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SOLVENT EXTRACTION STUDIES USING TETRACYCLINE AS COMPLEXING AGENT

XIV. STUDY OF THE BEHAVIOUR OF TETRACYCLINE AS AN EXTRACTING AGENT FOR SOME FISSION PRODUCTS*

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The behaviour of tetracycline as an extracting agent for strontium, iodine, barium, molybdenum, technetium, zirconium, niobium, cesium, ruthenium, tellurium and uranium has been studied and the influence of the acidity of the aqueous phase upon extraction of the elements mentioned has been examined. Experiments have been made to determine whether or not the species extracted into the organic phase is the complex formed between tetracycline and the elements considered as well as to determine the time of shaking necessary so that the equilibrium between the phases is attained. As a practical application, the possibility of using the tetracycline-benzyl alcohol system for separating the fission products ^{137}Cs, ^{140}Ba, ^{140}La, ^{141}Ce, ^{103}Ru, ^{95}Zr and ^{95}Nb from each other and from uranium is presented. The same study has been made for ^{131}I, ^{99m}Tc, ^{99}Mo, ^{132}Te, ^{239}Np and uranium and the steps necessary for the separation of these elements are proposed.

Introduction

Tetracycline (TC) has been used as complexing and extracting agent for several elements.[1–4]

NASTASI and LIMA[1] examined the behaviour of TC as complexing and extracting agent for uranium, thorium, scandium and the lanthanide elements. They also tested the 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 these elements.

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SAIKI et al.[2] used the TC-benzyl alcohol system for the extraction of lanthanides, zinc, scandium, uranium, thorium, neptunium and protactinium. Separations of those elements from one another, and of uranium from selenium, bromine, antimony, barium, tantalum and tungstem were carried out.

In the present work the extraction curves for strontium, iodine, barium, molybdenum technetium, zirconium, niobium, ruthenium and uranium were obtained by using the extraction system TC-benzyl alcohol.

The dependence of extraction on the acidity of the aqueous phases as well as on the nature of the electrolyte present was examined.

The application of tetracycline for separation of some fission products namely ^{95}Zr, ^{95}Nb, ^{141}Ce, ^{103}Ru, ^{140}Ba, ^{140}La and ^{137}Cs from each other and from uranium has been studied.

Individual separation of the fission products ^{131}I, ^{99}Mo, ^{99m}Tc and ^{132}Te as well as of uranium and neptunium with TC-benzyl alcohol is also presented.

Experimental

Preparation of solutions

Radioactive tracers of barium (^{139}Ba) and ruthenium (^{103}Ru) were obtained by irradiating 20 mg of BaO and of $RuCl_3$ for 1 and 40 hours, respectively, in a thermal neutron flux of about 10^{12} n · cm^{-2} · s^{-1}. After the irradiation, both compounds were dissolved with 0.1M solutions of nitric, hydrochloric and perchloric acids, depending on the medium of the extraction experiments. ^{99}Mo was obtained by irradiation of 100 mg of MoO_3 for 8 hours under the same thermal neutron flux mentioned before. The oxide was dissolved with 10M sodium hydroxide solution. In order to obtain ^{99m}Tc, a solution of ^{99}Mo kept at a pH of 4.2 was percolated over an alumina column (5.0 cm high and 1.2 cm of diameter). Thus, ^{99}Mo was held in alumina from which carrier free ^{99m}Tc was milked with 0.2M sodium perclorate, chloride, nitrate or sulfate solutions, depending on the medium in which the behaviour of ^{99m}Tc would be studied. Strontium chloride, nitrate or perchlorate solutions were added to a carrier-free ^{90}Sr solution resulting in 10^{-5}M strontium solutions. Radioactive tracers of cesium (^{134}Cs) and tellurium (^{123m}Te) were obtained by irradiating 1 mg of CsCl and 200 mg H_2TeO_6, respectively, for 8 hours, in the same thermal neutron flux as above. After the irradiation, the compounds were dissolved with water.

Carrier-free radioactive tracers of zirconium and niobium (^{95}Zr and ^{95}Nb) were obtained by irradiating natural uranium oxide (2.6 g of U_3O_8) for 100 hours with thermal neutron (~ 10^{12} n · cm^{-2} · s^{-1}). A cooling time of 2 months elapsed before the irradiated oxide was worked out. The extraction curves of ^{95}Zr and ^{95}Nb were obtained in the presence of the other fission products as well as that of uranium.

In order to obtain carrier-free ^{131}I, 0.25 g of U_3O_8 was irradiated for 4 hours in the same thermal neutron flux mentioned before and cooled for 5 days. In both cases, the irradiated U_3O_8 was dissolved with 4 M HNO_3, or concentrated $HClO_4$, H_2SO_4 or HCl depending on the case to be studied. The uranyl nitrate, perchlorate, sulfate or chloride solutions containing the carrier-free radioisotopes under study were used for the extraction experiments.

In order to study the behaviour of tetracycline as extracting agent for uranium, natural uranium oxide (U_3O_8) was dissolved either with 4 M nitric acid solution or with concentrated $HClO_4$, H_2SO_4 or HCl. The solutions thus obtained were used for the extraction experiments, after being conveniently diluted.

Tetracycline hydrochloride was dissolved with benzyl-alcohol previously washed with distilled water.

Determination of the percent extraction of metals

The concentration of barium, strontium and cesium solutions used for extraction experiments was $1 \cdot 10^{-5}$M, and the concentration of molybdenum, ruthenium and tellurium was $1 \cdot 10^{-4}$M. The concentration of uranium solution was $2.9 \cdot 10^{-4}$M. The fission products ^{95}Zr, ^{95}Nb, ^{131}I and ^{99m}Tc were carrier-free. The concentration of tetracycline in benzyl alcohol was $2 \cdot 10^{-2}$M. In order to examine the individual extraction behaviour of Ba, Sr, Cs, Mo, Ru, Te, Ru and Tc the extraction system was made up of tetracyclinebenzyl alcohol solution. The aqueous phases contained each of the elements under study, with a unit volume ratio being kept.

In the cases of ^{131}I, ^{95}Zr and ^{95}Nb the extraction curves were obtained using as aqueous phases a convenient volume of the fission product mixture solution containing those radioisotopes besides the other fission products and also uranium. It must be pointed out that the concentration of uranium in the aqueous phases used in these cases was $1.8 \cdot 10^{-2}$M.

Extraction curves of all the elements under study were obtained in several media constituted by $NaNO_3$, NaCl, Na_2SO_4 or $NaClO_4$ solutions, the final concentration of each electrolyte being 0.1M.

The acidity of the aqueous phases varied from 10 M to 10^{-10}M. In order to attain equilibrium the phases were mechanically shaken for 30 minutes at 25.0 ± 0.5 °C. The phases were separated, centrifuged and the pH's of the aqueous phases measured. Activities of the radioisotopes were measured in a single channel gamma-ray spectrometer coupled to a 5.08 cm × 4.45 cm well type NaI(Tl) scintillation detector. In the case of samples containing more than one radioelement a Ge(Li) detector coupled to a 4096-channel analyzer was used. A Geiger-Müller detector was used to measure the activities of ^{90}Sr samples. For the determination of extraction curves of uranium, the concentration of this element in both phases was determined by using the epithermal neutron activation analysis method.[5] In this case use was made of a 7.5 cm × 7.5 cm well type NaI(Tl) scintillation detector coupled to a 400-channel analyzer.

Results

Extraction experiments carried out by agitating alcohol alone with aqueous solutions of radioactive tracers of the elements under study showed that technetium as pertechnetate ions as well as molybdenum and iodine ions are extracted into benzyl alcohol, as can be seen in Fig 1 to 3, respectively. The extraction of these three elements into benzyl alcohol depends on the acidity as well as on the nature of the electrolyte present in the aqueous phase. On the other hand, benzyl alcohol alone does not extract the other elements studied namely, zirconium, niobium, ruthenium, barium, strontium, tellurium, cesium and uranium.

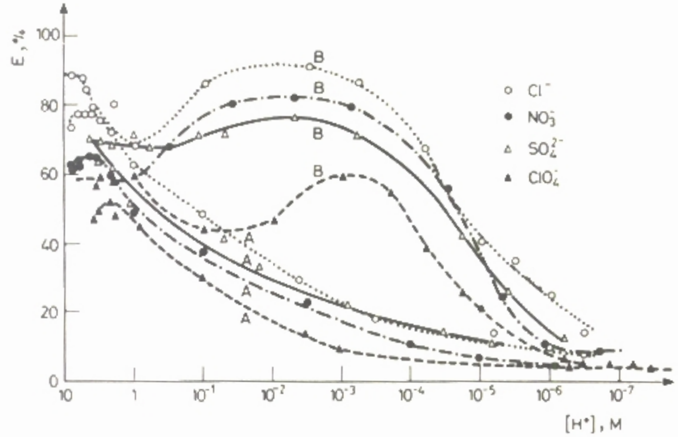

Fig. 1. Extraction curves for technetium. Curves A: benzyl alcohol alone; curves B: tetracycline-benzyl alcohol system technetium carrier-free; [NaX] = 0.1M, (X = Cl^-, NO_3^-, ClO_4^- or SO_4^{2-}), [TC] = $2 \cdot 10^{-2}$ M

Extraction experiments carried out in the presence and absence of tetracycline showed that the addition of the latter into benzyl alcohol enhances molybdenum extraction in the acidity range from 10M to 10^{-9}M (Fig. 2); nevertheless, in the case of technetium (Fig. 1) the addition of tetracycline makes a difference only when the acidity of the aqueous phases is below 1.0M. The extraction curves depicted in Fig. 3 show that the extraction of iodine is due only to the presence of benzyl alcohol.

In order to determine the agitation time necessary for the equilibrium between the phases to be attained in the case of each element, both organic and aqueous phases were shaken for times varying from 10 to 120 minutes, and the percent extraction of metal was calculated for each element in each case. The back-extraction curves of the elements were determined for a shaking time of 30 minutes and the results obtained showed that for all elements studied, except for ruthenium, equilibrium is reached within 30 minutes.

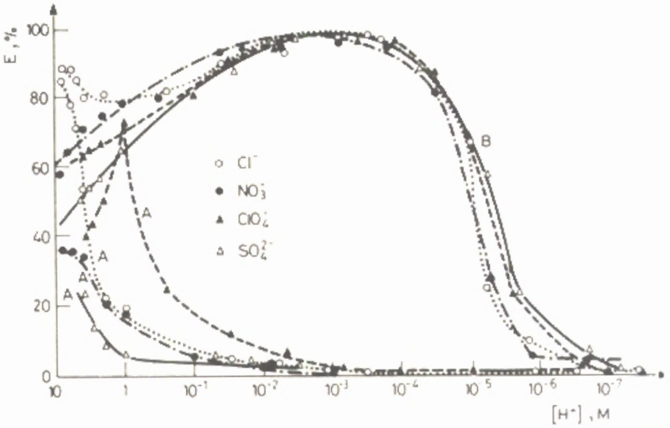

Fig. 2. Extraction curves for molybdenum. Curves A: benzyl alcohol alone; curves B: tetracycline-benzyl alcohol system; $[Mo] = 5 \cdot 10^{-4}M$, $[NaX] = 0.1M$, ($X = Cl^-, ClO_4^-, NO_3^-$ or SO_4^{2-}), $[TC] = 2 \cdot 10^{-2}M$

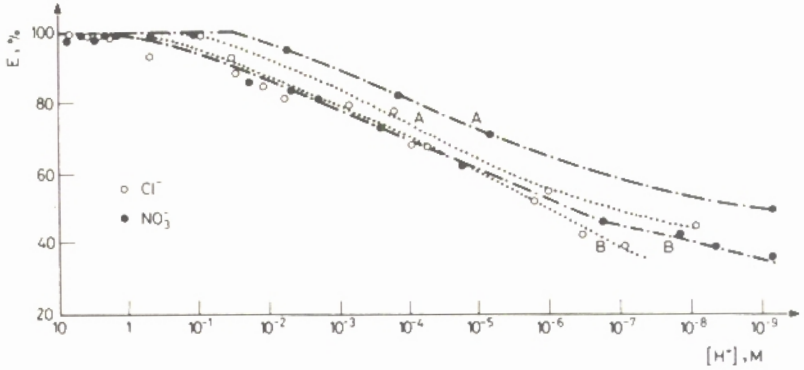

Fig. 3. Extraction curves for iodine. Curves A: benzyl alcohol alone; curves B: tetracycline-benzyl alcohol system iodine carrier-free; $[NaX] = 0.1M$, ($X = Cl^-, NO_3^-$), $[TC] = 2 \cdot 10^{-2}M$

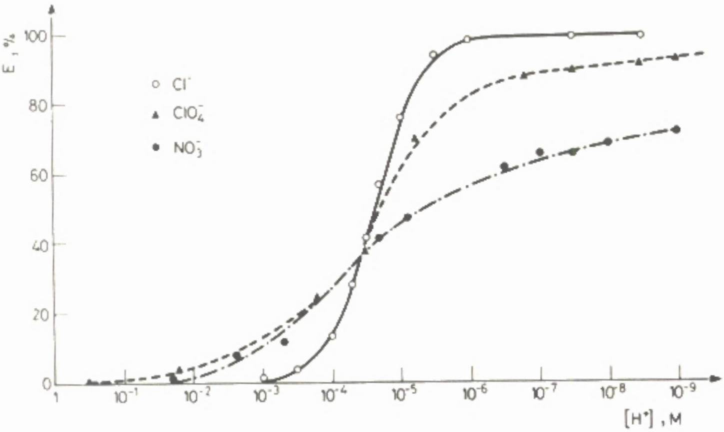

Fig. 4. Extraction curves for strontium; [TC] = 2 · 10^{-2}M, [NaX] = 0.1M, (X = Cl^-, NO_3^- or ClO_4^-), [Sr] = 1 · 10^{-5}M

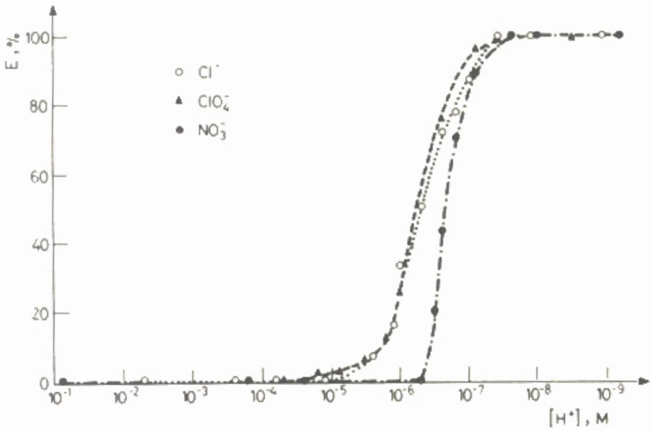

Fig. 5. Extraction curves for barium; [TC] = 2 · 10^{-2}M, [NaX] = 0.1M, (X = Cl^-, NO_3^- or ClO_4^-), [Ba] = 1.0 · 10^{-5}M

Cesium and tellurium are not extracted into the tetracycline-benzyl alcohol solution under the experimental conditions employed.

Figures 4 to 9 present the extraction curves of the elements strontium, barium, niobium, zirconium, ruthenium and uranium, as a function of the acidity of the aqueous phases, the elements being present in the different media considered.

The extraction curves of technetium depicted in Figure 1 show that the highest percent metal extractions are obtained in chloride medium. In the presence of NaCl,

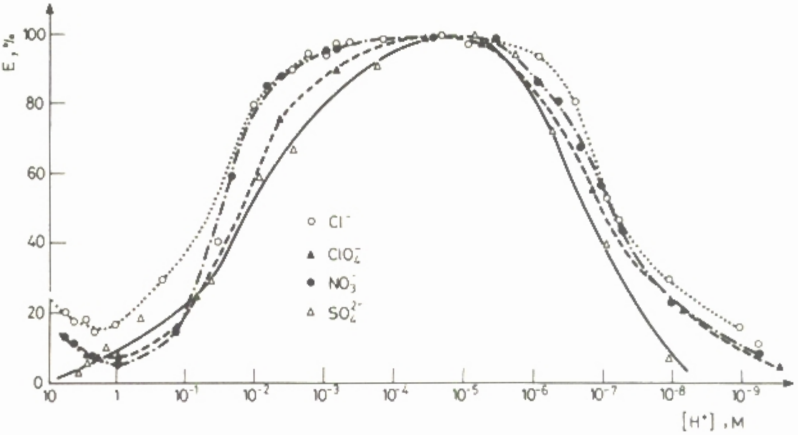

Fig. 6. Extraction curves for niobium; [TC] = $2 \cdot 10^{-2}$M, [NaX] = 0.1M, (X = Cl^-, NO_3^-, ClO_4^- or SO_4^{2-}), ^{95}Nb, carrier-free

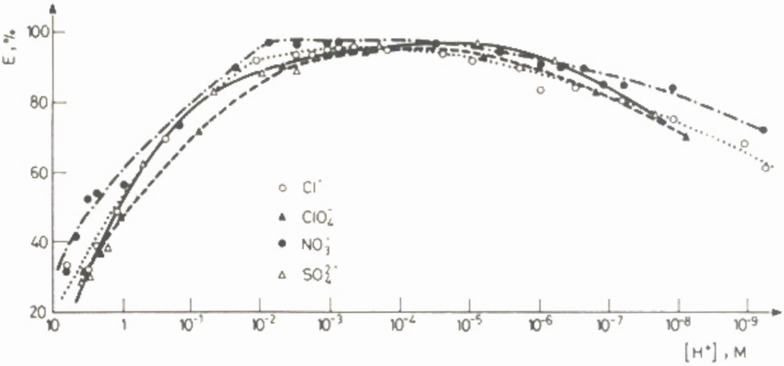

Fig. 7. Extraction curves for zirconium; [TC] = $2 \cdot 10^{-2}$M, [NaX] = 0.1M, (X = Cl^-, NO_3^-, ClO_4^- or SO_4^{2-}), ^{95}Zr, carrier-free

technetium is extracted in the pH interval from 1.0 to 3.0 to the extent of 90%, but the extraction decreases as the pH is raised above 3.

Figure 2 presents the extraction curves of molybdenum. The results show that at acidity values smaller than 1.0M there is no influence of the nature of the electrolyte upon the extraction of molybdenum; nevertheless, in the acidity range from 1.0M to 10M, the presence of Cl^- enhances the extraction of molybdenum. The extraction of molybdenum is 95% when the pH of the aqueous phase is kept within the range from 2.0 to 4.0.

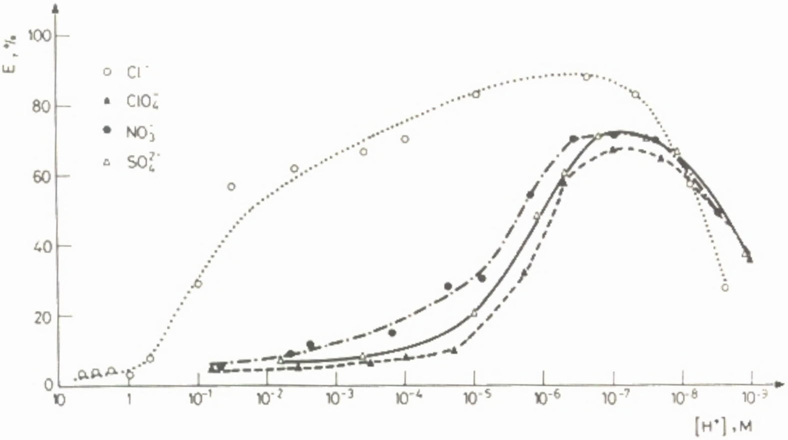

Fig. 8. Extraction curves for ruthenium; $[TC] = 2 \cdot 10^{-2}$ M, $[NaX] = 0.1$M, ($X = Cl^-, NO_3^-, ClO_4^-$ or SO_4^{2-}), $[Ru] = 1 \cdot 10^{-4}$ M

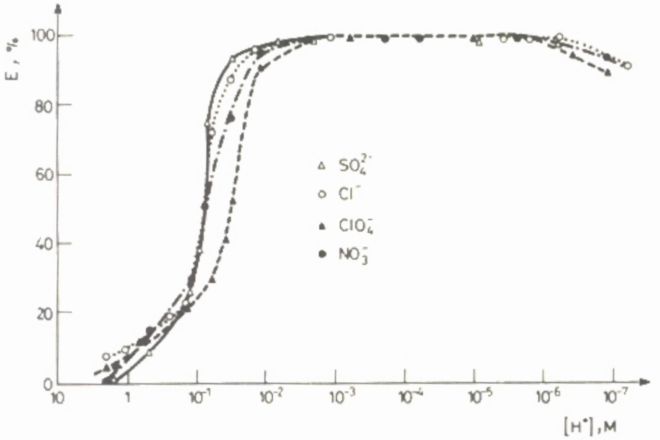

Fig. 9. Extraction curves for uranium; $[TC] = 2 \cdot 10^{-2}$ M, $[NaX] = 0.1$M, ($X = Cl^-, NO_3^-, ClO_4^-$ or SO_4^{2-}), $[U] = 2.9 \cdot 10^{-4}$ M

The extraction of iodine (Fig. 3) is due only to the presence of benzyl alcohol and the extraction does not depend on the nature of the electrolyte employed.

The extraction curves of strontium presented in Fig. 4 show that only in the presence of NaCl is the extraction of strontium quantitative, being essentially complete at pH 5.8.

It can be seen in Fig. 5 that the extraction of barium in the presence of NaCl or $NaClO_4$ starts at pH 5.0 and 4.5, respectively, and is complete at pH 7.4. However, when the extraction experiments are carried out in the presence of $NaNO_3$, the extraction curve shifts towards higher pH values and the extraction of barium does not start before pH 6.4.

The extraction curves of niobium and zirconium depicted in Figs 6 and 7, respectively, show that there is no influence of the nature of electrolyte upon the extraction of these elements. More than 90% of niobium and zirconium is extracted into the organic phase when the extraction operation is carried out in the pH range from 2.0 to 6.0.

As is shown in Fig. 8, the extraction of ruthenium is greatly enhanced in the presence of NaCl, but it must be pointed out that a treatment of the solution in order to obtain ruthenium in a definite chemical form has not been made.

In order to verify the influence of the nature of the electrolyte upon the extraction of uranium (Fig. 9), distribution ratios (D) were calculated, and a statistical test[6] applied to the values found for log D as a function of pH showed that the straight lines obtained for the behaviour of extraction in the presence of Cl^-, NO_3^- and SO_4^{2-} are coincident at a confidence level of 95%. However, when the extraction experiments were made in the presence of ClO_4^- the extraction curves shifted towards higher pH values.

Practical applications

Separation of ^{95}Zr, ^{95}Nb, ^{141}Ce, ^{140}Ba, ^{140}La, ^{103}Ru and ^{137}Cs from uranium

U_3O_8 (2.6 g) was irradiated for 100 hours in a thermal neutron flux of about 10^{12} n · cm^{-2} · s^{-1} and cooled for 2 months. The irradiated U_3O_8 was dissolved with 4M nitric acid solution. The solution so obtained was used after proper dilution to carry out the extraction experiments whose aim was to isolate uranium. The main gamma-ray emitter fission products present after a 2-month cooling time are ^{95}Zr, ^{95}Nb, ^{103}Ru, ^{137}Cs, ^{141}Ce, ^{140}Ba and ^{140}La. The extraction operations were performed as mentioned before. The concentration of uranium was $1.8 \cdot 10^{-2}$M and the fission products were carrier-free.

Figure 10 shows the extraction curves for the fission products studied and for uranium. Since cesium is not extracted into the organic phase under the experimental conditions employed, the separation of uranium from cesium, barium, cerium and lanthanum is feasible provided the extraction operation is carried out at a convenient pH value. The extraction of uranium at pH 1.8 is practically complete while the elements mentioned are not extracted into the organic phase at this pH value. Futhermore, at this same pH value it is possible to separate uranium from ruthenium almost completely inasmuch under these conditions only 5% of ruthenium is extracted into the organic phase.

A partial separation of uranium from zirconium is possible when the acidity of the aqueous phase is 2.0M. In this case 55% of zirconium is extracted into the organic phase while uranium remains in the aqueous phase. In order to obtain a complete separation between uranium and zirconium, a multiple extraction operation has to be used. The same curves presented in Fig. 10 show also that for isolating uranium from niobium several extraction operations will be necessary in order to obtain a complete separation between these elements.

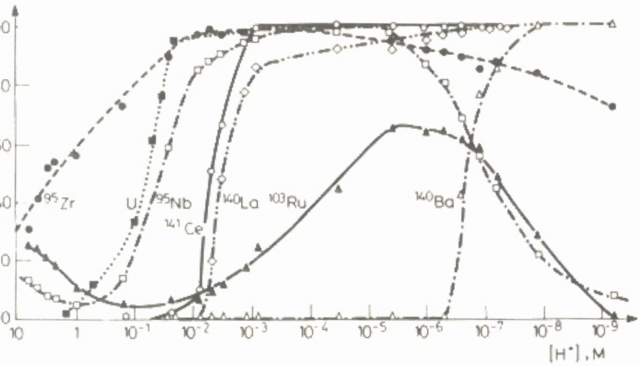

Fig. 10. Extraction curves for uranium and fission products ^{95}Zr, ^{95}Nb, ^{141}Ce, ^{140}La, ^{103}Ru and ^{140}Ba; $[TC] = 2 \cdot 10^{-2}$ M, $[NaNO_3] = 0.1$M, carrier-free fission products

Separation of ^{95}Zr, ^{95}Nb, ^{141}Ce, ^{140}Ba, ^{140}La, ^{103}Ru and ^{137}Cs one from the other

Barium can easily be isolated from zirconium, niobium, cerium, lanthanum, ruthenium and cesium by means of two extraction operations carried out at properly chosen pH values.

From the extraction curves shown in Fig. 10 it can be seen that an extraction operation performed at pH 9.0 allows ruthenium and cesium to be isolated from the mixture of fission products. At this pH value, barium, together with the other fission products considered present in the solution, is quantitatively extracted into the organic phase, while ruthenium and cesium remain in the aqueous phase. From the organic phase containing the other fission products together with barium, this last is stripped into the aqueous phase by performing another extraction operation at pH 4.5.

From the extraction curves shown in Fig. 10 it can also be seen that from uranium-free fission product mixture the separation of zirconium and niobium from barium, cerium, lanthanum, ruthenium and cesium can be achieved, provided the extraction operation is carried out at pH 1.7. In this case 90% of zirconium and 65% of niobium is extracted into the organic phase together with only 5% of ruthenium, while the other fission products remain in the aqueous phase.

After isolating zirconium and niobium from the mixture (pH 1.7), the separation of barium, cerium and lanthanum from both ruthenium and cesium is performed when the pH of the aqueous phase is 9.0. Cerium, lanthanum and barium are quantitatively extracted while ruthenium and cesium remain in the aqueous phase. Although barium is extracted together with cerium and lanthanum, barium is stripped when another extraction operation is made at pH 4.5. Under such conditions, cerium and lanthanum remain in the organic phase being separated from barium.

The aqueous phase resulting from the extraction of cerium, lanthanum and barium at pH 9.0 can be used to obtain ruthenium or cesium. These two elements can be separated when the extraction operation is carried out at pH 5.5. Thus 55% of ruthenium is extracted into the organic phase while cesium remains in the aqueous phase. More than one extraction operation is necessary to obtain a complete separation between ruthenium and cesium.

The extraction curves of Figure 10 show also that a single extraction operation is not enough to separate cerium from lanthanum neither zirconium from niobium. In order to obtain these separations, multiple countercurrent extraction procedures[1] have to be used in both cases.

Separation of ^{99}Mo, ^{99m}Tc, ^{131}I, ^{132}Te and ^{239}Np from uranium

U_3O_8 (0.25 g) was irradiated for 4 hours with thermal neutrons (10^{12} n · cm^{-2} · s^{-1}) and cooled for 5 days. The solution containing uranium, ^{239}Np and fission products (^{131}I, ^{132}Te, ^{99}Mo and ^{99m}Tc) obtained by dissolving the U_3O_8 with 4M nitric acid solution was used to perform the extraction experiments made to isolate the fission products of interest from one another and from uranium. The uranium concentration was $1.8 \cdot 10^{-2}$M and the fission products were carrier-free. The extraction operations were made as mentioned before.

Figure 11 shows the extraction curves obtained for the short-lived fission products studied, uranium and ^{239}Np. Tellurium is not extracted into the organic phase. The steps for the separation of those fission products are described.

With only one extraction operation ^{99}Mo and ^{99m}Tc can be partially separated from uranium since within the acidity range from 2.0 to 8.0M, the extraction of these radioisotopes is about 60% while uranium is not extracted. Within the same acidity range it is also possible to separate uranium from iodine since iodine is quantitatively extracted into the organic phase. The extraction curves presented in

Figure 11 show that the separation of uranium from tellurium and neptunium is possible. At pH 1.7 the extraction of uranium is nearly complete while tellurium and neptunium are not extracted. The separation of neptunium from tellurium is possible when the pH of the aqueous phase is kept within the range from 4.0 to 6.0, since the extraction of neptunium is higher than 80% while tellurium is not extracted.

In can be seen in Fig. 11 that separation of technetium and molybdenum from iodine would only be possible by means of a multi-stage extraction procedure. The extraction curves for technetium and molybdenum are too close to one an other to allow the separation of both elements using the system TC-benzyl alcohol.

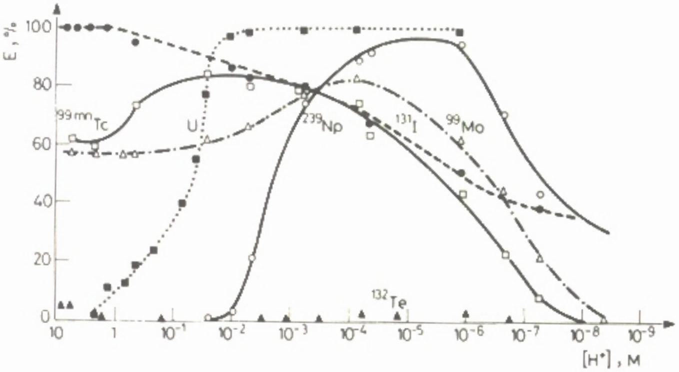

Fig. 11. Extraction curves for uranium, neptunium and fission products ^{131}I, ^{99m}Tc and ^{99}Mo; [TC] = $2 \cdot 10^{-2}$M, |[NaNO$_3$]| = 0.1M, carrier-free fission products

Based on all information obtained from extraction experiments it is seen that the tetracycline-benzyl alcohol system can be used for isolating fission products present in their mixture, as well as for the separation of uranium from some fission products.

Separation of some genetically related fission products

In the present paper the solvent extraction technique has been employed for isolating genetically related pairs of nuclides. Either the parent nuclide or its daughter is extracted into the organic phase, while the daughter or parent, respectively, remains in the aqueous phase. After a suitable length of time required for regeneration of the daughter, the process may be repeated until the parent has decayed completely.

The parent – daughter pairs which have been studied are ^{90}Sr – ^{90}Y, ^{140}Ba – ^{140}La and U – ^{239}Np and they have been obtained as mentioned before.

Separation of ^{90}Sr – ^{90}Y. The extraction curves obtained for both strontium and yttrium (Fig. 12) show that these two elements can be completely separated from each other. By keeping the pH of the aqueous phase at 2.5, yttrium is quantitatively extracted while strontium remains in the aqueous phase.

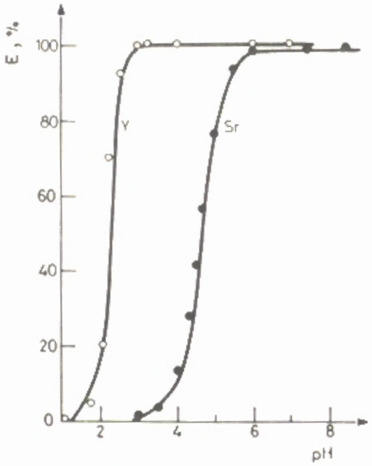

Fig. 12. Extraction curves for strontium and yttrium; $[Tc] = 2 \cdot 10^{-2}$ M, $[NaNO_3] = 0.1$M, $[Sr] = [Y] = 1 \cdot 10^{-5}$M

Separation of ^{140}Ba – ^{140}La. After chemical separation of barium from the fission product mixture as mentioned before, ^{140}La can be removed from the generator. The results obtained (Fig. 10) show that extraction of lanthanum is complete at pH 4.5 while barium is not extracted into the organic phase.

^{140}La can be milked periodically from its parent (^{140}Ba) until this last has decayed completely.

Separation of U – ^{239}Np. The experimental results indicate that uranium is extracted efficiently (95%) into the organic phase, whereas neptunium is poorly extracted (only 2%) when the extraction operation is carried out at pH 1.7 (Fig. 11).

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