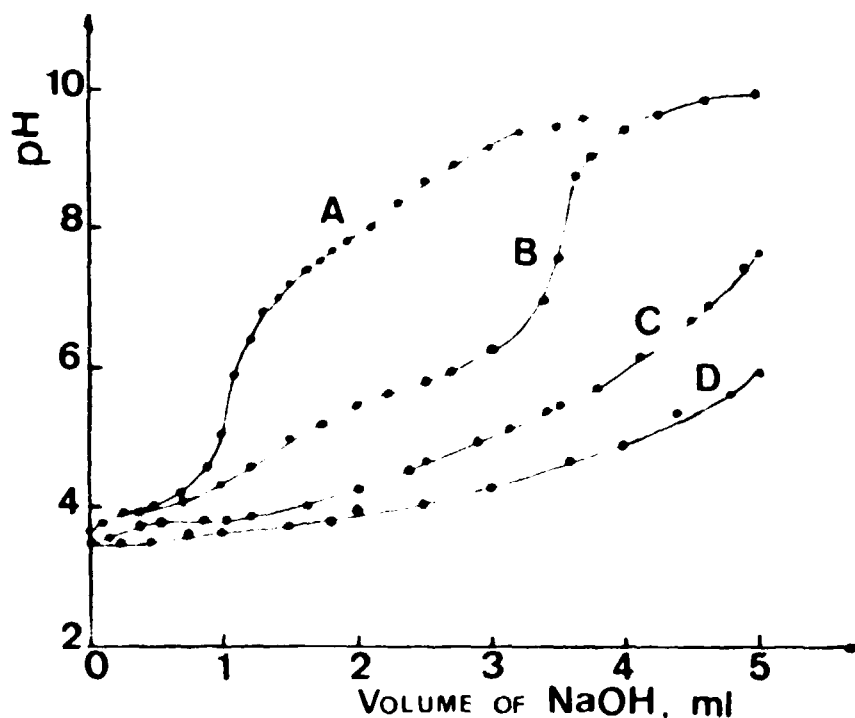


Figure 3 — Potentiometric titration of 0.010M TC with 0.010M NaOH.
La–TC, ratio A — no La; B — 1:1; C — 1:2; D — 1:3.

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For conductimetric titrations with lanthanum ions two tetracycline derivatives (anhydrotetracycline, ATC, and dedimethylamino-tetracycline, DTC, Figure 5) were used, as well as the tetracycline ligand (TC) used throughout in this work. TC and ATC were titrated in aqueous solutions and DTC in methanol, since its solubility in water is rather small. Formation of complexes with a metal-ligand ratio equal to 1:1, 1:2 and 1:3 was thus confirmed, Figures 6 and 7. It is thus seen that the lanthanide is not coordinated through the nitrogen of group B (Figure 5) (dimethylamino) since this group is not present in the DTC. The same conclusion was drawn by means of solvent extraction technique, since the compounds formed with ATC and DTC are both extractable into benzyl alcohol.
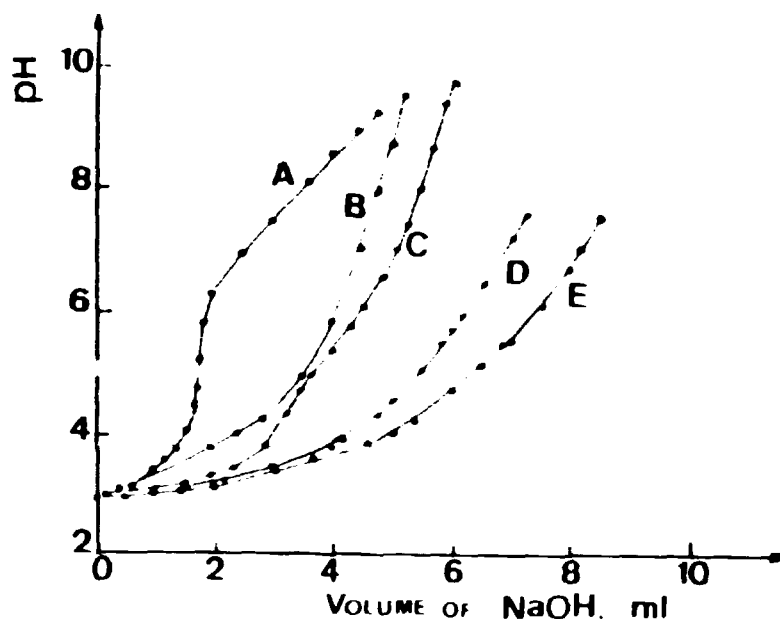


Figure 4 — Potentiometric titration $9.2 \times 10^{-3}$ M TC with 0.10M NaOH.
Th—TC, ratio A — no Th; B — 1:1; C — 1:2; D — 1:3; E — 1:4.

Figure 8 shows the results of conductimetric titrations of TC with thorium ions, indicating the formation of the species in which the metal:ligand ratios are equal to 1:1, 1:2, 1:3 and 1:4.

Absorption infrared spectra of TC, La—TC and Th—TC complexes were made. The compounds were emulsified in mineral oil (Nujol). The La—TC and Th—TC compounds were prepared in accordance with the procedure presented by Baker and Brown[6]. The spectra showed the following characteristics (Figures 9 and 10):

a) TC, La—TC and Th—TC have the same absorption bands in the interval from 200 to 1500 cm$^{-1}$ (in Figures 9 and 10 the whole spectrum is not represented).

b) The compound La—TC obtained at pH = 3.0 and the one obtained at pH = 4.5 are the same.

c) TC presents three absorption bands at 1580, 1610 and 1670 cm$^{-1}$ which are not present in the spectrum of La—TC nor in the spectrum of Th—TC; instead a large band, at approximately 1600 cm$^{-1}$, is presented by La—TC (Figure 9) and by Th—TC (Figure 10). Since the absorption corresponding to the value at 1670 cm$^{-1}$ is due to the vibration of the group —C=O it is seen that lanthanum and thorium are linked to the TC molecule by the tricarbonylmethane group A.
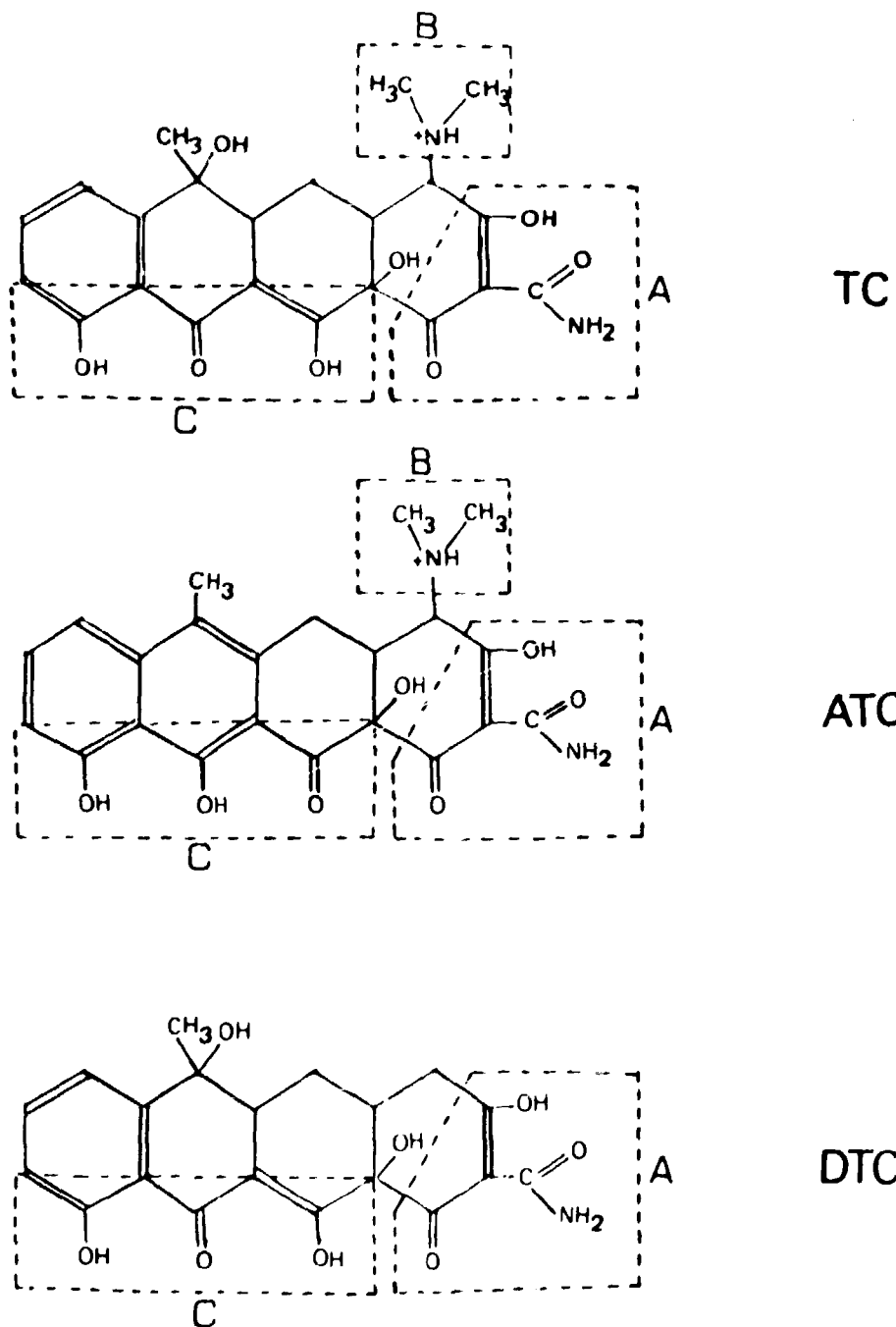
Figure 5 — Formulae of Tetracycline (TC), Anidrotetracycline (ATC) and
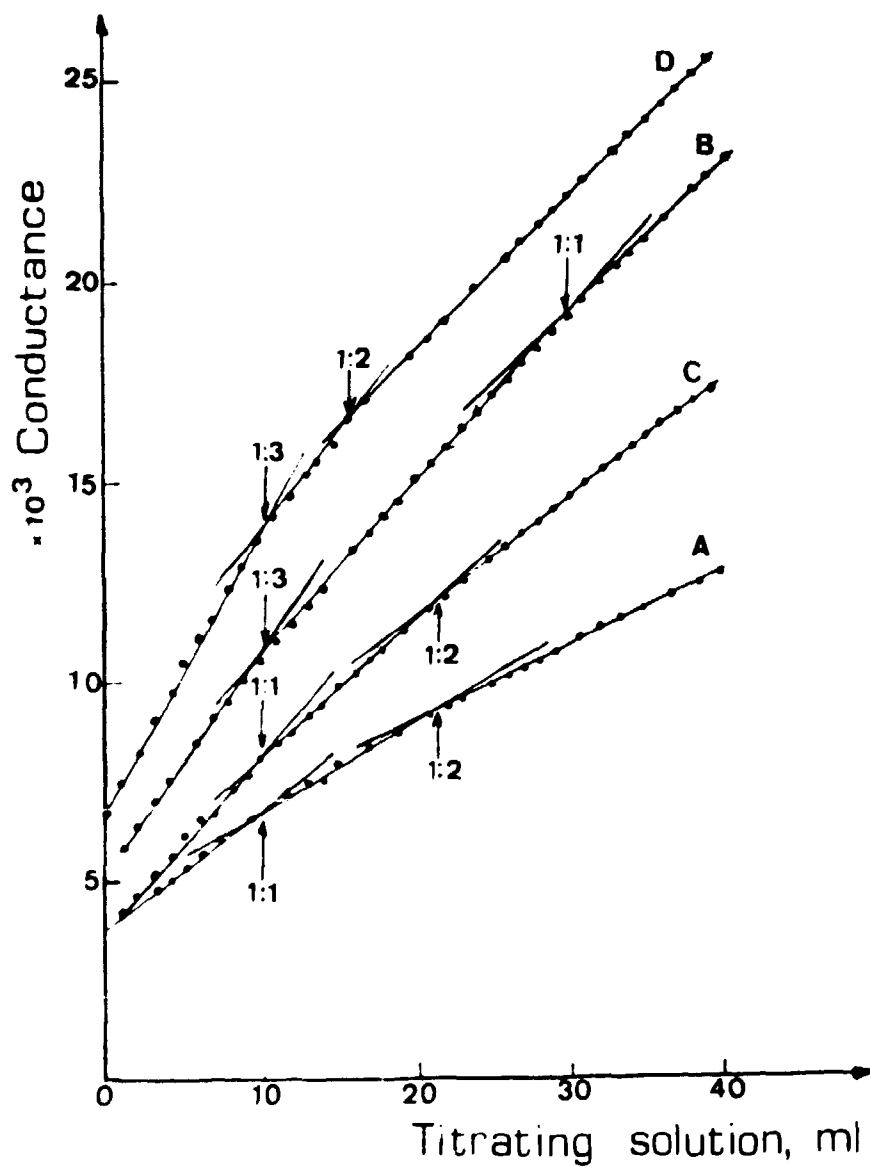Dedimethylaminotetracycline (DTC)

**Figure 6** — Conductimetric titrations of TC an ATC. Curves A and C — 10ml of 0.010M LaCl₃ + 20ml of water. Titrating solutions: 0.010M TC (A) and 0.10M ATC (C). Curves B and D — 30ml of 0.010M TC solution (B); 30ml of 0.10M ATC solution (D). Titrating solution: 0.010M LaCl₃. TC—tetracycline, ATC — anhydrotetracycline.
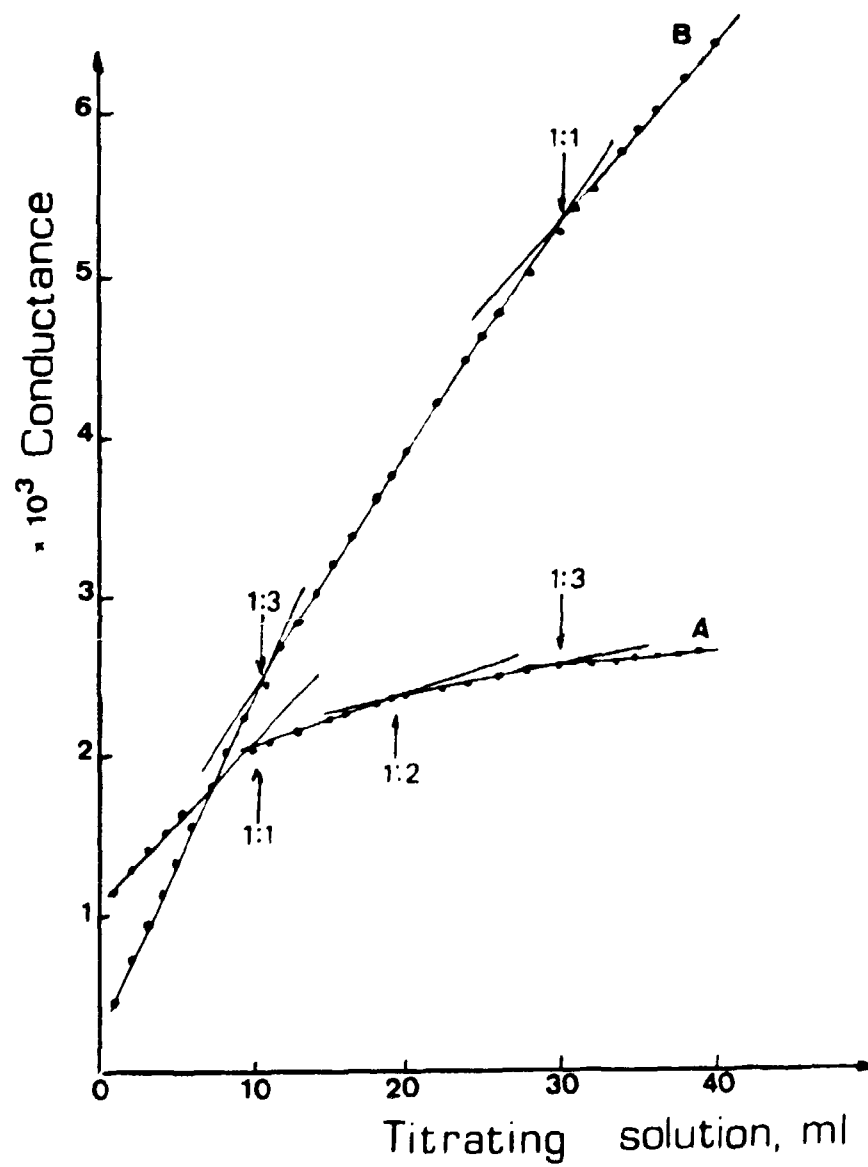
**Figure 7** — Conductimetric titration of DTC. Curves A — 10ml of 0.010M LaCl₃ + 20ml methanol. Titration with 0.010M DTC. B — 30ml 0.010M DTC. Titration with 0.010M LaCl₃. DTC — dedimethylaminotetracycline.
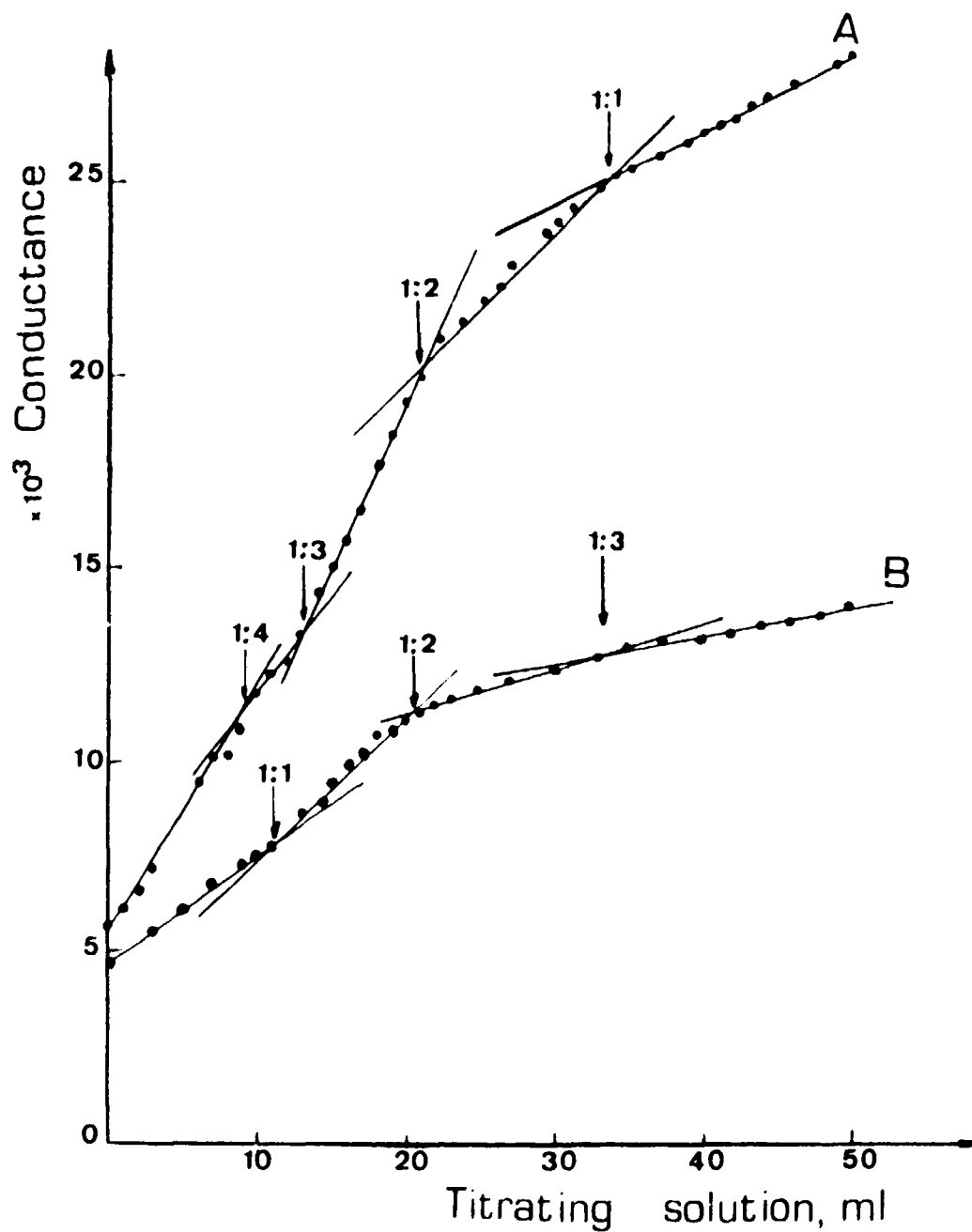
**Figure 8** — Conductimetric titration of TC: A – 40ml 9.2 × 10⁻³M TC + 110ml of water titrated with 0.01M Th(NO₃)₄; B – 10ml of 0.01M Th(NO₃)₄ + 140ml of water titrated with 9.2 × 10⁻³M Th. (in curve B formation of the 1:4 complex is not indicated since solutions corresponding to this proportion are too dilute for detection by the conductometer).

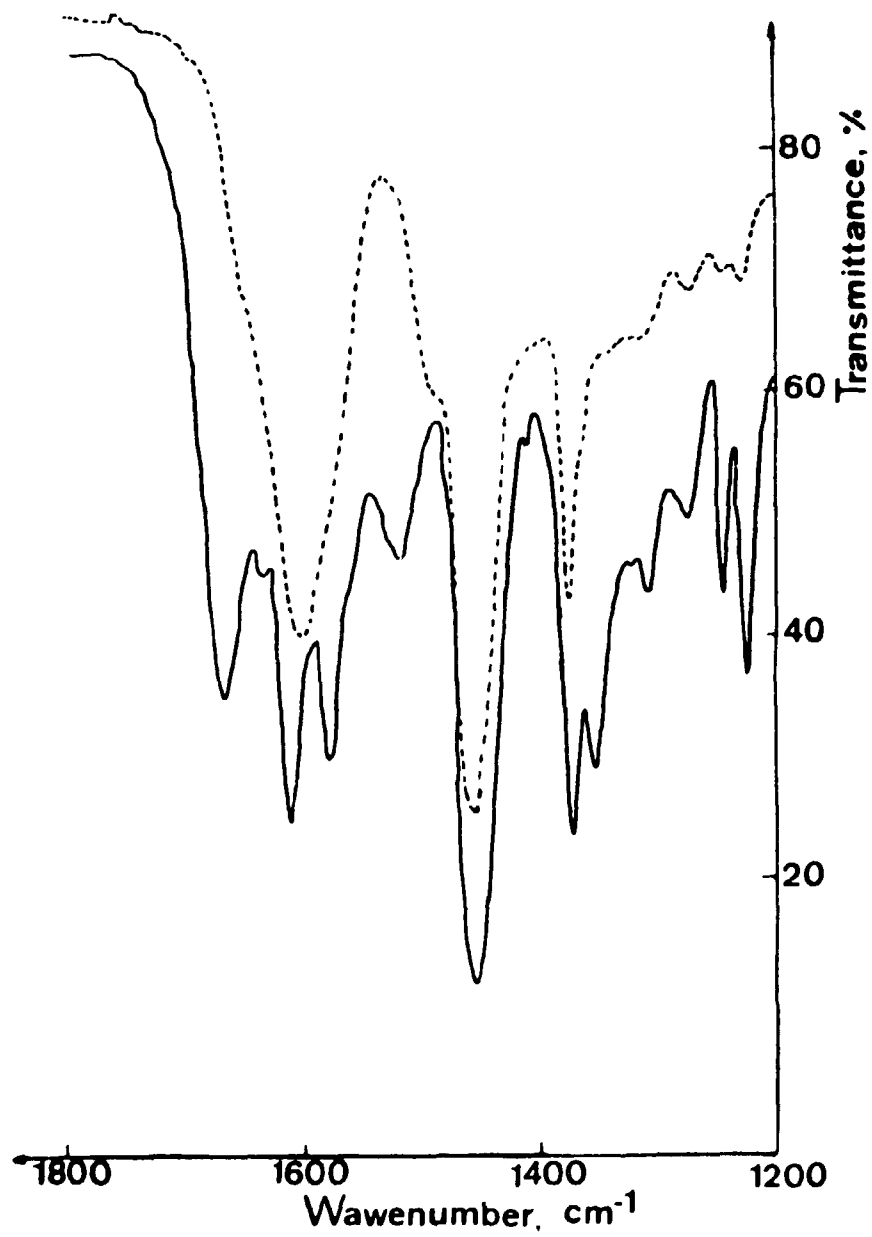**Figure 9 –** Infrared absorption spectrum of TC and La—TC compounds. Curves:TC—full line, La—TC – dotted line.
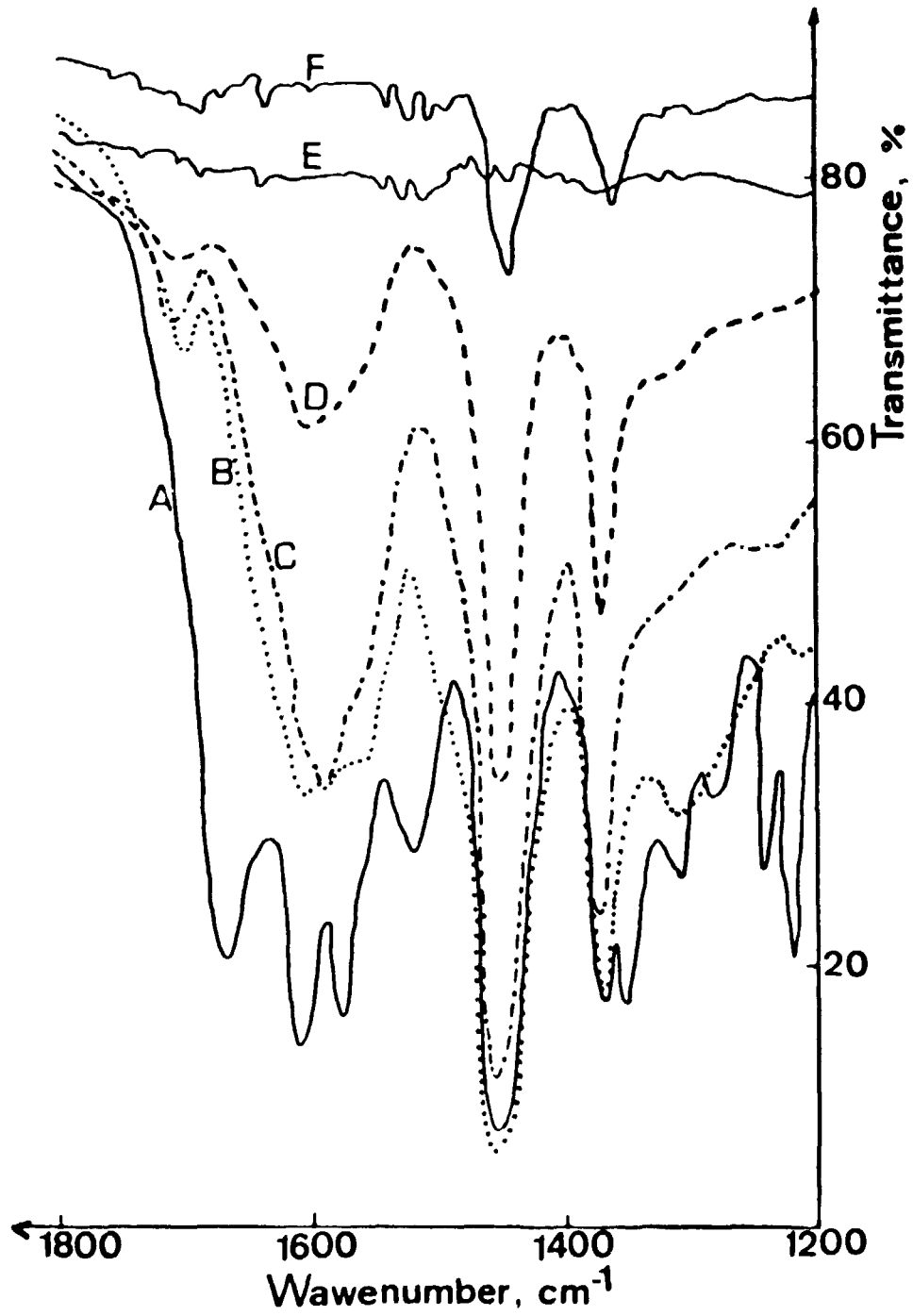
**Figure 10** — Infrared absorption spectrum of Th–TC compounds: A — TC; B — Th(TC); C — Th(TC)$_2$;
D — Th(TC)$_4$; E — KBr cells; F — Nujol oil.

Based on all information obtained from potentiometric and conductimetric titrations for TC, ATC and DTC, as well as the information from the absorption spectra in the infrared region for the solid for the solid compounds La-TC and Th-TC, prepared in accordance with the method of Baker and Brown[6], it is seen that the complexation of the lanthanides and of thorium occurs through the hydrogen position of the tricarbonylmethane group in the TC molecule whose ionization constant is $10^{-3.39}$, that is $pK_1 = 3.39$, at 25°C and ionic strength of 0.10M in $NaClO_4$.

Williamson and Everett[28] have also shown, by nuclear magnetic ressonance, that the trivalent ions $Nd^{+3}$, $Tb^{+3}$, $La^{+3}$, $V^{+3}$ and the bivalent ones $Cu^{+2}$, $Mn^{+2}$, $Co^{+2}$ $Ca^{+2}$ and $Mg^{+2}$ are linked to the TC molecule by the tricarbonylmethane group.

## I.2 — Stability Constants Calculation

To calculate stability constants the following correlation was used:

$$D = I_o/I_a = K_D \beta_N |A|^N / \sum_{n=0}^{N} \beta_n |A|^n \tag{1}$$

where

$D$ — distribution ratio of metal M;

$I_o, I_a$ — activities of the tracer in the organic and aqueous phases, respectively;

$K_D$ — distribution constant of the complex $MA_N$;

$A$ — concentration of the ligand ion in the aqueous phase;

$N$ — valence of metal;

$\beta_n (n = 1,2 \ldots N)$ — formation constants for the complexes $MA_n$ (charges are omitted for simplicity).

By using labelled radioelements the concentrations of the metal to be extracted (tracer plus carrier) can be made much smaller than the initial concentration of the ligand. The amount of ligand in the complex molecule can thus be neglected and the concentration of free ligand TC, $|A|$, was calculated by means of the following equations[21]:

$$pA = pK_1 - pH - \log C_o V_o/(1 + D'V_o V^{-1}) (1 + K_1 |H|^{-1})V \tag{2}$$

where

$V_o$ and $V$ — volumes of organic and aqueous phases, respectively;

$C_o$ — initial concentration of TC in the organic phase;

$D'$ — distribution ratio for the ligand. $(D' = |HA|_o/(|A| + |HA|)$; $D'$ values are presented in Reference 21.

$K_1$ — first dissociation constant of TC.

The formation or stability constants of lanthanides and thorium with TC were determined by the methods of average number of ligands, two parameters and least squares; for thorium the limiting value was also applied, besides the three ones mentioned[21,24].

General correlations used for calculating the stability constants were presented in References (21) and (24).

Values of stability constants for $Ln(TC)_n$ complexes are presented in Tables II, III and IV; for $Th(TC)_n$ complexes they are presented in Table V.

## TABLE II

Stability Constants for the Complexes of Lanthanides With
Tetracycline Determined by the Average Number Method

| Element | $\log \beta_1$ | $\log k_2 . k_3$ | $\log \beta_3$ |
|---|---|---|---|
| La | 2.82 | 6.08 | 8.90 |
| Ce | 3.10 | 6.32 | 9.42 |
| Pr | 3.59 | 6.52 | 10.11 |
| Nd | 3.62 | 6.22 | 9.84 |
| Sm | 3.45 | 6.78 | 10.23 |
| Eu | 3.53 | 6.38 | 9.91 |
| Gd | 3.60 | 6.64 | 10.24 |
| Tb | 3.78 | 6.81 | 10.59 |
| Dy | 3.72 | 6.82 | 10.54 |
| Ho | 3.53 | 6.88 | 10.41 |
| Er | 3.71 | 7.01 | 10.72 |
| Tm | 3.99 | 6.77 | 10.76 |
| Yb | 4.26 | 6.69 | 10.95 |
| Lu | 4.20 | 6.22 | 10.42 |

$[NaClO_4] = 0.10M$, temperature $= 25.0 \pm 0.5\,^{\circ}C$

The constants $\beta_n$ and $k_n$ are expressed in units corresponding to $(litre)^n/(mol)^n$ and $(litre)/(mol)$ respectively.

## TABLE III

Stbility Constants for the Complexes of Lanthanides With
Tetracycline Determined by the two Parameters Method

| Element | $\log \beta_1$ | $\log \beta_2$ | $\log \beta_3$ |
|---|---|---|---|
| La | 2.95 | 6.90 | 8.85 |
| Ce | 3.10 | 6.20 | 9.30 |
| Pr | 3.25 | 6.50 | 9.75 |
| Nd | 3.20 | 6.40 | 9.60 |
| Sm | 3.30 | 6.60 | 9.90 |
| Eu | 3.35 | 6.70 | 10.05 |
| Gd | 3.35 | 6.70 | 10.05 |
| Tb | 3.45 | 6.90 | 10.35 |
| Dy | 3.45 | 6.90 | 10.35 |
| Ho | 3.50 | 7.00 | 10.50 |
| Er | 3.65 | 7.30 | 10.95 |
| Tm | 3.70 | 7.40 | 11.10 |
| Yb | 3.55 | 7.10 | 10.65 |
| Lu | 3.50 | 7.00 | 10.50 |

## TABLE IV

Stability Constants for the Complexes of Lanthanides With
Tetracycline Determined by the Least Squares Method

| Element | log $\beta_1$ | log $k_2 \cdot k_3$ | log $\beta_3$ |
|---------|---------------|---------------------|----------------|
| La | 3.50 ± 0.16 | 5.84 ± 0.26 | 9.35 ± 0.22 |
| Ce | 3.31 ± 0.24 | 6.16 ± 0.30 | 9.47 ± 0.22 |
| Pr | 2.86 ± 0.12 | 7.45 ± 0.24 | 10.32 ± 0.18 |
| Nd | 2.92 ± 0.38 | 6.67 ± 0.41 | 9.59 ± 0.15 |
| Sm | 2.81 ± 0.77 | 7.20 ± 0.78 | 10.01 ± 0.14 |
| Eu | 3.97 ± 0.14 | 5.93 ± 0.38 | 9.90 ± 0.37 |
| Gd | 3.79 ± 0.14 | 6.53 ± 0.17 | 10.32 ± 0.13 |
| Tb | 3.78 ± 0.19 | 6.73 ± 0.23 | 10.52 ± 0.15 |
| Dy | 2.70 ± 0.59 | 7.72 ± 0.59 | 10.43 ± 0.06 |
| Ho | 3.53 ± 0.33 | 7.26 ± 0.33 | 10.79 ± 0.12 |
| Er | 3.73 ± 0.21 | 7.14 ± 0.22 | 10.87 ± 0.11 |
| Tm | 4.26 ± 0.10 | 6.78 ± 0.12 | 11.05 ± 0.08 |
| Yb | 3.55 ± 0.35 | 7.33 ± 0.44 | 10.88 ± 0.27 |
| Lu | 4.48 ± 0.09 | 6.36 ± 0.11 | 10.84 ± 0.11 |

## TABLE V

Stability Constants for the Complexes of Thorium with
Tetracycline

| Method | log $\beta_1$ | log $\beta_2$ | log $\beta_3$ | log $\beta_4$ | $K_D$ |
|--------|---------------|---------------|---------------|---------------|-------|
| Two parameters | 7.3 | 13.8 | 19.5 | 24.4 | — |
| Limiting value | 7.1 | 13.5 | 18.5 | 24.0 | 500 |
| Average number | 7.6 | 14.1 | 19.6 | 24.6 | — |
| Least squares | 7.0 ± 0.4 | 14.2 ± 0.3 | 18.9 ± 0.5 | 24.6 ± 0.3 | 507 ± 46 |

$[NaClO_4] = 0.10M$, temperature $= 25.0 \pm 0.5\,^{\circ}C$.

For $Ln(TC)_n$ complexes the calculation of $\log \beta_2$ by the least squares method, was not performed by the computer program since the value of $a_2$ [*] was rejected by the program as a consequence of a too large standard deviation for $a_2$. A new set of values for $a_0$, $a_1$ and $a_3$ was recalculated and in this way instead of $\beta_2$ values, the product $k_2 \cdot k_3$ (product of consecutive equilibrium constants) is reported. The omission of the $a_2$ parameter would not mean that the corresponding complex does not exist, but only that the stability constant cannot be calculated because of uncertainties in the corresponding experimental data, probably because the concentration of $MA_2$ is not high enough to influence the measurements.

Also, application of the method of average number of ligands to calculate $\beta_2$ values for lanthanides complexes resulted in values with negative signs for $\beta_2$. The difficulty found in the

[*] Note $y = \sum_{n=0}^{N} a_n |A|^n$

$$y = D^{-1} |A|^N \quad \text{and} \quad a_n = \beta_n / K_D \beta_N$$

(3)

calculation of $\beta_2$ by this method and by the least squares method, may support the conclusion that the calculation of this value, by the method of two parameters, might be dubious, the reason being the same, that is, the concentration of $MA_2$ would be rather small. The stability constants of $Th(TC)_n$ complexes presented in Table V show that a good agreement is found for all four methods.

Figure 11 presents the experimental values of log D versus pA (dots) as well as the calculated curves for log D using the calculated formation constants values. It is seen that the constants calculated by the two-parameters method give a curve that is mostly displaced from the experimental poinds, comparatively to the three other methods. This displacement can be explained considering that the two-parameters method gives only approximate values for the constants, since the correlations used for calculations are exact only if there are at most two chemical species present and if the ratio of two consecutive constants $k_n$ is tne same[27].
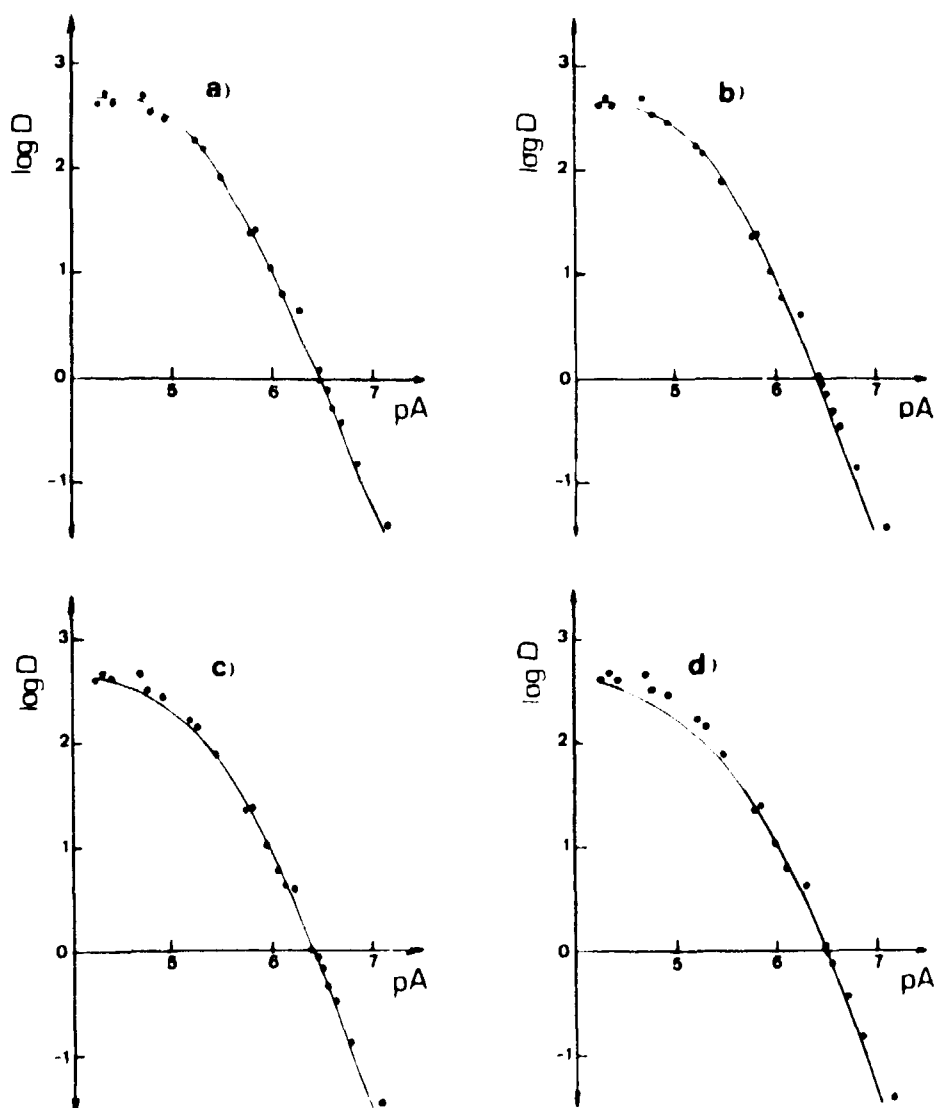


**Figure 11** — Distribution ratio of Th versus pA. Dots represent experimental values and the curves are calculated values using constants obtained by the four methods: a) least squares; b) limiting value; c) average number; d) two-parameter.

## II — SEPARATION STUDIES

### II.1 — Extraction Behavior of the Lanthanide Elements

Preliminary experiments had shown that the presence of a salting-out agent such as NaCl, at a concentration equal to 1.0M, would greatly enhance the metal extraction at any given pH, Table VI.

### TABLE VI

Percent Europium Extracted (%E) in the Presence or Absence of Sodium Chloride

| pH | %E | |
|---|---|---|
| | NaCl 1.0M | 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.

The dependence of extraction of the lanthanides on hydrogen ion concentration, using NaCl 1.0M as supporting electrolyte, was studied between pH 1.50 and 3.50. Figure 12 presents the extraction curves for the lanthanides. Only those corresponding to lutetium, neodymium, praseodymium, cerium and lanthanum are presented since the curves for the elements promethium through ytterbium are too close one to the other.
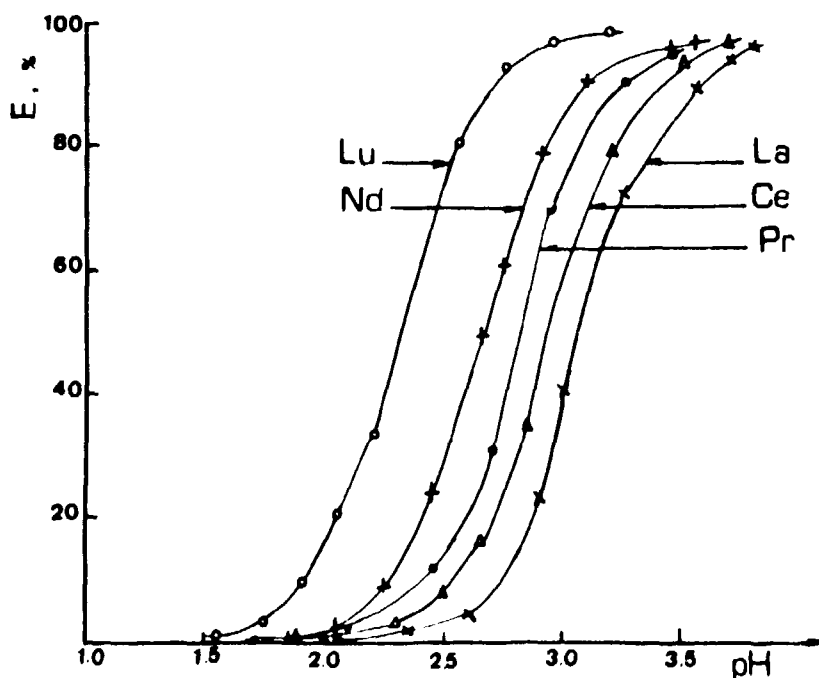


**Figure 12**   Extraction curves for the lanthanide elements. Concentration of tetracycline solution: $10^{-2}$M. Concentration of metal ions = $10^{-5}$M, NaCl = 1.0M.

The dependence of the extraction of the lanthanides on tetracycline concentration was studied for a tetracycline concentration range varying from $1.25 \times 10^{-3}$M to $20.0 \times 10^{-3}$M. In this case the pH value at which each set of experiments for a specific lanthanide was carried out, was held constant. The least squares method was used to determine the slopes of the plots of log D versus pH and of log D versus tetracycline concentration for each of the lanthanides. The values obtained are shown in Table VII and VIII, respectively.

## Table VII

Slopes of the Lines $\log D = a\,pH + b$ for the Lanthanide Elements

| Element | 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 | 2.46 | 2.45 | 2.61 | 2.37 |
| $\sigma a$ | 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 |
| 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 |

$\sigma a$: Standard Deviation of a.
c.c.: Correlation Coefficient.
[TC] = 0.010M
Ionic strenght: 1.0M (NaCl)
Lanthanide concentration: $10^{-5}$M.

## Table VIII

Slopes of the Lines: $\log D = a \log |TC| + b$ for the Lanthanide Elements

| Element | 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 |
| pH | 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 |
| $\sigma a$ | 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 |

$\sigma a$: 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 $1.25 \times 10^{-3}$M to $20.0 \times 10^{-3}$M.
Lanthanide concentration: $10^{-5}$M.
Ionic strength: 1.0M (NaCl).

Since hydrolysis of the lanthanide elements is not likely to occur in the pH range in which the partition experiment were carried out and since it has been shown[17] that Cl ions are not co-extracted with the lanthanide-TC complex, the lower than 3 slopes found for the log D versus pH would indicate a step wise formation of the complexes, with the species $(LnTC)^{2+}$ and $(LnTC_2)^+$ present in the aqueous phase together with $Ln^{+3}$ ions.

### II.2 — Multi-Stage Separation of the Lanthanides

From the straight lines log D - f(pH) of each of the lanthanide elements, the distribution ratios, D, for all the lanthanides at any pH value, can be evaluated. The separation factors, $\alpha = D_1/D_2$, of any pair of lanthanides can thus be calculated, giving an indication of the feasibility of separation between the two elements. Separation factors, $\alpha$, for lanthanides, calculated for solutions of pH equal to 2.50 are presented in Table IX.

**TABLE IX**

Separation Factors $\alpha = D_1/D_2$ for the Lantanide Elements

| Element | 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 |

$D_1$ and $D_2$: Distribution ratio for the lanthanides

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

Aqueous phase pH: 2.50

Ionic Strength (NaCl): 1.0M.

Taking into account the values of distribution ratios, D, theoretical distribution curves $T_{n,r}$ (fraction of element present in each tube) as function of the corresponding serial number of the tubes, for various D were drawn for the lanthanides. The theoretical value of the fraction $T_{n,r}$ of the solute present in the $r^{th}$ tube after n transfers is given by Craig[8] as:

$$T_{n,r} = \frac{n!}{r!(n-r)!} \times \frac{D^r}{(D+1)^n}$$ (4)

where

D is the distribution ratio.

The theoretical curves drawn for lanthanum and thulium showed that a 10-step extraction procedure would be enough for separating lanthanum from thulium (separation factor 52.55). A higher number of steps would be necessary for obtaining the separation between praseodymium, europium and ytterbium, since separation factors of 4.05, 5.38 and 21.77 were obtained for the pairs Pr-Eu, Eu-Yb and Pr-Yb, respectively.

Figure 13 presents the theoretical and experimental distribution curves for lanthanum and thulium. It shows that these two elements were completely separated in a 10-step extraction experiment. Figure 14 shows that a 23-step process yielded a complete separation of praseodymium from ytterbium. However, a higher number of steps would be necessary in order to obtain complete separation of europium from praseodymium 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 experimental curves was not met, their agreement is seen to be rather fair. Brown et al.[7] have also found a shifting of the experimental curv : relatively to the theoretical ones when studying the countercurrent extraction of the rare earth acetylacetonates.
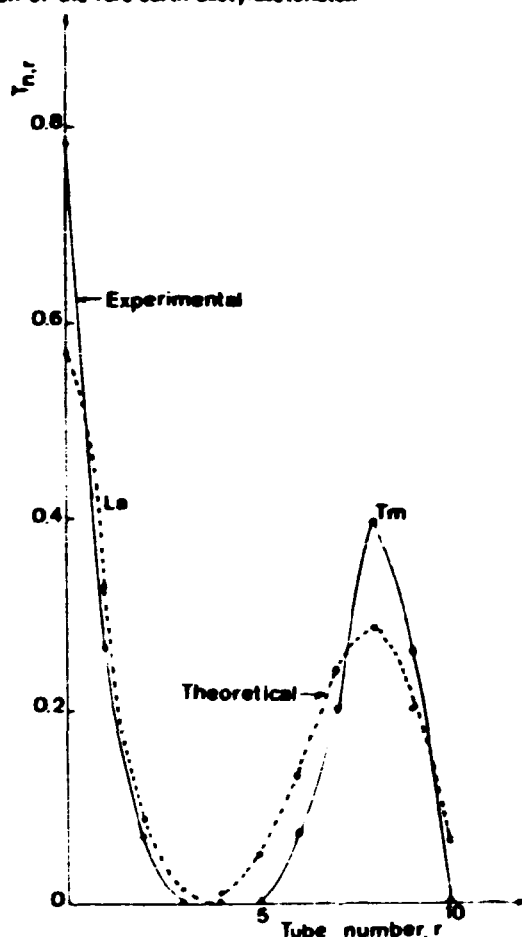


**Figure 13** — Distribution curves for lanthanum and thulium for a 10-step countercurrent extraction process. Concentrations of metal ~ $10^{-5}$M, TC = $10^{-2}$M and NaCl = 1.0M. pH of aqueous phase = 2.50.
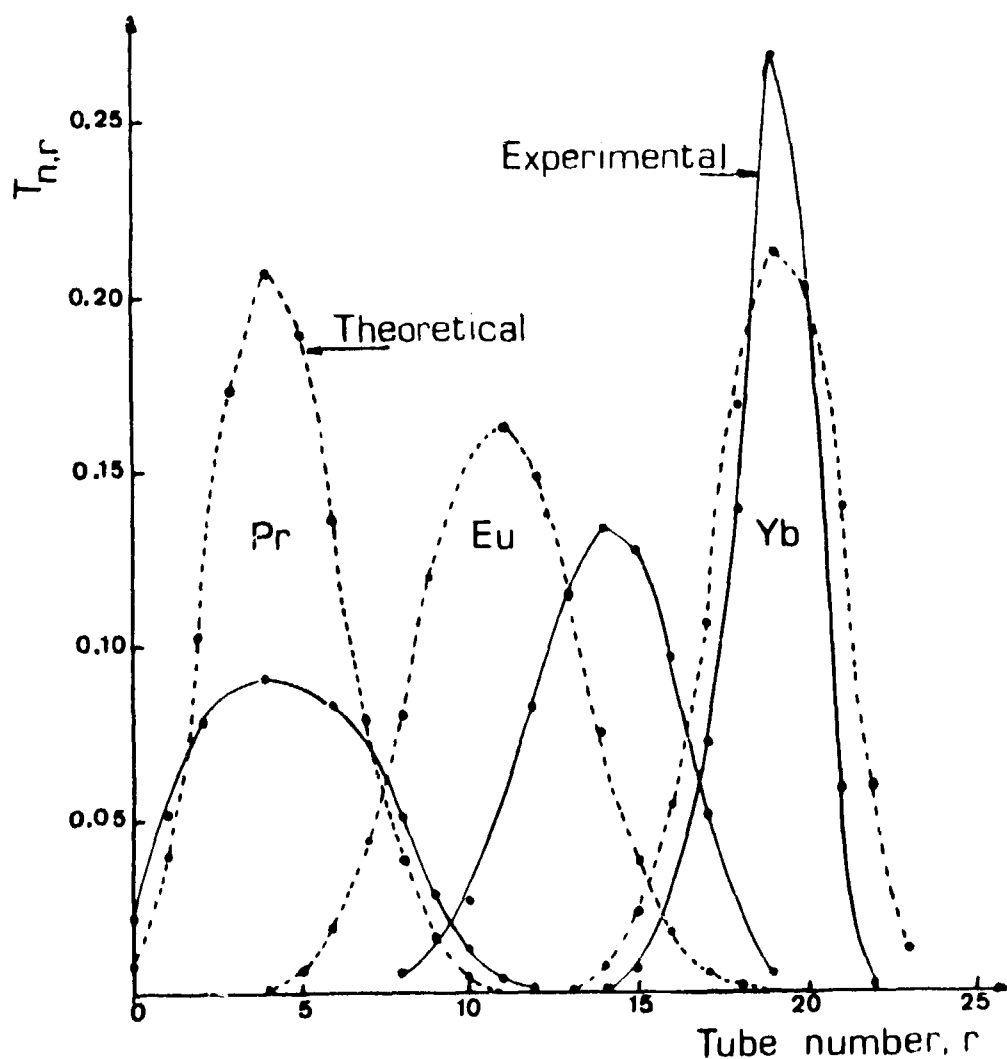
**Figure 14** — Distribution curves for praseodymium, europium and ytterbium for a 23-step countercurrent extraction process. Concentration of metal $\sim$ $10^{-5}$M, TC = $10^{-2}$M, and NaCl = 1.0M, pH of aqueous phase = 2.50.

## II.3 — Separations Based on the Choice of pH

### II.3.1 — Separation of Neptunium from Uranium

Figure 15 shows the extraction curves for uranium and neptunium. It can be seen that in this case it is rather simple to obtain separation between uranium and neptunium by a proper choice of the pH value at which the extraction procedure is to be carried out. From Figure 15 it can be seen that neptunium can be isolated from irradiated uranium if the extraction operation is carried out a pH = 1.7, for instance. To demostrate the effectiveness of such separation procedure an extraction experiment was carried out in which the aqueous phase consisted of a solution made up by dissolving $U_3O_8$ irradiated for 8 hours with epithermal neutrons and let to cool for 16 hours in order that $^{239}$Np could grow. NaCl was used as the salting-out agent. Table X shows the results.
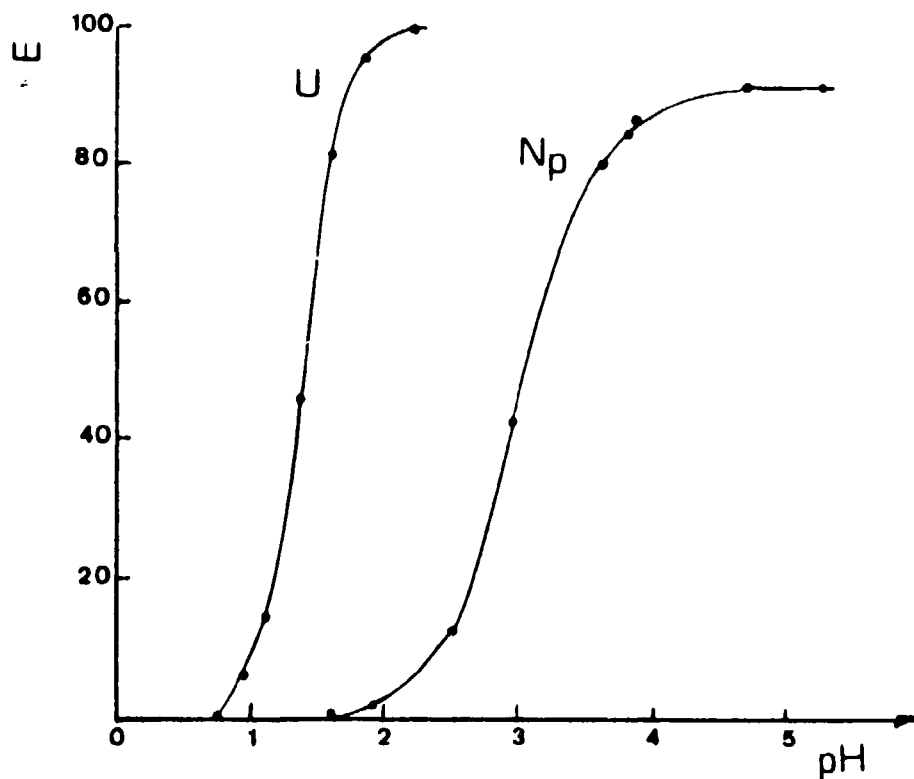
**Figure 15** — Extraction curves of U and Np. Concentration of NaCl = 1.0M, TC = $10^{-2}$ M, U = 5 x $10^{-5}$ and $^{239}$ Np carrier free.

**Table X**

Separation of Neptunium From Uranium

| Equilibrium pH | Percent Metal in Organic Phase | |
|---|---|---|
| | U | Np |
| 1.90 | 96 | 2.5 |
| 2.00 | 97 | 5.0 |
| 2.50 | 99 | 10 |
| 4.35 | 97 | 95 |
| 4.70 | 98 | 95 |

[U]   = $10^{-5}$ M
[TC]  = 0.010M
[NaCl] = 1.0 M

Extraction conditions are described at length in reference 16.

### II.3.2 – Separation of Scandium from Zinc

Figure 16 shows the extraction curves for zinc and scandium into TC-benzyl alcohol solutions and Table XI shows the numerical results for a separation experiment. From Figure 16 it can be seen that if the extraction operation is performed at a pH of about 2.5, a good separation between scandium and zinc is obtained with the former being extracted and the latter element remaining in the aqueous phase.
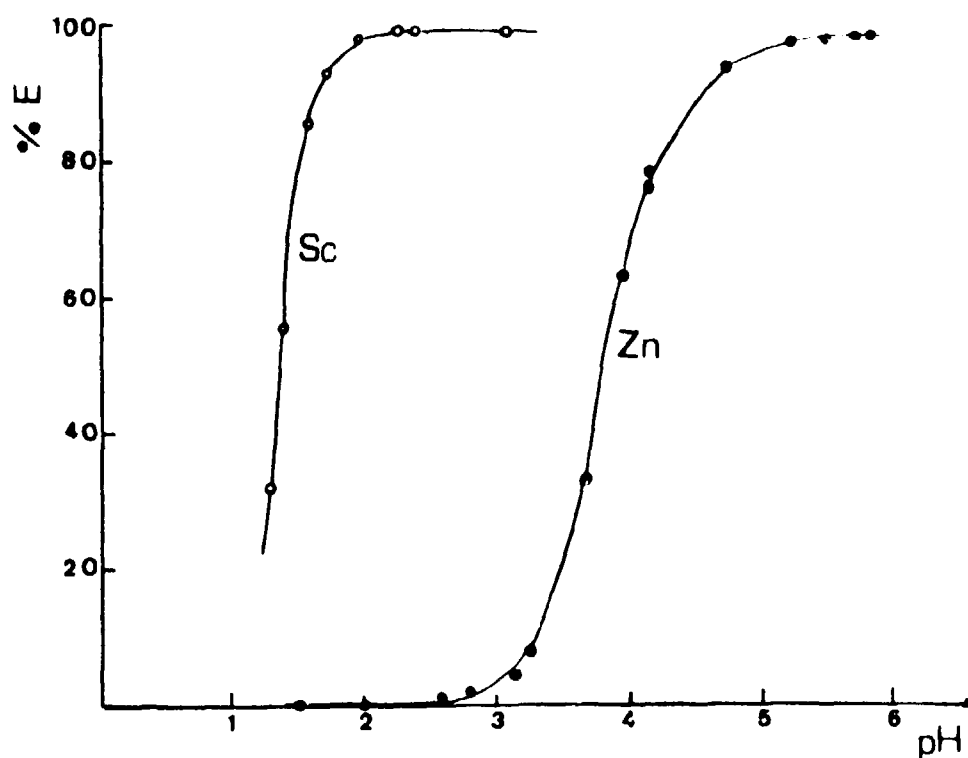


**Figure 16** – Extraction curves for scandium and zinc. Concentration of $Sc = 1.0 \times 10^{-5}M$, $Zn = 1.0 \times 10^{-4}M$, $NaClO_4 = 0.10M$ and $TC = 0.01M$.

### Table XI

Separation of Scandium from Zinc

| Scandium | | Zinc | |
|---|---|---|---|
| pH | %E | pH | %E |
| 2.45 | 94.6 | 2.45 | 1.7 |
| 2.55 | 97.3 | 2.55 | 2.2 |
| 2.95 | 97.6 | 2.75 | 3.1 |

Concentrations:
$[TC] = 0.010M$; $[Sc] = 10^{-5}M$; $[Zn] = 8 \times 10^{-5}M$; $[NaClO_4] = 0.10M$.

**II.4 — Separation Based on the Addition of Masking Agent to the Extraction System.**

**II.4.1 — Separation of Uranium from Scandium and Lanthanides**

Previous experiments had shown that in the absence of tetracycline, uranyl ions, lanthanides and scandium ions, are not extracted into pure benzyl alcohol(no TC dissolved in the alcohol), as well as the EDTA complexes of lanthanides and scandium ions. Uranyl-EDTA complexes are practically nonexisting.

Figure 17 shows the extraction curves for scandium, uranium, thulium, europium and lanthanum obtained for the extraction system TC-benzyl alcohol. It can be seen in Figure 17 that separation of uranium from scandium, thulium, europium and lanthanum would only be possible by use of a multi-stage extraction procedure.
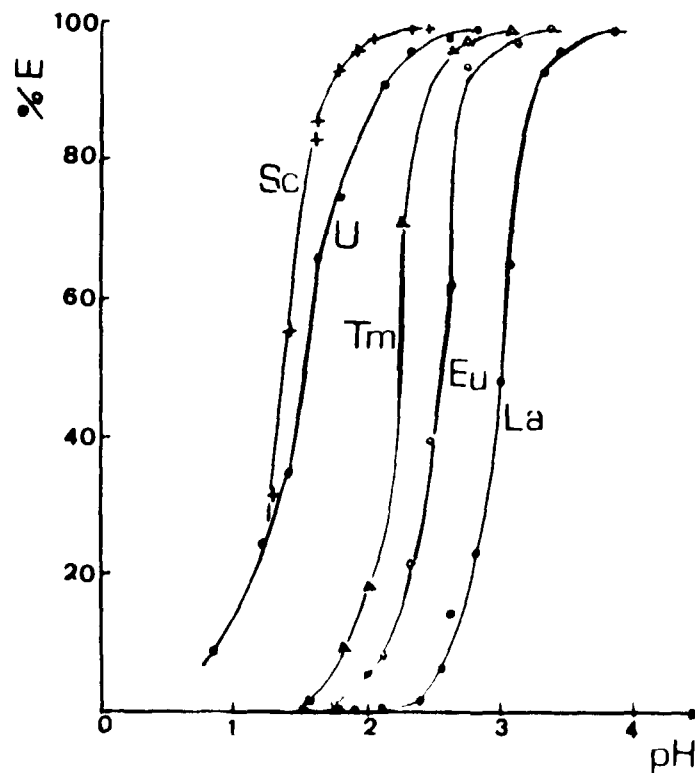


Figure 17 — Extraction curve for U, Sc and lanthanide elements without masking agent. Concentration of $NaClO_4 = 0.10M$, $U = 7.0 \times 10^{-5}M$, $TC = 0.010M$, $Sc = 1.0 \times 10^{-5}M$ and lanthanides from $10^{-4}$ to $10^{-5}M$.

However, masking of scandium and tetracycline reaction as well as lanthanides and tetracycline reaction with EDTA, with the formation of non-extractable Sc-EDTA and lanthanide-EDTA complexes, gives an excellent separation of uranium from scandium and the lanthanides, Figure 18. In this case uranium is extracted into the organic phase as the uranyl-TC complex while scandium and the lanthanide elements remain in the aqueous phase as non-extractable EDTA complexes. The stability constants for the lanthanide-EDTA and Sc-EDTA complexes[25] are higher than the ones for the lanthanides-TC complexes. Consequently, TC does not displace the lanthanides and scandium from their respective EDTA complexes, which remain in the aqueous phase while uranium is extracted into the organic-phase.
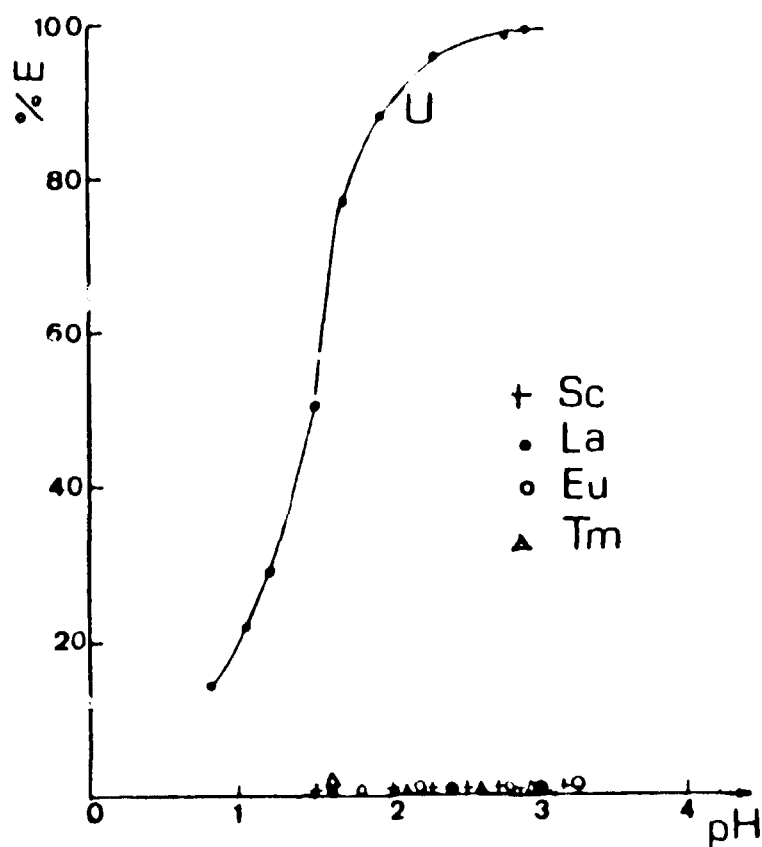
**Figure 18** — Extraction curve for U, Sc and lanthanide elements using EDTA as masking agent. Concentration of $NaClO_4 = 0.10M$, $U = 8.0 \times 10^{-5}M$, $EDTA = 2.5 \times 10^{-3}M$.

**II.4.2 — Separation of $^{233}Pa$ from Thorium**

Figure 19 presents the extraction c···es for uranium, thorium and protactinium. It shows that a single extraction operation will not allow protactinium to be isolated neither from uranium nor from thorium, just by changing the pH of the aqueous phase. Figure 20 shows the extraction curves for thorium and protactinium when NaF is added as masking agent to the extraction system. In this case, masking of Pa-TC reaction by fluoride ions hinders the extraction of protactinium into the organic phase until the pH value of 3.0 is reached. At this pH value thorium extraction has reached its maximum value (95%) while protactinium extraction corresponds to 4.4% only. In this way, the choice of suitable pH value at which the extraction operation is to be carried out for an extraction system to which NaF is added, can yield the separation between protactinium and thorium.
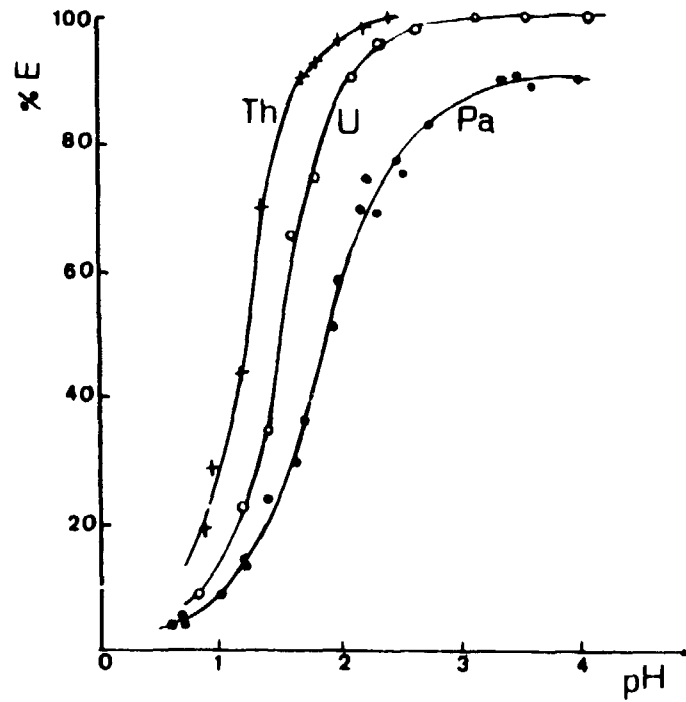
Figure 19 — Extraction curves for thorium, uranium and protactinium. Concentration of TC = 0.010M, Th = 5.0 x $10^{-4}$M, U = 7.0 x $10^{-5}$M and NaClO$_4$ = 0.10M. Shaking time = 30 min. Temperature = 25.0 ± 0.5 °C.
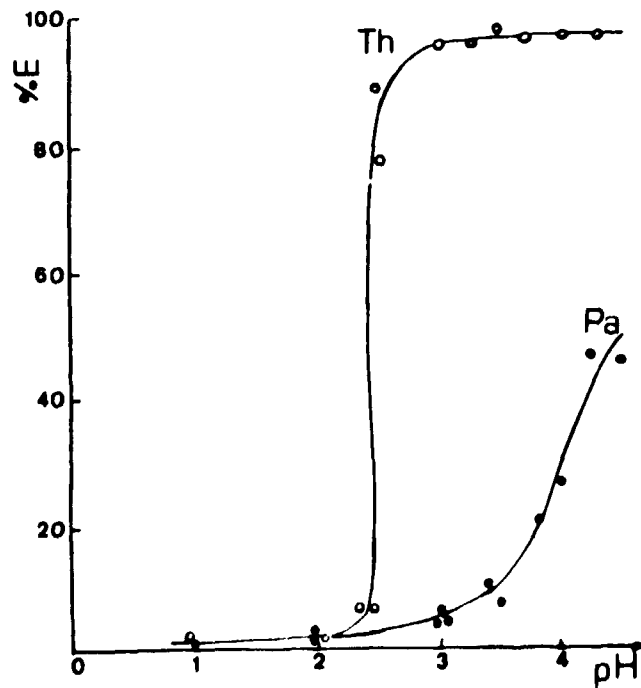


Figure 20 — Extraction curves for thorium and $^{233}$Pa using NaF as a masking agent. Concentration of NaF = 4.9 x $10^{-3}$M, Th = 2.0 x $10^{-5}$M, NaClO$_4$ = 0.10M and TC = 0.010M.

The concentration of masking agent NaF and the concentration of thorium initially present in the extraction system, influence the separation factor value. Such influences are shown in Table XII and XIII, respectively.

Results of Table XIV show that although benzyl alcohol alone does not extract protactinium within the pH range from 0.75 to 3.39, increasing losses of protactinium with increasing pH values were detected for the same pH interval. It is also shown that although no protactinium losses occurred when $10^{-2}$ M TC-benzyl alcohol solutions were used, increasing losses of protactinium were detected as the concentration of TC in benzyl alcohol decreases, Table XV.

## Table XII

Separation Between $^{233}$Pa and Th as Function of

NaF Concentration

| NaF (M) | %E of Th | %E of Pa | Separation Factor |
|---------|----------|----------|-------------------|
| $1.2 \times 10^{-3}$ | 97.0 | 42.7 | 43 |
| $4.9 \times 10^{-3}$ | 95.0 | 4.4 | 430 |
| $1.2 \times 10^{-2}$ | 92.9 | 1.8 | 713 |

$[Th] = 2.0 \times 10^{-5}$ M; pH = 3.0; $[TC] = 0.010$M.

## Table XIII

Separation Between $^{233}$Pa and Th as Function of

Th Concentration

| Th (M) | %E of Th | %E of Pa | Separation Factor |
|--------|----------|----------|-------------------|
| $2.0 \times 10^{-5}$ | 95.0 | 4.4 | 430 |
| $1.1 \times 10^{-4}$ | 93.1 | 8.6 | 143 |
| $2.0 \times 10^{-4}$ | 77.9 | 7.6 | 43 |

$[NaF] = 4.9 \times 10^{-3}$ M; pH = 3.0; $[TC] = 0.010$M.

## TABLE XIV

### Extraction of Protactinium With Pure Benzyl Alcohol and Percentage of Losses (%P)

| pH | %E | %P |
|------|-----|------|
| 0.75 | 1.9 | 2.2 |
| 1.06 | 1.9 | 14.5 |
| 1.67 | 2.5 | 59.1 |
| 2.55 | 2.5 | 52.9 |
| 2.88 | 1.7 | 77.0 |
| 3.39 | 0.8 | 78.1 |

$[Th] = 2.9 \times 10^{-4} M$; $[U] = 5.0 \times 10^{-5} M$;
$[NaClO_4] = 0.10M$; Shaking Time: 30 min,
Temperature $= 25.0 \pm 0.5\,^{\circ}C$.

## TABLE XV

### Percentage of $^{233}Pa$ Losses (%P) as Function of Tetracycline Concentration

| TC (M) | %P |
|--------|------|
| $1 \times 10^{-2}$ | – |
| $4 \times 10^{-3}$ | 1.9 |
| $3 \times 10^{-3}$ | 2.3 |
| $1 \times 10^{-3}$ | 6.5 |
| $5 \times 10^{-4}$ | 16.0 |
| $2.5 \times 10^{-4}$ | 22.0 |
| $1 \times 10^{-4}$ | 58.8 |

pH = 3.30; $[NaClO_4] = 0.10M$.

### II.4.3 — Separation of Uranium from Protactinium and Thorium

As shown in Figure 21 uranium can be isolated from protactinium and from thorium when DTPA is used as masking agent. If prior to the extraction operation carried out with TC-benzyl alcohol, DTPA is added to the aqueous phases containing uranium, thorium and protactinium, only uranium will be extracted into the organic phase, since DTPA will mask thorium and protactinium reactions with tetracycline.

Figure 22 shows the extraction curves for uranium and thorium when EDTA was used as the masking agent. It can be seen in this Figure 22 that masking of the reaction of thorium and tetracycline with EDTA is not effective to prevent thorium extraction together with uranium. However, masking of thorium and tetracycline reaction with DTPA, gives an excellent separation of uranium and thorium, with thorium remaining in the aqueous phase. The pH range at which the amount of thorium extracted is practically nil, lies between 2.0 and 2.6.

Although the stability constant of the complex Th-EDTA is high[25] ($log \beta$ - 23.2) thorium was partially extracted into the organic phase (TC-benzyl alcohol) under the experimental conditions described, indicating a displacement of thorium by TC from the complex Th-EDTA.
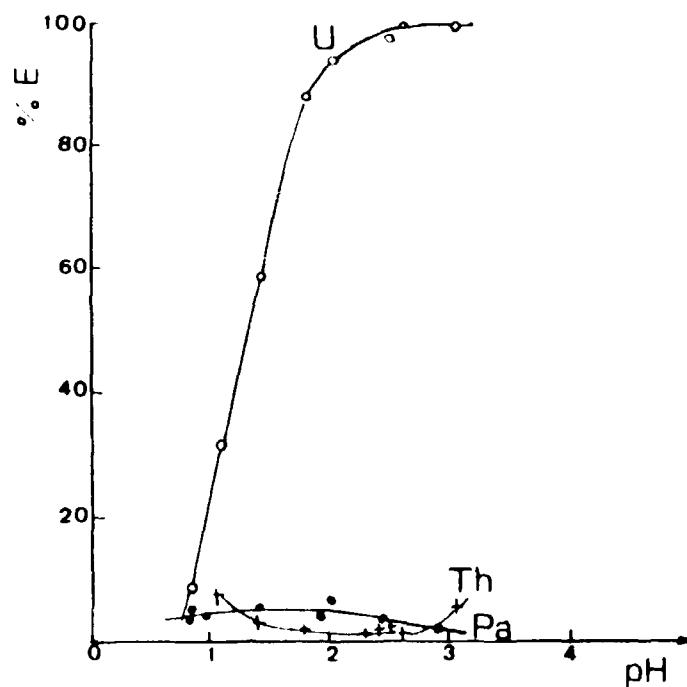
Figure 21 — Extraction curves for uranium, thorium and $^{233}$Pa using DTPA as masking agent. Concentration of DTPA $= 2.5 \times 10^{-3}$M, U $= 7.0 \times 10^{-5}$M, Th $= 5.0 \times 10^{-4}$M and TC $= 0.010$M.
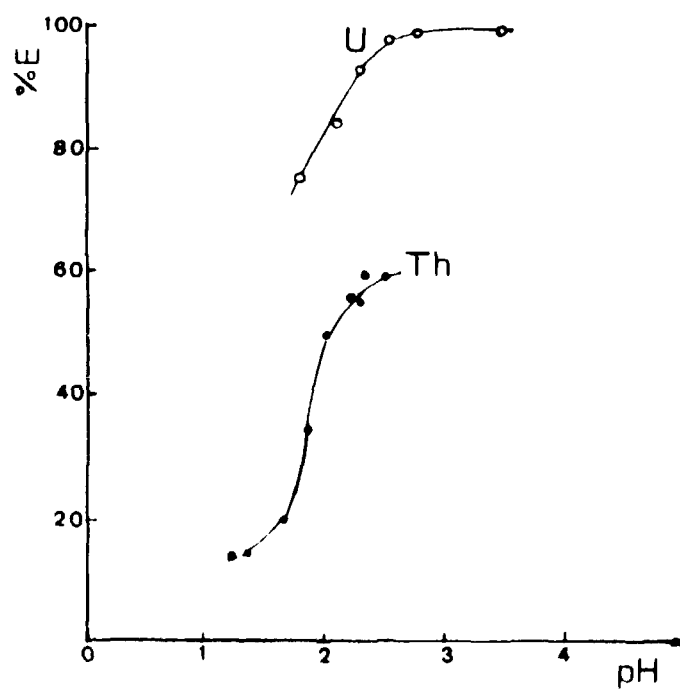


Figure 22 Extraction curves for uranium and thorium using EDTA as a masking agent. Concentration of U $= 6.0 \times 10^{-5}$M, Th $= 5.0 \times 10^{-4}$M, TC $= 0.010$M, EDTA $= 2.5 \times 10^{-3}$M and NaClO$_4 = 0.10$M.

Preliminary experiments had shown that the complexes Th—EDTA, Th—DTPA, are not extracted into pure benzyl alcohol.

The stability constant of Th—DTPA complex is rather high[25] ($\log \beta > 27$) and there is no displacement of thorium by TC in the Th—DTPA complex at pH values between 2.0 and 2.6. Consequently, the extraction of thorium into TC-benzyl alcohol solutions does not take place when DTPA is present.

The amount of uranyl-DTPA complex formed, if any, is very small and the uranyl-TC complex is preferentially formed. The result is that uranium is extracted into the organic phase as the complex uranyl TC and thorium remains in the aqueous phase as the Th-DTPA complex (which is too stable to be broken by tetracycline) allowing in this way, a separation between thorium and uranium.

### II.4.4 – Separation of Uranium from Se, Br, Sb, Ba, Ta, W

The presence of several elements, viz., selenium, bromine, antimony, barium, tantalum and tungsten interfere with the determination of uranium when use is made of epithermal neutron activation analysis, since the radioisotopes of those elements have photopeaks with energies too close to the 74.6 keV $^{239}$U photopeak.

Experiments were carried out to show the usefulness of the extraction system tetracycline-benzyl alcohol in order to isolate uranium from each one of the mentioned elements.

As it is shown in Items II.4.4 a-b-c-d separation of uranium from antimony, tantalum, bromine (as bromide), and selenium (hexavalent state) can be achieved by carrying out the extraction operation at a suitable pH value for each case. Virtually nothing of the interfering elements is extracted while uranium is extracted to an extent of about 99%.

#### a. Separation Uranium-Antimony

Figure 23 shows the separation of uranium from antimony. It is seen that the separation is rather efficient at a pH interval from 4.6 to 6.0. Extraction experiments carried out with buffered solution at pH 5.5 (0.1M sodium acetate and 0.02M acetic acid) have shown that separation of uranium from antimony is complete giving extraction values of 99.5% for uranium and 0.7% for antimony.

#### b. Separation Uranium-Tantalum

In this case fluoride ions are present since tantalum was dissolved with drops of concentrated HF, which partly complexes uranium and prevents a complete extraction of uranium as the uranyl-TC complex until the pH has reached a value above 3.3. Results for separation of uranium from tantalum are presented in Figure 24. It is seen that such a separation is effective at a pH interval from 3.3 to 4.8. Extractions of 99.3% for uranium and 0.3% for tantalum, were obtained when the extraction operation was carried out with a buffered solution at pH 4.50 (0.1M sodium acetate and 0.2M acetic acid).

#### c. Separation Uranium-Bromine

Preliminary experiments showed that bromate ions are extracted directly into benzyl alcohol. However, bromide ions are neither extracted into benzyl alcohol nor into tetracycline-benzyl alcohol solution, making possible the separation of bromine, as bromide ions, from uranium. Figure 25 shows results and conditions for such a separation.
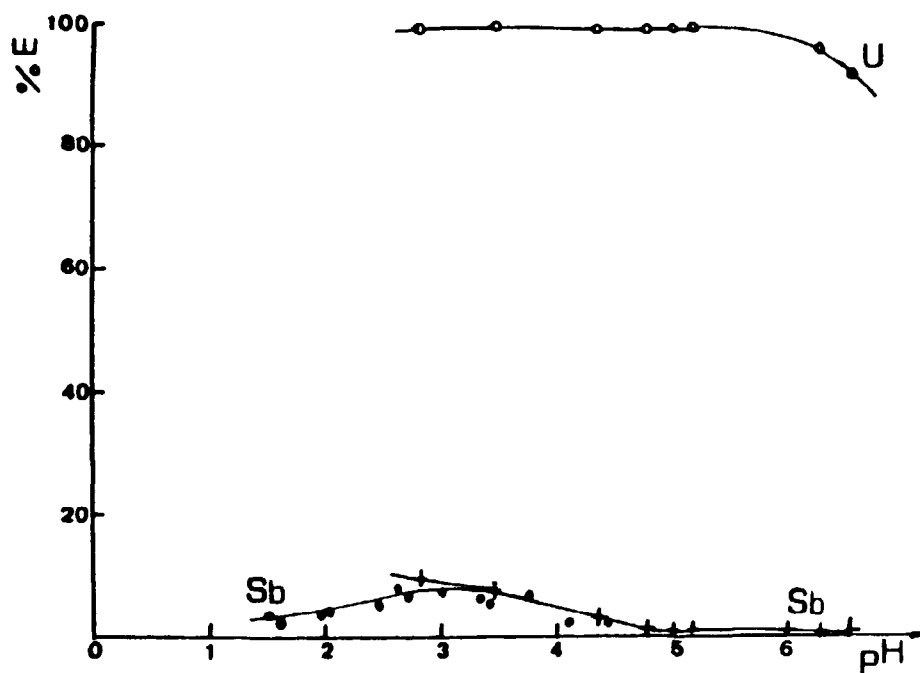
**Figure 23** — Extraction curves for uranium and antimony. (+) — mixture Sb – U; (●) – Sb alone. Concentration of U = 8 x $10^{-5}$ M, Sb= 5 – 17 x $10^{-5}$ M, $NaClO_4$ = 0.10M and TC = 0.010M.



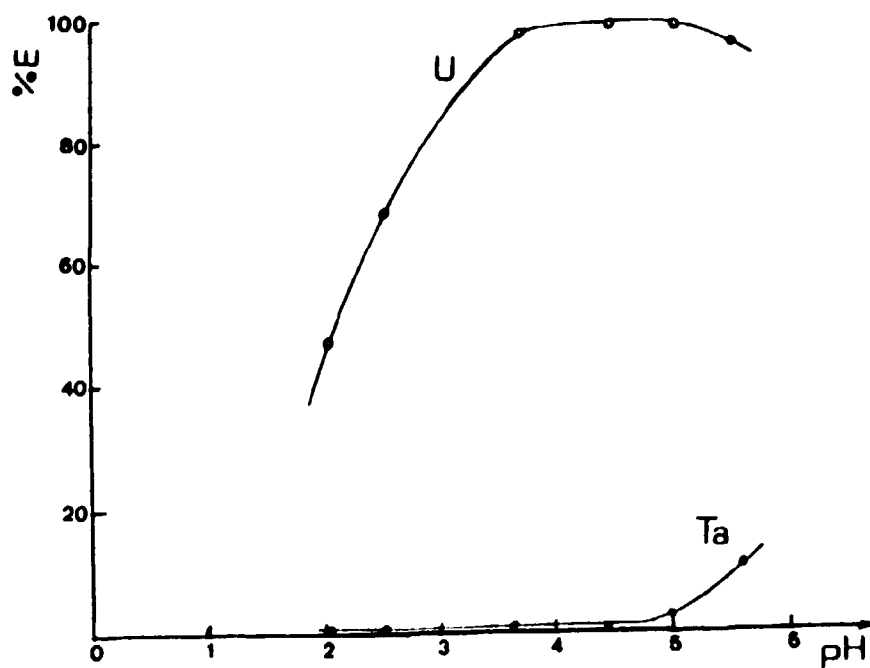**Figure 24** — Extraction curves for uranium and tantalum. Concemtration of U = 8 x $10^{-5}$ M, Ta = $10^{-5}$ M. $NaClO_4$ = 0.10M and TC = 0.010M.
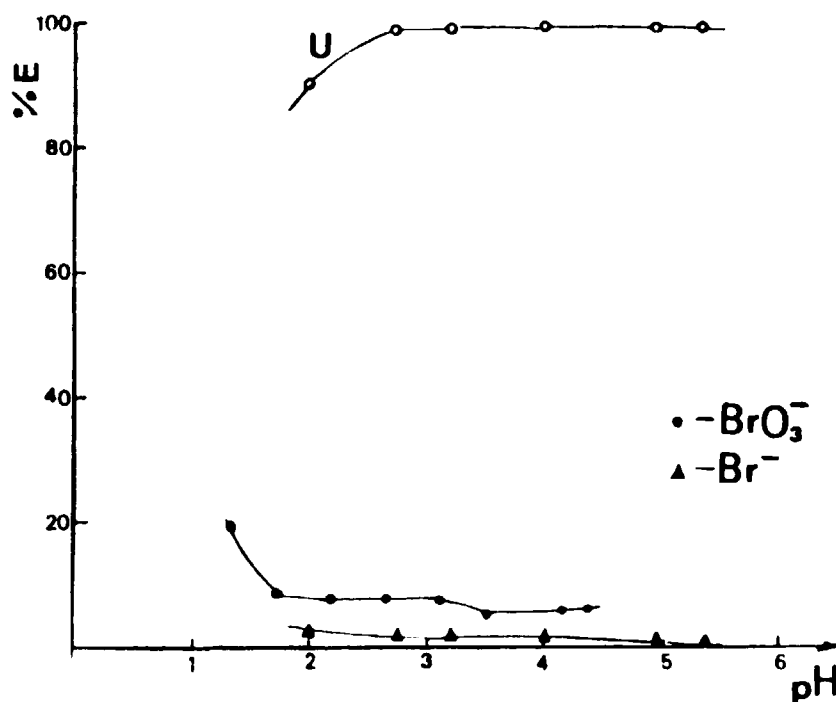
Figure 26 — Extraction curves for uranium and bromine (bromide and bromate). Concentration of U = 8 x 10⁻⁵M, Br = 1.1 x 10⁻⁵M, NaClO₄ = 0.10M and TC = 0.010M.

### d. Separation Uranium-Selenium

Results for the extraction of Se(VI) and Se(IV) are presented in Figure 26. Se(IV) and Se(VI) are both extracted into pure benzyl alcohol, without TC, in the pH interval of 2.0 to 3.0, to the extent of 6 to 15%. However Se(VI) is not extracted into TC-benzyl alcohol organic phase in the pH interval from 4.0 to 5.0. In this way it is possible to separate uranium from selenium using TC-benzyl alcohol, by oxidising Se(IV) to Se(VI) with hydrogen peroxide and carrying the extraction at a pH interval from 4.0 to 5.0. Hydrogen peroxide does not interfere with the extraction of uranium.

By using buffered solution of acetic acid and sodium acetate, at pH = 5.5, the percentage of extraction of uranium and Se(VI) were 97.4% and 2.9%, respectively.

### e. Separation Uranium Barium

In the case of barium, extraction experiments were accomplished with and without addition of the masking agent EDTA. Although the percentage of barium extracted into the organic phase is low (< 5.5%) in the absence of the masking agent, it can be seen in Figure 27 that when EDTA is added to the extraction system, barium is practically totally held in the aqueous phase. The addition of EDTA does not interfere with the extraction of uranium into tetracycline-benzyl alcohol solution.

### f. Separation Uranium-Tungsten

Figure 28 presents the results for the separation of uranium from tungsten, with and without hydrogen peroxide as masking agent for the complexation reaction of tungsten by tetracycline. Hydrogen peroxide will form peroxotungstates which are not extracted into the TC-benzyl alcohol organic phase.
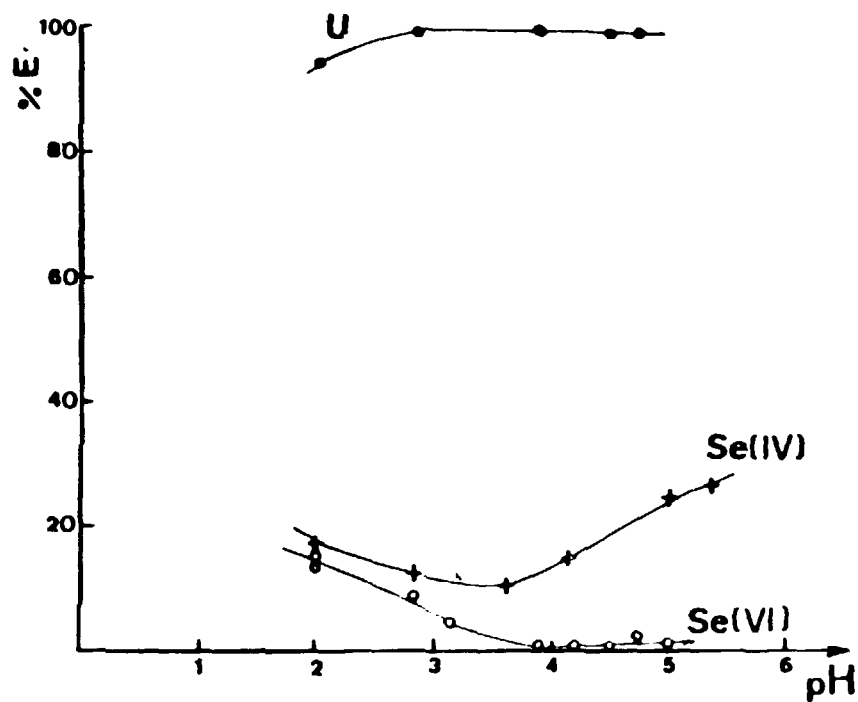
**Figure 26** — Extraction curves for uranium and selenium. Concentration of $U = 8 \times 10^{-5}M$, $Se = 10^{-4}M$, $NaClO_4$ = 0.10M, $H_2O_2$ = 3.15% and TC = 0.010M.
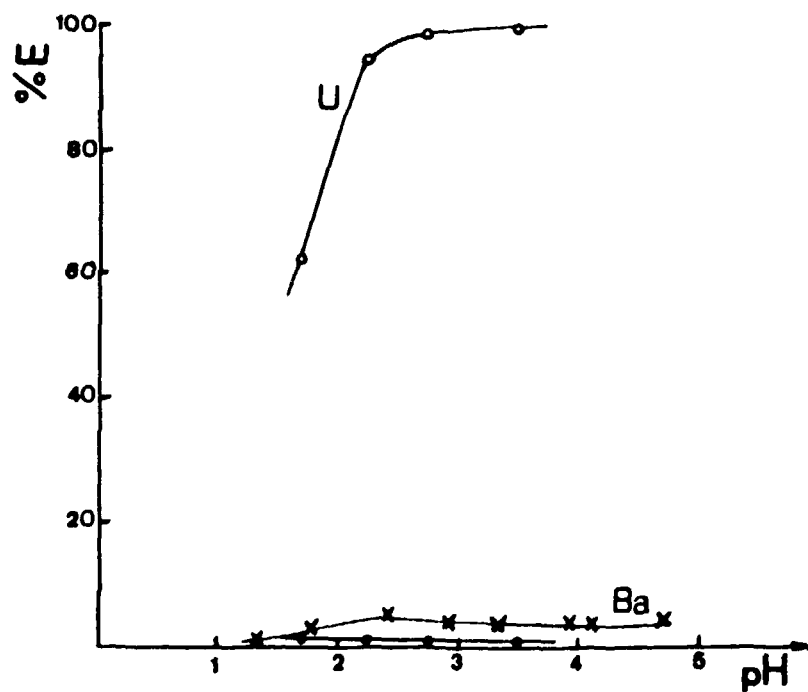


**Figure 27** — Extraction curves for uranium and barium. Concentration of $U = 8 \times 10^{-5}M$, $Ba = 4 \times 10^{-4}M$, EDTA = 2.5 $\times$ $10^{-3}$ and TC = 0.010M. (x) — Ba without masking agents; (●) Ba with EDTA.
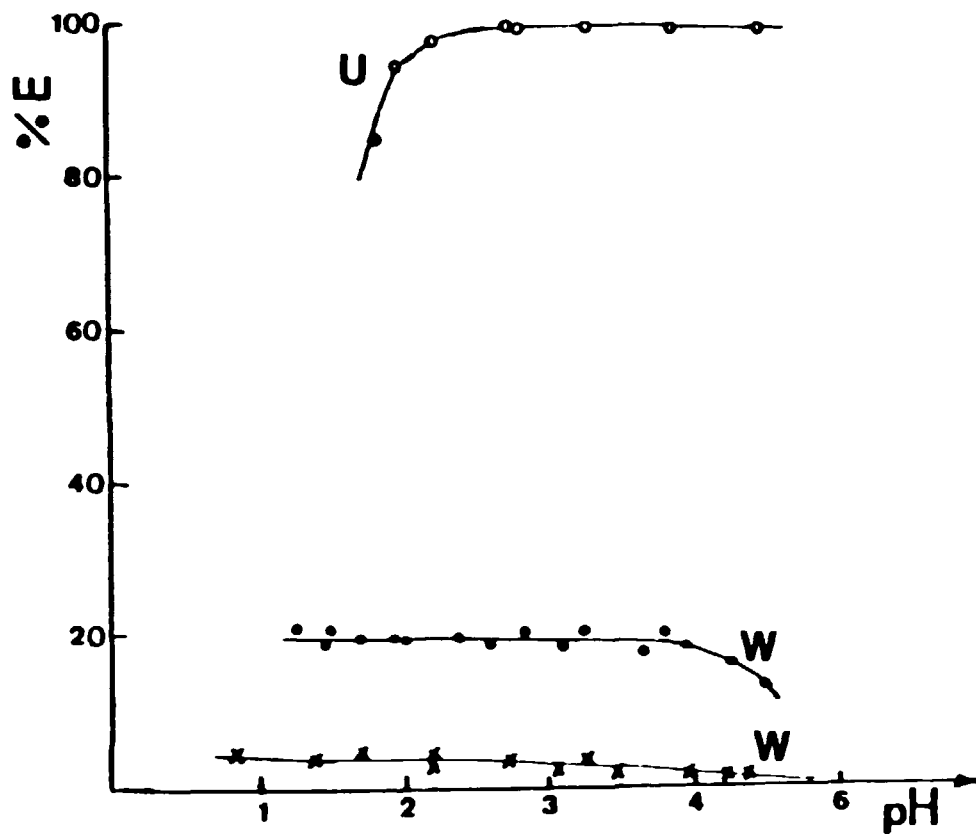
Figure 28 — Extraction curves for uranium and tungsten. Concentration of U = 8 x 10⁻⁵M, W = 10⁻⁴ — — 10⁻⁶M, NaClO₄ = 0.10M, H₂O₂ = 3.15% and TC = 0.010M. (●) tungsten without masking agents, (x) tungsten with H₂O₂.

Figure 29 shows a Periodic Table of the Elements in which are marked the chemical elements that have been studied, in connection with their reactions with TC or its derivatives.

Figure 29 — Elements studied in connection with their reactions with TC or its derivatives.

## ACKNOWLEDGEMENTS

## RESUMO

Constitui o presente trabalho uma revisão dos trabalhos que vêm sendo desenvolvidos na Área de Radioquímica-COURP sobre o complexante tetraciclina, usado em processos de extração com solventes, para várias separações radioquímicas.

Foram obtidas as curvas de extração para os elementos lantanídicos, zinco, escândio, urânio, tório, neptúnio e protactínio. Foram realizadas separações, entre si, de alguns dos elementos mencionados, bem como as separações entre urânio e os elementos seguintes: selênio, bromo, antimônio, bário, tântalo e tungstênio. Em todos os casos foi usada uma solução tetraciclina (TC) em álcool benzílico. Cloreto de sódio foi usado como agente salificante caso das separações dos elementos lantanídicos, e, no caso dos demais elementos, foi usado perclorato de sódio.

Foram determinadas as constantes de estabilidade dos complexos formados entre a tetraciclina e os elementos lantanídicos, e também com o tório. Os métodos de cálculo usados foram o do número médio de ligantes, o do valor limite (para o tório), o dos dois parâmetros e o dos quadrados mínimos ponderados. Os valores (log) das constantes de estabilidade dos complexos Ln(TC)$_3$ dos lantanídios vão desde $9,35 \pm 0,22$ para o lantânio até $10,84 \pm 0,11$ para o lutécio. O valor (log) da constante de estabilidade do complexo Th(TC)$_4$ é $24,6 \pm 0,3$.

Para as determinações foram usados os radioisótopos dos respectivos elementos. Quando havia mais de um radioisótopo em um experimento foi usado um analisador multicanal acoplado a um detector de Ge-Li ou de NaI(Tl) para as contagens. No caso de estar presente apenas um radioisótopo, as contagens foram realizadas no sistema integral utilizando um analisador monocanal e um detector de NaI(Tl). A determinação do urânio foi feita por meio da técnica de análise por ativação com nêutrons epitérmicos Os radioisótopos utilizados foram obtidos pela irradiação de alvos apropriados no reator piscina do IPEN. Nos experimentos que envolviam o elemento tório foi usado o radioisótopo natural $^{234}$Th.

Algumas separações, como no caso dos pares de urânio-neptúnio e escândio-zinco, foram obtidas simplesmente por meio do acerto do valor do pH da fase aquosa antes da operação de extração. Outras separações foram feitas à custa da adição de um agente mascarante.

Urânio foi separado de escândio e lantanídios quando à mistura inicial foi adicionada uma solução de ácido etilenodiaminotetraacético (EDTA), que não interfere com a extração do urânio mas retém os elementos mencionados na fase aquosa.

Da mesma forma, o ácido dietilenotriaminopentaacético (DTPA) foi usado como mascarante para o tório, permitindo a separação entre este elemento e urânio.

O uso do fluoreto de sódio, como agente mascarante para o protactínio, levou à separação entre este elemento e tório, e o DTPA mascarando tanto tório como protactínio mostrou-se útil para separar ambos estes elementos do urânio.

Para obter a separação dos lantanídios entre si foi necessário empregar um procedimento de extração com vários estádios, uma vez que as constantes de estabilidade destes elementos são muito próximas.

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