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SOLVENT EXTRACTION STUDIES USING TETRACYCLINE AS A COMPLEXING AGENT. XIII. APPLICATION OF TETRACYCLINE FOR SEPARATION OF INTERFERING ELEMENTS IN ACTIVATION ANALYSIS OF URANIUM*

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Tetracycline in solution of benzyl alcohol was used as an extracting agent to separate uranium from interfering elements in the determination of uranium and of isotopic ratio $^{235}U/^{238}U$ by neutron activation analysis. Separation gives a recovery of 97% for uranium and the interferences from matrices of pitch-blende and monazite are eliminated.

INTRODUCTION

Separation of uranium from several elements using solvent extraction and tetracycline /TC/ as a complexing agent has been previously reported[1]. Ethylenediamine-tetraacetic acid /EDTA/ was used as a masking agent for

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lanthanides and diethylenetriaminepentaacetic acid /DTPA/ for lanthanides and thorium, allowing the complexation of uranium by TC whose complex was extracted by benzyl alcohol. Lanthanides and thorium are complexed by the masking agents and are not extracted into the TC-benzyl alcohol solution.

Although solvent extraction studies for tetracycline complexes have been carried out for several elements, it has not yet been fully exploited in the separation of elements present in real samples.

This study is now extended to chemical separation of interfering elements in activation analysis of uranium and in the determination of the isotopic ratio $^{235}U/^{238}U$, by neutron activation in samples of pitchblende and monazite.

Many other extractants such as tributyl phosphate, trioctylphosphine oxide and acetylacetone can be used in this type of separation. However, due to the fact that TC forms complexes with many elements a study should be carried out in order to apply it to various practical and useful separation. In this way TC will be an attractive alternative for many practical problems of radiochemical separations.

Thermal neutron activation allows uranium and isotopic ratio $^{235}U/^{238}U$ determinations, but in some cases the interference problems become serious since some of the elements of the matrix form, by /n,γ/ reactions, the same radioisotopes produced by fission of ^{235}U. Interfering elements may also form radioisotopes that emit γ-rays with energies close to the ones emitted by ^{239}Np or by fission products of ^{235}U. Besides, the Compton continuum consequent of the activation of various interferers makes difficult the detection of the γ-rays of ^{239}Np and of the fission products.

Use of epithermal neutrons for activation of uranium cannot always be a purely instrumental technique. Depending on the relation between concentration of uranium and interferers such as thorium and some lanthanides, which have high resonance integrals, such an exclusive instrumental technique cannot be applied.

Delayed neutron activation analysis is a method of broad application but when thorium is presnet in amounts larger than the amount of uranium, as in the case of monazite, for instance, the interference caused by thorium becomes appreciable.

EXPERIMENTAL

Reagents and solutions

Reagents used were of analytical grade and the solutions were prepared with deionized water distilled in a quartz apparatus. Benzyl alcohol and water were saturated with water and benzyl alcohol, respectively, to avoid a variation in volumes of the organic and aqueous phases during extraction.

A standard solution of uranyl nitrate was prepared by dissolution of U_3O_8, previously calcinated to 800 °C, in a few drops of concentrated HNO_3 and by heating. After eliminating the excess of acid by evaporation, the solution was diluted to give a concentration of 10^{-3}M in uranium.

Tetracycline solution in a concentration of 0.010M was prepared by dissolution of tetracycline hydrochloride /Laboraterápica Bristol SP/ in benzyl alcohol.

Procedure

100 mg of rocks were dissolved in about 10 ml of concentrated HNO_3 and 10 ml of 48% HF, both added in

small portions, and some drops of concentrated H_2SO_4. The mixture was heated and after dissolution the excess of acids was eliminated by evaporation of the solution to dryness. The residue was taken up in water. Solutions of DTPA and $NaClO_4$ were added to the sample solution and the volume was completed to 10 ml with water. The final concentration of DTPA and $NaClO_4$ were 0.010M and 0.10M, respectively.

This solution and 10 ml of 0.010M TC solution in benzyl alcohol were transferred into a separatory funnel. The pH of the aqueous phase was adjusted to 3.5 using dilute solutions of NaOH or $HClO_4$. The funnel was shaken for 30 min at a temperature of 25 °C. The aqueous phase was discarded. The organic phase was separated by decantation followed by centrifugation and 5 ml of this phase was transferred to another funnel and washed with 5 ml of an aqueous solution containing 0.10M $NaClO_4$ and 0.010M DTPA /see Table 1/. The pH of this solution was equal to 3.5. After phase separation, 50 μl of organic phase were pipetted on a small piece of Whatman No 41 filter paper. After drying under an infrared lamp, the paper was folded and introduced into an aluminum envelope for thermal neutron irradiation.

The uranium standards were prepared by pipetting 50 μl of a 5.0×10^{-5}M $UO_2/NO_3/_2$ solution onto the filter paper. Both sample and standard were irradiated together for 8 h in the IEA-R1 reactor at a neutron flux of approximately 10^{12} $n.cm^{-2}s^{-1}$. After a cooling time of 15 to 24 h, activity measurements were carried out using a Ge/Li/ detector whose resolution was 2.45 keV FWHM for the 1332 keV photopeak of ^{60}Co. The Ge/Li/ detector was coupled to a 4096-channel analyser and this to a minicomputer.

TABLE 1

Extraction values of U and of interferers into the organic phase

Element	Extraction percent	
	Before washing	After washing
U	97.8	97.1
Sm	- *	-
Fe	0.6	-
Zn	-	-
Ag	1.8 **	0.4 **
Th	2.3	-
Na	-	-
Ta	12.8 **	5.3 **
W	15.1	11.5
Mo	64.2	32.5

* Indicate that extraction is negligible.
** Ag and Ta are partially removed by adsorption into flask walls or in the interface.

RESULTS AND DISCUSSION

Interference studies and selection of γ-ray photopeaks

A natural uranium standard with 1.6 μg of U was irradiated in a flux of about 10^{12} n.cm^{-2}.s^{-1} for 8 h. Activity measurements were made 15 h after irradiation using ^{239}Np and fission product photopeaks. This cooling time was chosen in order to reduce the short-life radioisotope interferences and to attain the radioactive equilibrium between the fission products ^{99}Mo and ^{97}Zr and their respective daughters ^{99m}Tc and ^{97}Nb. The following γ-ray peaks were chosen to determine concentration and isotopic ratio of U in the samples: 106 and 277 keV for ^{239}Np; 141 keV for ^{99}Mo-^{99m}Tc; 668 keV for ^{132}Te-^{132}I; 293 keV for ^{143}Ce; 530 keV for ^{133}I and 658 and 743 keV for ^{97}Zr-^{97}Nb.

The 228 keV peak of ^{239}Np was not chosen due to the interference of 230 keV peak of ^{132}Te. Also the 556 keV peak of ^{91m}Y fission product was not used due to the interference of the 554 peak of ^{82}Br originated from bromine activation of the filter paper used as supporting material for irradiation.

The elements Th, Ta, Ag, W, Na, Zn, Fe, lanthanides and Mo are considered as interferers since ^{233}Pa, ^{182}Ta, ^{110m}Ag, ^{187}W, ^{59}Fe and several radioisotopes of lanthanides such as ^{153}Sm, ^{141}Ce, ^{152}Eu, ^{147}Nd have γ-ray energies close to the ones emitted by ^{239}Np or by fission products of ^{235}U. Na and Zn, by activation, form ^{24}Na and ^{65}Zn whose γ-spectrum has a Compton continuum that interferes, in a general way, with counting. Mo is also considered an interferer because it forms in the ^{99}Mo, by /n,γ/ reaction, which is the same radioisotope produced in the fission of ^{235}U.

Solvent extraction using DTPA as masking agent

Data for extraction of U, Th, Zn, Mo, Ta, W and lanthanides with TC-benzyl alcohol solution were presented in Refs 1 and 2. It was verified that without masking agent U could not be separated from Fe, Th, Mo, W and Sm with a single extraction. In the range of pH 2.5 to 3.0 only Na, Ag and Zn could be eliminated from U. Na and Ag are not extracted and loss of Ag and Ta occurred during the extraction.

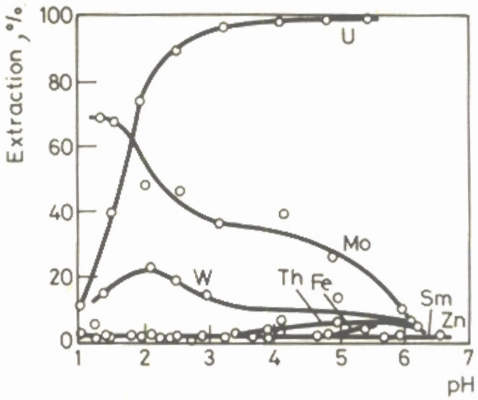

Fig. 1. Extraction curves with tetracycline-benzyl alcohol solution in the presence of DTPA and standard ore solution. TC = 0.010M; $NaClO_4$ = 0.10M; DTPA = 0.010M. Elements = 2.0×10^{-3}M to 1.0×10^{-5}M

However, if DTPA is added to the aqueous phase such a separation becomes possible as can be seen in Fig. 1.

Determination of amount of interferers extracted into the organic phase

These experiments were carried out as described in the procedure using ^{24}Na, ^{65}Zn, ^{59}Fe, ^{110m}Ag, ^{234}Th, ^{182}Ta, ^{187}W, ^{153}Sm and ^{99}Mo radioactive tracers. Results of the amount extracted into the organic phase are presented in Table 1. It is seen that extraction of U is practically quantitative and that the elements Sm, Zn, Na remain in the aqueous phase. Ag and Th are slightly extracted and even this extraction can be reduced to negligible amounts by washing the organic phase with an aqueous solution of 0.10M $NaClO_4$ and 0.010M DTPA. Mo, W and Ta are partially extracted into the organic phase. However, after two washings of the organic phase with the mentioned aqueous solution their amount may be reduced to values that do not interfere with the U determination by activation with thermal neutrons.

Application

1. Analysis of uranium

The proposed method was applied to the analysis of uranium in a standard ore with 0.527% U_3O_8 /IAEA, S-7, pitchblende, Lot No. 43/ and in two samples of monazite. The results are presented in Table 2.

Application of a Student t test[4] on the mean values obtained at a confidence level of 95% shows that the results found for the concentration of uranium in the IAEA ore can be considered as equal to the value of the IAEA certificate[3]. The relative errors were lower than 3%, which is considered as a good result. Besides the total error of the method, calculated using the criterion developed by McFarren et al.[5] and by Eckschlager[6], was lower than 20%, which allows one to classify the method as "excellent".

In spite of the fact that Mo and W were not completely eliminated, it was observed that their remaining amount did not interfere with the results.

2. Determination of $^{235}U/^{238}$ ratio

Table 3 shows the results obtained for isotopic determination of uranium.

A statistic t test[4] at a confidence level of 95% applied to these results of isotopic ratio shows that the rocks analyzed have the isotopic ratio of natural uranium, i.e., $^{235}U/^{238}U$ ratio is equal to 7.252×10^{-3} /values for ^{238}U and ^{235}U taken from Holden[7]/.

TABLE 2

Results of uranium analysis in pitchblende and monazite samples

	Pitchblende /a/		Monazite 1 /b/	Monazite 2 /c/
	U_3O_8, %	Relative error, %	U_3O_8, %	U_3O_8, %
^{239}Np 106 keV	0.528±0.008[x]	0.2	0.991±0.017	0.0332±0.0024
^{239}Np 278 keV	0.527±0.006	0	0.973±0.016	0.0316±0.0006
^{99}Mo 140 keV	0.531±0.016	0.8	0.971±0.030	0.0327±0.0019
^{143}Ce 293 keV	0.528±0.024	0,2	1.07 ±0.11	/d/
^{133}I 530 keV	0.533±0.022	1.1	0.977±0.077	0.0313±0.0024
^{97}Nb 658 keV	0.510±0.038	3.2	1.009±0.044	/d/
^{97}Zr 744 keV	0.514±0.030	2.4	0.990±0.082	0.0350±0.0024
^{132}I 668 keV	/e/	/e/	0.903±0.056	/e/

/a/, /b/ and /c/ results are mean of 6, 5 and 4 determinations, respectively.
/d/ - Results with relative standard deviations higher than 10%.
/e/ - Calculation was not possible /peak was not detected/.
/x/ - Standard deviation.

TABLE 3

Determination of $^{235}U/^{238}$ ratio

		Pitchblende [a] x 10^3	Monazite 1 [b] x 10^3	Monazite 2 [c] x 10^3
^{239}Np	^{99}Mo 140 keV	7.29±0.18 [*]	7.07±0.21	7.16±0.16
106 keV	^{143}Ce 293 keV	7.29±0.44	7.36±0.58	/d/
relative to	^{133}I 530 keV	7.31±0.29	7.14±0.49	6.85±0.71
	^{97}Nb 658 keV	7.00±0.58	7.38±0.20	7.09±0.54
	^{97}Zr 744 keV	7.20±0.57	7.28±0.46	7.65±0.32
^{239}Np	^{99}Mo 140 keV	7.30±0.21	7.20±0.18	7.51±0.32
278 keV	^{143}Ce 293 keV	7.28±0.37	7.50±0.64	/d/
relative to	^{133}I 530 keV	7.32±0.30	7.28±0.47	7.18±0.52
	^{97}Nb 658 keV	7.01±0.52	7.52±0.24	7.45±0.73
	^{97}Zr 744 keV	7.08±0.42	7.38±0.50	/d/

/a/, /b/ and /c/ results are mean of 6, 5 and 4 determinations, respectively.
/d/ - Results with relative standard deviations higher than 10%.
/*/ - Standard deviation.

For the determination of uranium concentration and $^{235}U/^{238}U$ ratio in pitchblende and monazite 1 samples, the relative standard deviations were lower than 10%. For analysis of monazite 2, some results presented relative standard deviations higher than 10% due to bad counting statistics and in this case the results are not presented.

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