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SOLVENT EXTRACTION STUDIES USING TETRACYCLINE AS COMPLEXING AGENT. VIII. SEPARATION OF Se, Br, Mo, Sb, Ba, Ta, W, Au and Hg FROM URANIUM

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A study of the separation of uranium from Se, Br, Mo, Sb, Ba, Ta, W, Au and Hg is presented. Separations were carried out by solvent extraction technique using tetracycline as complexing agent and benzyl alcohol as organic phase. Masking agents were required for some of the separations.

INTRODUCTION

In previous work the use of the antibiotic tetracycline (TC) for separation of uranium from neptunium[1], thorium[2], scandium and lanthanides elements[3] has been described. Separations were performed using solvent extraction technique with benzyl alcohol-tetracycline solutions as the organic phase.

This paper presents the studies in connection with the separation of uranium from the elements Se, Br, Mo, Sb, Ba, Ta, W, Au and Hg. These elements interfere in the determination of uranium by activation analysis using epithermal neutrons[4], since their radioisotopes ^{79m}Se, ^{81m}Se, ^{80m}Br, ^{82m}Br, ^{90}Mo, ^{101}Mo, ^{122m}Sb, ^{131}Ba, ^{182}Ta, ^{182m}Ta, ^{187}W, ^{198}Au, ^{197m}Hg have gamma rays with energies too close or with, practically, the same value as the photopeak of 74 keV of ^{239}U.

EXPERIMENTAL

All reagents used were of analytical grade. Benzyl alcohol and water phases were mutually saturated with each other before use. When buffer solutions were used as aqueous phases the benzyl alcohol was presaturated with these solutions. pH = 4.5 (sodium acetate 0.1M and acetic acid 0.2M): pH = 5.5 (sodium acetate 0.1M and acetic acid 0.02M).

Radioactive tracers for the various elements were obtained by irradiation of compounds of the elements, in accordance with Table 1, in a thermal neutron flux of 5×10^{12} n cm^{-2} sec^{-1}, for times from 8 min up to 24 hours, depending of the nuclear characteristics of the stable irradiated isotopes as well as of the produced radioisotopes. Containers for irradiations were made up of aluminium sheets. For mercury, bromine (bromid and selenium, which were irradiated in solutions, quartz ampoules were

Experimental procedure

5 ml of a 10^{-2}M solution of tetracycline in benzyl alcohol were added to a separatory funnel as well as 5 ml of the aqueous solution containing the element to be extracted. The concentration of $NaClO_4$ in the aqueous solution was equal to 0.10M. When masking agents were used the same $NaClO_4$ aqueous solution was used but for the buffer the pH adjustment was made by adding diluted solutions of NaOH or $HClO_4$.

The funnels were mechanically shaked for 30 min at a temperature equal to $25.0 \pm 0.5^{\circ}C$ and afterwards the phases were separated by centrifugation. pH measurements were made in a Metrohn Herisau equipment, Model E-350B, with scale up to 0.1 pH units. Activities of the radioisotopes were measured in a single channel analyser coupled to a well type NaI(Tl) detector or, when counting interferences would so require, in a 4096 channels analyser coupled to a Ge-Li detector. Uranium concentrations in both phases were determined by epithermal neutron activation analysis[4].

TABLE 1

Radioactive tracer solutions

Element	Compound	Dissolution with	Stock solution concentration (M)	Radioisotope
Se	Se (metal)	HNO_3	10^{-3}	^{75}Se
Br	$KBrO_3$	H_2O	10^{-3}	^{82}Br
Br	KBr	H_2O	10^{-2}	^{82}Br
Mo	MoO_3	NaOH	3.5×10^{-3}	^{99}Mo
Sb	Sb (metal)	Acqua Regia	10^{-3}	^{124}Sb
Ba	$Ba\,CO_3$	HCl 0.2M	4×10^{-3}	^{131}Ba, ^{133}Ba
Ta	Ta (metal)	HF 28M	10^{-2}	^{182}Ta
W	$(NH_4)_{10}W_{12}O_{41}5H_2O$	H_2O	10^{-4}	^{187}W
Au	Au (metal)	Acqua Regia	10^{-3}	^{198}Au
Hg	$Hg\,Cl_2$	HNO_3 0.1M	10^{-3}	^{203}Hg
U	U_3O_8	HNO_3	10^{-3}	^{239}U

RESULTS AND DISCUSSION

a. Separation uranium-selenium

Results for the extraction of uranium (UO_2^{2+}) by the 0.01M tetracycline solution in benzyl alcohol are presented in Fig. 1. Uranium is extracted in a rather large pH interval, namely from 2.5 to 6.0.

Results for the extraction of Se(VI) and of uranium, when both elements were present in the same aqueous solution, are presented in Fig. 2.

Se(IV) and Se(VI) are both extracted by pure benzyl alcohol, without tetracycline, in the pH interval of 2.0 to 3.0 in the extent of 6 to 15%. However, results presented at Fig. 2, show that it is possible to separate uranium from selenium, with tetracycline-benzyl alcohol, in the pH inter-

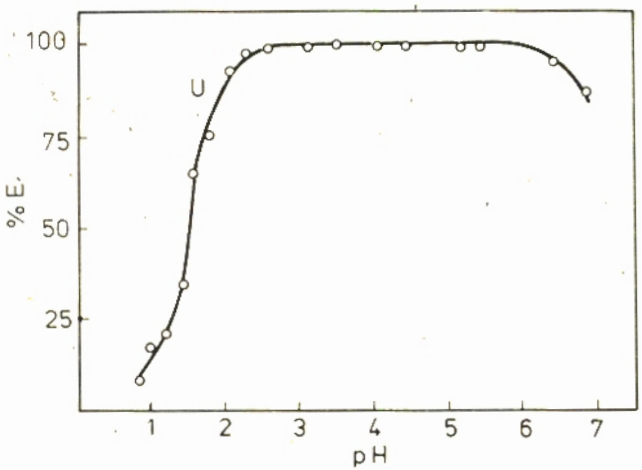

Fig. 1. Extraction curve for uranium. Uranium = $8x10^{-5}$M; TC = 0.01M; $NaClO_4$ = 0.10M

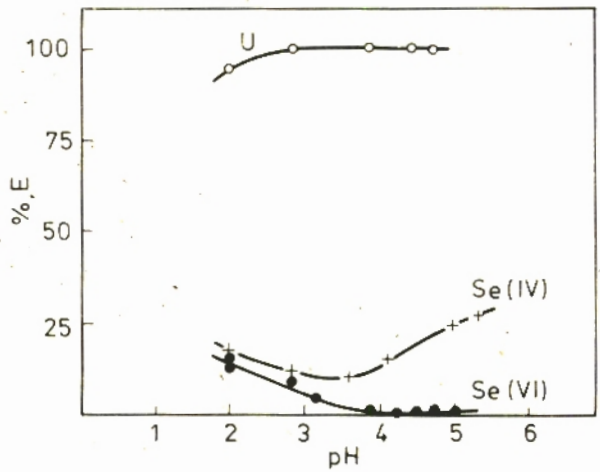

Fig. 2. Extraction curves for uranium and selenium. Uranium = $8x10^{-5}$M; Se = 10^{-4}M; $NaClO_4$ = 0.10M; H_2O_2 = 3.15% and TC = 0.01M

val from 4.0 to 5.5. Hydrogen peroxide used to oxidize Se(IV) to Se(VI) does not interfere with the extraction of uranium.

By using buffered solutions of acetic acid and sodium acetate, at pH = 5.5 the percentages of extraction of uranium and selenium (VI) were, 97.4% and 2.9% (mean values of three replicates) respectively.

b. Separation uranium-bromine

Preliminary experiments showed that the BrO_3^- anions are extracted directly by benzyl alcohol without tetracycline. However Br^- ions are not extracted into pure benzyl alcohol and into tetracycline-benzyl alcohol solution, making possible the separations of bromine as bromide ions from uranium. Fig. 3 shows that results and conditions for such a separation.

c. Separation uranium-molybdenum

Mo(VI) is extracted into the organic phase even in the presence of masking agents (EDTA and DTPA). In fact molybdenum is extracted directly into benzyl alcohol, in the absence of tetracycline, and the complete separation uranium-molybdenum is not possible.

d. Separation uranium-antimony

Fig. 4 shows the separation of uranium from antimony(III). It is seen that the separation is rather efficient at a pH interval 4.6 to 6.0.

Extractions carried out with buffered solutions at pH = 5.5 have shown that the pH value is not changed after equilibration of both phases and that separation of uranium from antimony is complete giving extraction values of 99.5% and 0.7% for uranium and antimony, respectively.

Extraction of antimony (III) by benzyl alcohol alone, without tetracycline, does not take place.

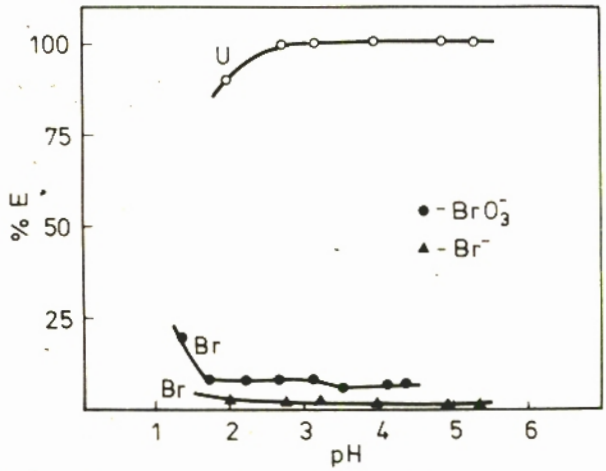

Fig. 3. Extraction curves for uranium and bromine (bromine and brom
Uranium = $8x10^{-5}$M; Br = $1.1x10^{-5}$M; $NaClO_4$ = 0.10M; TC = 0.

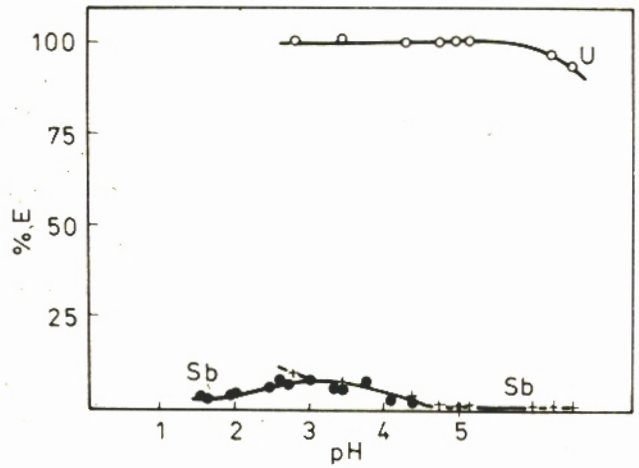

Fig. 4. Extraction curves for uranium and antimony. (+) - mixture Sb-U; (●) - Sb alone. Uranium = $8x10^{-5}$M; Sb = $5\text{-}17x10^{-5}$M; $NaClO_4$ = 0.10M; TC = 0.01M

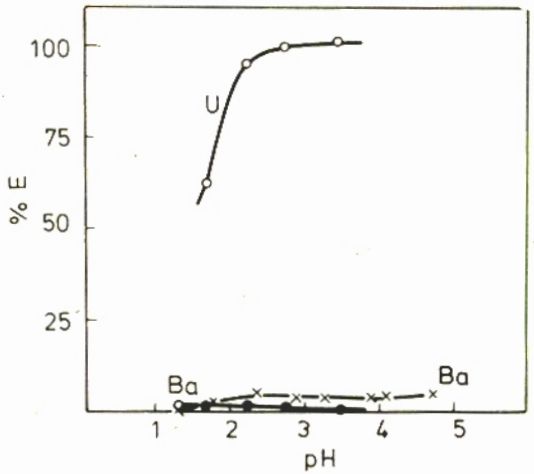

Fig. 5. Extraction curves for uranium and barium. (x) - Ba without masking agents; (●) Ba with EDTA. Uranium = 8×10^{-5}M; Ba = 4×10^{-4}M; $NaClO_4$ = 0.10M; EDTA = 2.5×10^{-3}M; TC = 0.01M

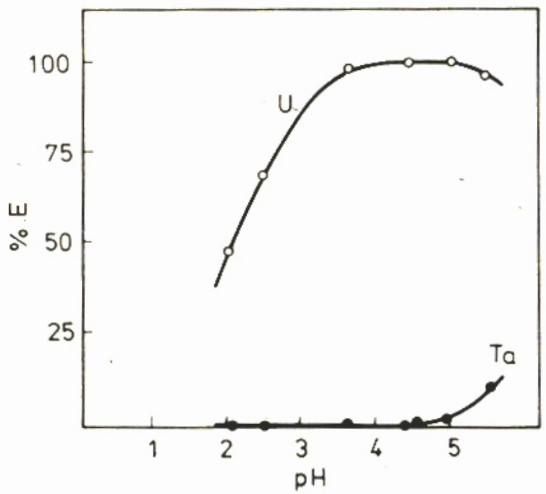

Fig. 6. Extraction curves for uranium and tantalum. Uranium = 8×10^{-5}M; Ta = 10^{-5}M; $NaClO_4$ = 0.10M; TC = 0.01M

e. Separation uranium-barium

Fig. 5 presents the results for the extraction of barium with and without masking agent (EDTA). EDTA is a masking agent for the complexation reaction of barium with tetracycline, making possible a rather complete separation of barium from uranium.

f. Separation uranium-tantalum

Results for separation of uranium from tantalum are presented in Fig. 6. It is seen that such a separation is effective in a pH interval from 3.3 to 4.8. The difference observed in the uranium extraction curves of Fig. 1 and Fig. 6 is due to the presence of fluoride ions in the experiments corresponding to Fig. 6. Fluoride ions are present since tantalum was dissolved with hydrofluoric acid which complexes uranium and prevents a complete extraction of uranium as the complex uranium-tetracycline until pH has reached a value above 3.3. For the separation uranium-tantalum it was also verified that it is possible to use buffered aqueous solution at a pH = 4.50 with an extraction of 99.3% and 0.3% for uranium and tantalum, respectively.

g. Separation uranium-tungsten

Fig. 7 presents the results for the separation of uranium from tungsten with and without hydrogen peroxide as masking agent for the complexation of tungsten by tetracycline. Hydrogen peroxide will form peroxotungstates[5] which are not extracted into the organic phase tetracycline benzyl alcohol.

h. Separation uranium-gold

Separation of uranium from gold is performed by using pure benzyl alcohol as organic phase (Fig. 8). At pH values smaller than 1.0 extrac-

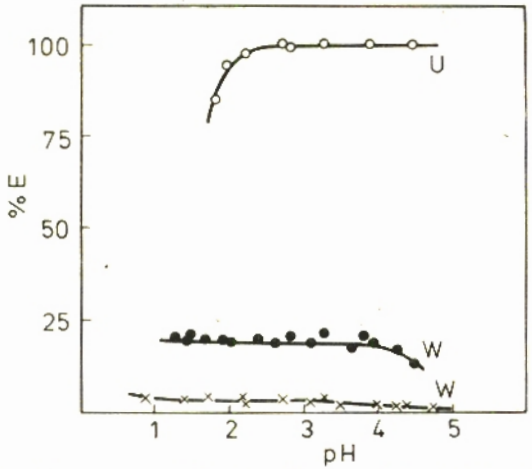

Fig. 7. Extraction curves for uranium and tungsten. (●) tungsten without masking agents; (x) tungsten with H_2O_2. Uranium = $8x10^{-5}$M; tungsten = 10^{-4} – 10^{-6}M; $NaClO_4$ = 0.10M; H_2O_2 = 3.15%; TC = 0.01M

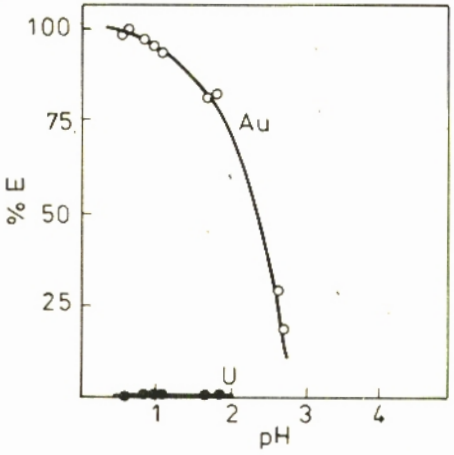

Fig. 8. Extraction curves for uranium and gold with pure benzyl-alcohol. Uranium = $8x10^{-5}$M; Au = $2x10^{-5}$M; $NaClO_4$ = 0.10M

tion of gold by pure benzyl alcohol is practically complete. Uranium is not extracted into the organic phase at this pH value when no tetracycline is present in the organic phase. Separation of uranium from gold at pH values higher than 1.0 by using tetracycline-benzyl alcohol as organic

phase is not efficient due to loss of gold in the interface of both phases as well as in the walls of the separating funnels.

i. Separation uranium-mercury

For the system uranium-mercury it was observed that losses of mercury ocurred when no masking agent was used or when the masking agent was EDTA. These losses, as in the case for gold, occur at the interface and at the walls of the separating funnels.

With buffered aqueous solution, at pH = 5.5, and EDTA as masking agent, the following results were obtained for extraction and losses of mercury: uranium extraction into the organic phase: 98.2% (mean value of three replicates); mercury extraction into the organic phase: 1.1% (mean value of five replicates); - loss of mercury at the interface or at walls: 38.9% (mean value of duplicate).

It is thus seen that it is possible to separate uranium from mercury but recovery of mercury is not complete.

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