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AN IMPROVED METHOD FOR DETERMINATION OF URANIUM ISOTOPIC COMPOSITION IN URINE BY ALPHA SPECTROMETRY

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A comparative study of source preparation techniques to determine uranium isotopic composition by alpha spectrometry, namely electrodeposition and chemical stripping with polymeric membranae containing trioctylphosphine oxide (TOPO), is presented. The mean yield obtained for electrodeposition and TOPO deposition were 85% and 74%, respectively. The mean activity ratio $^{235}U/^{238}U$ were 0.044 and 0.042 and the ratio $^{234}U/^{238}U$ were 0.994 and 1.009, using electrodeposition and TOPO deposition techniques, respectively. The method of uranium separation from urine using an ion-exchange resin Dowex 1x8, chloride form and citrate form, was also studied. The obtained global yields of these methods were 50% and 41%, respectively.

The determination of uranium in urine is important to control the internal contamination, as well as the workers' equivalent dose. When the uranium isotopic composition is known, the fluorimetric technique is suitable, due to its high sensitivity and quickness. Otherwise it is necessary to use techniques such as alpha spectrometry or mass spectrometry.

Determination of uranium isotopic composition by alpha spectrometry requires a very high degree of chemical purification because interferents give rise to self-absorption of the alpha particle in the sources, which is a critical point. We have had experience with solvent extraction techniques to separate uranium from urine, but these techniques are very time-consuming and, moreover, results obtained by these methods greatly depend on the skill of the individual investigator.

Several investigators have reported on the ion-exchange methods of analysis for uranium by alpha spectrometry,[1,3,4,5,6,10,11,13,14] but some methods are not directly applicable for the urine samples because this is a complex sample with variable interferents.

Iron is the principal interferent because it is able to form, as the uranium, anionic complex in strong hydrochloric acid, so that they are absorbed on an anion exchanger and in very diluted hydrochloric acid solutions, the complex ionic UO^2Cl^{4-} and $FeCl^{4-}$ are not stable so that they can be eluted from the column. Subsequently, in the alpha source preparation they are deposited jointly.

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The aim of this work is to study a simple, rapid and economic method to determine the uranium isotopic composition in urine by alpha spectrometry, using ion-exchange techniques.

The uranium separation from urine using ion-exchange column with Dowex 1x8 resin, citrate form and chloride form, was studied. The adopted procedure was based upon two methods from the literature.[9,12] Separation and radiochemical purification of uranium from other elements is achieved on a single anion exchange column by washing with HCl and IBMK solution.

Firstly, a comparative study for alpha source preparation techniques, namely electrodeposition and chemical stripping with polymeric membranae containing trioctylphosphine oxide (TOPO), was made. For the uranium electrodeposition, the conditions established by Mertzig[7] were used and for the TOPO deposition, the method developed by Sachett[2] was used.

Experimental

Alpha source preparation: Electrodeposition

The uranium was deposited on a polished 304-stainless steel disc 25 mm in diameter and about 1 mm thick, using a lucite cell with brass base as the cathode, a platinum wire of 1 mm in diameter as the anode and NH_4Cl as electrolyte applying a current of 1.2 A. The sample volume was 5 cm^3 in 1 M HCl and the electrolysis time was 60 minutes.

Alpha source preparation: TOPO deposition

The TOPO ($(CsH_{17})_3PO$) is a complex agent used for chemical separation of uranium. This agent has shown high solubility in ciclohexanone and high extraction coefficient in 1 M HNO_3 solutions, forming $UO_2(NO_3)_2 \cdot 2TOPO$.[2,8]

The uranium was deposited on the same type of steel used for electrodeposition, covered with a film having the following composition: 1.025 g of TOPO and 1.25 g of vinyl chloride acetate (VINNOL H 10/60), dissolved in 4 cm^3 ciclohexanone, and placed 20 minutes in an oven at 40°C. The disc was fixed in the lucite cell. The sample was dissolved in 3 cm^3 of 1 M HNO_3 and was stirred with a curled glass rod and rotated at approximately 50 rpm for 120 minutes. Then the disc was washed with distilled water and ashed in a muffle furnace for 60 minutes at 400°C.

To study the behavior of these two techniques, seven alpha sources with different quantities of natural uranium were prepared for each one. To determine the reproducibility and recovery of the two techniques, 20 sources with 16.5 µg of natural uranium were prepared.

The uranium chemical separation of urine

For the pre-treatment, 100 cm^3 of urine sample was evaporated to dryness and was oxidized by repeated digestion using 16 M HNO_3 and H_2O_2 (120 v), forming a white residue.

For the citrate form, as well as for the chloride form, the ion-exchange column with 1.0 cm diameter, was filled with 15 cm^3 of Dowex 1x8 (200-400 mesh) resin.

The uranium chemical separation of urine in the citrate form

The resin was slurred with 100 cm^3 of solution containing 10 g of citric acid, 3 g of sodium citrate and 2 g of ascorbic acid dissolved in distilled water and diluted with water to 1,000 cm^3.

The residue from pre-treatment was dissolved in 100 cm^3 of the above solution and passed through the resin. The resin was washed with 100 cm^3 of isobutyl methyl ketone (IBMK), acetone and 1 M HCl solution (1:8:1 v/v), then with 100 cm^3 of 6 M HCl. The uranium was eluted with 100 cm^3 of 1 M HCl.

The uranium chemical separation of urine in the chloride form

The resin was slurred with 50 cm^3 of 8 M HCl and the residue from the pre-treatment was dissolved in 8 M HCl and passed through the column. The resin was washed with 50 cm^3 of IBMK solution and then with 50 cm^3 of 6 M HCl. The uranium was eluted from the resin with 50 cm^3 of 1 M HCl, evaporated to dryness and oxidized with 2-3 cm^3 of 16 M HNO_3 and drops of H_2O_2 (120 v).

A constant flow rate of about 1 cm^3/min was maintained throughout the ion-exchange procedure. To determine the reproducibility and the chemical yield of the two methods, two urine samples with 16.5 µg of natural uranium were analyzed for each method.

Alpha counting system

The samples were alpha counted using a 300 mm Si surface barrier detector model 576A, EG&G ORTEC, in conjunction with Multiplexer Router model 476, EG&G ORTEC, and with ADCAM system coupled to a microcomputer. The vacuum system pressure was maintained around 10^{-2} mbar.

The nominal efficiency of the detector was 29% and the resolution was 15 keV at FWHM for the ^{241}Am alpha peak. The counting time was 60,000 sec.

The calibration in energy was performed using the three uranium isotopes: ^{238}U (4,200 keV), ^{235}U (4,400 keV) and ^{234}U (4,770 keV).

Results and Discussion

Alpha source preparation

The uranium recovery from urine by the two techniques for different concentrations, as well as the activity ratios of $^{234}U/^{238}U$ and $^{235}U/^{238}U$, are presented in Table 1. The curve of the obtained activity versus added uranium mass is shown in Figure 1.

As shown in Table 1, the obtained recoveries (R%) of the TOPO deposition sources were slightly lower than the case of electrodeposition for all concentrations. The activity ratios of $^{234}U/^{238}U$ and $^{235}U/^{238}U$ obtained for TOPO did not show any variation for different concentrations. This occurs because the film saturates and the uranium in excess is eliminated by washing, while in the electrodeposition technique, all uranium in solution is deposited, causing a larger self-absorption that results in a poorer resolution for concentrations above 80 µg, and the tail of ^{238}U affects the ^{235}U spectrum.

It is seen in the TOPO curve, Figure 1, that the activity starts to become constant when the mass of uranium is 20 µg. This is due to the film saturation because the exchange capacity of the TOPO membrane decreases when the uranium concentration surpasses a certain value. This value depends on the film thickness and varies from about 20 to 50 µg.[7]

The obtained reproducibility and resolutions of U-234 and U-238 are shown in Table 2. The better resolution presented by the TOPO sources can be explained by the uranium extraction selectivity by the TOPO, while the electrodeposition is not selective and any metal in solution can be deposited, increasing the self-absorption effects.

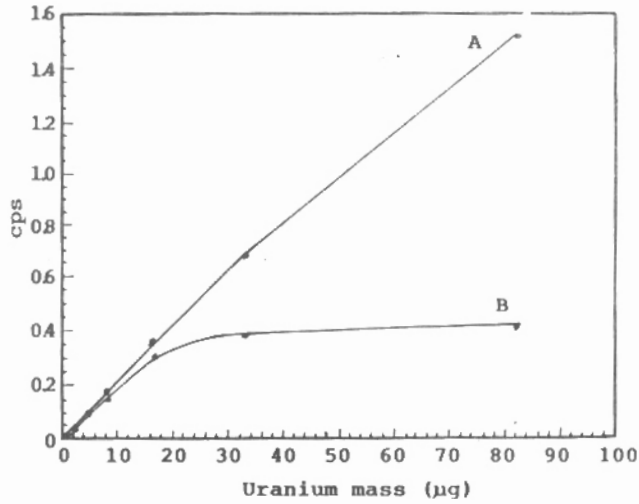

Figure 1. Counting rate x uranium mass for electrodeposition (A) and TOPO (B).

TABLE 1

Recovery and isotopic ratio for TOPO and electrodeposition

Mass of natural uranium (μg)	TOPO			Electrodeposition		
	R(%)	$^{234}U/^{238}U$	$^{235}U/^{238}U$	R(%)	$^{234}U/^{238}U$	$^{235}U/^{238}U$
0.82	67	0.862	0.065	81	0.846	0.041
2.47	73	1.049	0.052	76	0.995	0.046
4.80	72	0.998	0.042	80	1.006	0.048
8.25	70	1.000	0.046	85	1.008	0.043
16.50	73	1.006	0.046	85	1.008	0.045
33.00	46	1.004	0.044	81	0.999	0.045
82.50	20	0.999	0.048	72	0.998	0.097

TABLE 2

Comparative data between TOPO and electrodeposition

Data	TOPO	Electrodeposition
Number of sources	20	20
Yield	74 ± 6 %	85 ± 5 %
Resolution ^{238}U	50 ± 10 keV	75 ± 12 keV
Resolution ^{234}U	45 ± 9 keV	80 ± 7 keV
$^{234}U/^{238}U$	1.009 ± 0.010	0.994 ± 0.010
$^{235}U/^{238}U$	0.042 ± 0.003	0.044 ± 0.003

One drawback of the TOPO technique is that it requires more steps than the electrodeposition technique, namely the film preparation and the calcination. It also consumes more time for deposition. On the other hand, the electrodeposition is more expensive because it is necessary to use platinum, electrical connection and the electrolytic cell is corroded by the NH_4Cl, decreasing its lifetime.

Uranium chemical separation from urine

The obtained global yield of the ion-exchange in the chloride form was 50% and in the citrate form was 41%. The two methods were considered satisfactory, but the chloride form was chosen because of its simplicity, economy and quickness.

In the sorption solution, 8 M HCl, uranium is separated from aluminum, chromium and nickel. Cobalt, copper, etc., are separated from uranium by elution with 6 M HCl. The iron, which is the main interferent, was removed by elution with the IBMK solution because in this medium

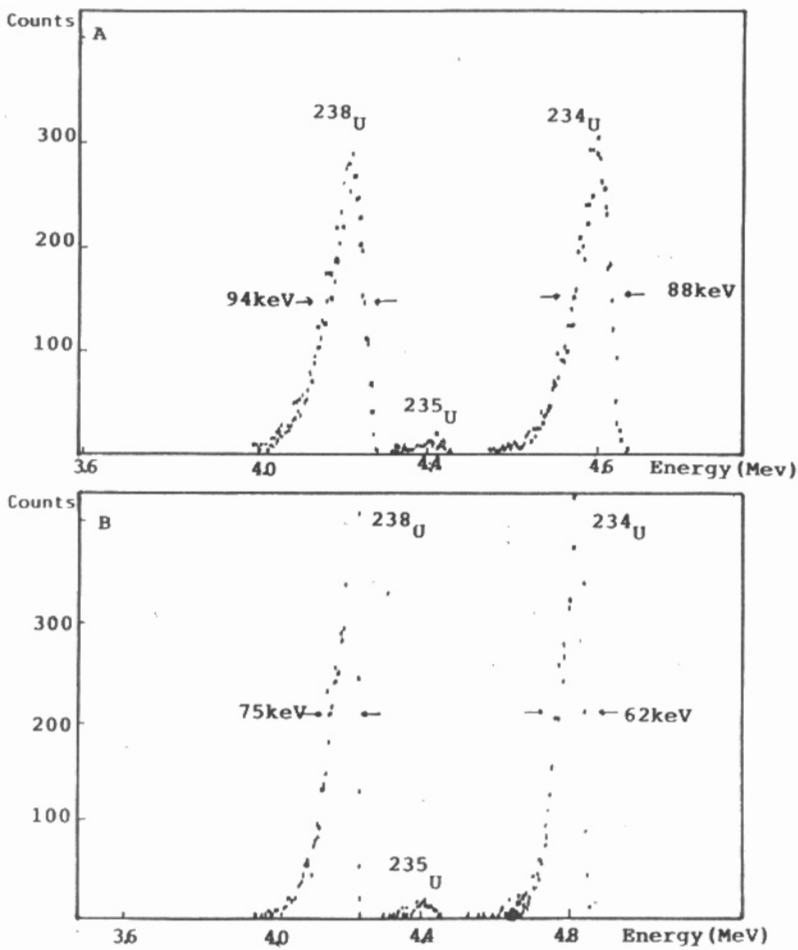

Figure 2. Energy spectra of urine sample with 16.5 μgU, after uranium chemical separation. Electrodeposition (A) and TOPO (B).

the Kd-values of iron and uranium are 1 and 1050, respectively.[9] In the subsequent uranium elution with 1 M HCl, an eluate is obtained containing only uranium because the co-absorbed zinc and cadmium are not eluted under these conditions.

By the high quality of the obtained spectra shown in Figure 2, the selectivity of the method for uranium can be seen. Since the ion-exchange separations presented in this paper can be performed in batches, several samples can be analyzed simultaneously and thus the method is suitable for the routine determination of uranium in urine.

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