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SOLVENT EXTRACTION STUDIES USING TETRACYCLINE AS A COMPLEXING AGENT. PART 6. SEPARATION OF URANIUM AND THORIUM WITH DTPA AS A MASKING AGENT

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Separation of thorium from uranium is accomplished by solvent extraction technique using benzyl alcohol as an extractant and tetracycline as a complexing reagent and diethylenetriaminepentaacetic acid as a masking agent for thorium.

INTRODUCTION

The antibiotic tetracycline (TC) and its derivatives have been used as complexing reagents for separation and determination of various cations.[1-4]

Extraction and separation studies of rare earth elements, scandium, uranium and thorium using benzyl alcohol and tetracycline have been carried out by Nastasi and Lima.[5-6] Stability constants for the complexes of the rare earths and tetracycline have been determined by Saiki and Lima.[7]

This paper presents the method for the separation of uranium and thorium by solvent extraction with benzyl alcohol-tetracycline and diethylenetriaminepentaacetic acid (DTPA) used as a masking agent for thorium.

EXPERIMENTAL

All reagents were of analytical grade and the corresponding solutions were prepared with water distilled in a quartz apparatus.

Uranium and thorium solutions were prepared by the dissolution of U_3O_8 and ThO_2, respectively, with some drops of 20% perchloric acid and concentrated nitric acid.

^{234}Th tracer was obtained by passing a uranyl nitrate solution through a column of alumina and removing ^{234}Th with hot HCl.[8]

For extraction experiments the solvent benzyl alcohol was first washed with distilled water. Tetracycline hydrochloride (Laborterápica Bristol) was dissolved in the alcohol to give a final solution of 0.010M. The solution was used within six hours after preparation. DTPA solution was standardized with KOH. EDTA, which had also been investigated as a masking agent, was dried at $80^{\circ}C$ for about four days and the solutions were prepared by dissolving it in NaOH solution to the desired concentration.

The extraction system consisted of 5 ml of the benzyl alcohol-tetracycline solution 0.01M and 5 ml of the aqueous phase (uranyl nitrate at a concentration of 7.0×10^{-5}M in uranium and/or thorium nitrate at a concentration of 5.0×10^{-4}M in thorium). Sodium perchlorate was added to the aqueous phase to reach a concentration corresponding to 0.10M.

The masking agent DTPA or EDTA was added to the aqueous phase to obtain a concentration of 2.5×10^{-3}M. pH of the aqueous phase was adjusted by adding perchloric acid or sodium hydroxide solutions. Both phases were then equilibrated by shaking mechanically for 30 min at $25^{\circ}C \pm 0.5^{\circ}C$. After this time the phases were separated by centrifugation.

Concentration of uranium in both phases was determined by activation analysis with epithermal neutrons[9] by measuring the activity corresponding to the 74 keV photopeak of ^{239}U. Thorium concentrations were determined by measuring the activities at 93 and 63 keV for the ^{234}Th tracer.

When the phases to be measured contained only uranium or only thorium activity determinations were made by using a well-type NaI(Tl) scintilla-

tion counter, 7 cm x 7 cm, and a 400-channel analyser. When both elements were present simultaneously counting was carried out using a Ge(Li) detector (27 cm^3 and with a resolution corresponding to 2.1 keV for the 1.33 MeV photopeak of ^{60}Co) and a 4096-channel analyser.

Fig. 1 shows the extraction curves for uranium and thorium. Separation of the two metals by pH change would be a rather inefficient method since the curves lie close to each other. Masking of thorium with EDTA was not effective to prevent the co-extraction of thorium and uranium. Fig. 2 shows both extraction curves when EDTA was tried as masking agent.

However, masking of thorium with DTPA, forming the non-extractable complex Th-DTPA, gives an excellent separation of both metals, with thorium remaining in the aqueous phase. The pH range at which thorium is practically non extracted corresponds to a value from 2.0 to 2.6. Fig. 3 shows the extraction curves of uranium and thorium in a mixture of uranyl nitrate and thorium nitrate.

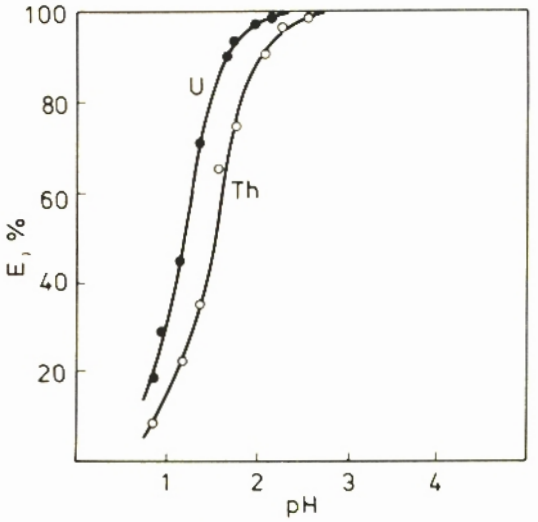

Fig. 1. Extraction curves for uranium and for thorium using only benzyl alcohol-TC solution. Uranium: 7.0×10^{-5}M, Thorium: 5.0×10^{-4}M, TC: 0.01M, $NaClO_4$: 0.10M

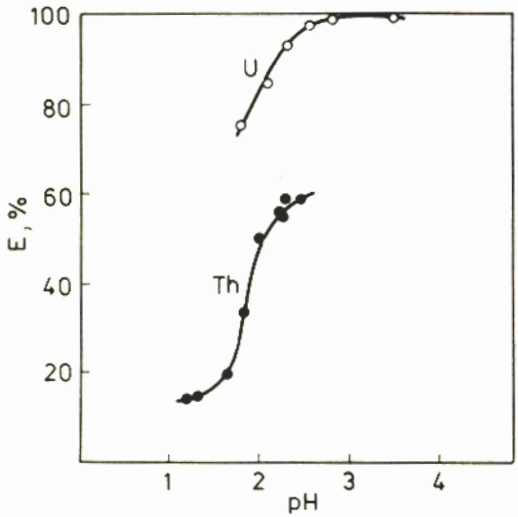

Fig. 2. Extraction curves for uranium and thorium using EDTA as a masking agent. Uranium: 6.0×10^{-5}, Thorium: 5.0×10^{-4}M, TC: 0.01M, EDTA: 2.5×10^{-3}M, $NaClO_4$: 0.10M

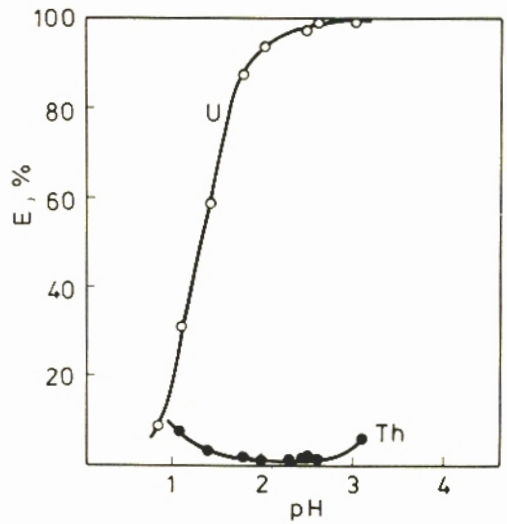

Fig. 3. Extraction curves for uranium and thorium using DTPA as a masking agent. Uranium: 7.0×10^{-5}M, Thorium: 5.0×10^{-4}M, TC: 0.01M, DTPA: 2.5×10^{-3}M, $NaClO_4$: 0.10M

Although the stability constant of the Th-EDTA complex is high,[10] ($\log \beta = 23.2$) thorium was partially extracted into organic phase under the experimental conditions described (Fig. ?). Preliminary experiments had shown that the complex Th-EDTA as well as Th-DTPA were not extracted into benzyl alcohol if tetracycline was not present in the organic phase. The same is true for uranium (UO_2^{2+}) and thorium, which are not extracted by pure benzyl alcohol.

The stability constant of the Th-DTPA complex is rather high,[10] ($\log \beta > 27$) and there is no displacement of Th by TC in the Th-DTPA complex. Consequently, the extraction of Th by benzyl alcohol-TC does not take place when DTPA is present. The amount of U-DTPA (uranyl) formed is very small and the complex U-TC (uranyl) is preferentially formed. The result is that uranium is extracted by the organic phase benzyl alcohol-TC as U-TC complex and thorium remains in the aqueous phase as Th-DTPA complex (which is too stable to be broken by tetracycline) allowing, in this way, a separation of thorium and uranium.

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