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Implementation of alpha-spectrometry for uranium isotopes in excreta samples

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The measurement of radioactivity concentrations in excreta is an important tool for the monitoring of possible radionuclide intakes by occupationally exposed workers. For this purpose, a radiochemical procedure for the determination of alpha-emitting isotopes of uranium in excreta has been optimized. The main steps involved in this procedure are pre-concentration, dissolution of sample, separation by ion-exchange resin, electrodeposition and alpha-spectroscopy. ^{232}U tracer is used to monitor chemical recoveries and correct the results to improve precision and accuracy. The quality control of radiochemical analysis in urine and faecal samples has been performed with participation in intercomparison exercises. The results obtained from these samples, with chemical recoveries (80–95%), are shown to be highly consistent. The method offers good prospects to be applied in routine monitoring programme of workers.

Introduction

When handling unsealed radioactive material, internal exposures cannot always be ruled out. In these cases the protection of the workers requires individual monitoring as well as the monitoring of the working environment.

The surveillance program for uranium at Brazilian Nuclear Facilities is most based on excreta analysis. The procedure for internal monitoring for the workers handling both natural uranium and enriched uranium at Instituto de Pesquisas Energéticas e Nucleares (IPEN) used to be fluorimetry.[1] A revision of bioassay programme was carried out and it has shown the need to implement a new analytical procedure, mainly to measure enriched uranium. According to the International Commission on Radiological Protection, ICRP-78,[2] the method of measurement for ^{234}U, ^{235}U and ^{238}U is radiochemical separation and alpha-spectrometry on urine and faeces samples with typical detection limit of 10 mBq·l^{-1} and 10 mBq, respectively.

The determination of low concentrations of these elements in biological samples requires time consuming and tedious chemical procedures. An essential feature of these methods is the pre-concentration and purification of the actinides of interest. This is important to isolate them from the large amounts of inactive substances present in the sample and also to separate them from radioisotopes that may interfere with alpha-spectrometry.[3]

In this paper, a procedure for the determination of uranium isotopes in excreta samples is presented. The main steps involved in this procedure are pre-concentration, dissolution of sample, separation by ionic exchange resin, electrodeposition on stainless steel discs and counting by alpha-spectrometry. The accuracy and reliability of our analytical procedure was confirmed by participation in international intercomparison exercises runs. The establishment of an internal exposure monitoring programme based on the measurement of excreta samples is also discussed.

Experimental

All the reagents were of analytical grade and the solutions were prepared with deionized water. The radionuclide ^{232}U in nitric solution with a specific activity of approximately 0.02 Bq·ml^{-1}, used as tracer, was supplied by Institute of Radiation Protection, IRD-RJ, Brazil. The anionic resin Dowex 1X8 (100–200 mesh, chloride form) for uranium isotopes separation was also used. Electrodeposition cells, stainless steel discs of 25 mm in diameter for plating (cathode) and platinum electrode (anode) and alpha-spectrometer were also employed in this procedure.

Procedures

Basic features of the determination method for uranium in urine and faeces samples are illustrated in Fig. 1.

Sample preparation (pre-concentration step)

Urine: Plastic containers are used for the sample collection of twenty-four hour urine samples. The total volume of the sample is recorded and one liter of urine sample is transferred into a glass beaker. The containers are rinsed with 100 ml conc. HNO_3 and the rinsing liquid is added to the sample. Aliquots of 20 ml of 30%

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H_2O_2, 1 ml of conc. H_3PO_4 and 2 ml $CaCl_2 \cdot H_2O$ 0.7M are added to the sample. Next, 2 ml of ^{232}U tracer solution (approximately 40 mBq) is added to quantify chemical recovery. The sample and tracer are equilibrated by heating and magnetic stirring for one hour. The sample is removed from the heat, cooling to room temperature and conc. NH_4OH is slowly added until precipitation occurs. The precipitate is allowed to settle overnight and separated by decanting and centrifugation. The supernatant is discarded and the precipitate is transferred to a centrifuge tube. The beaker is washed 3 times with 50 ml of 1.25% ammonia solution and the rinsing liquid transferred to the centrifuge tube. After centrifuging, the supernatant is discarded and the precipitate is dissolved in 10 ml conc. HNO_3. The solution is transferred to Teflon beaker and evaporated to dryness in a hot plate. Wet-ashing of the residue is carried out with small amounts of concentrated HNO_3 and concentrated HCl twice.

Faeces: The faeces are collected in appropriate containers during a period of 48 hours and frozen. The frozen material is transferred to a porcelain capsule and placed in a closed furnace and the temperature is gradually raised in increments of 50 °C, until 450 °C is reached and dry-ashed for 24 hours.

The ashes were weight and transferred to a Teflon beaker. Next, the ^{232}U yield tracer is added into the sample. The wet-ashing is carried out with conc. HNO_3 and conc. HF. The solution was evaporated to dryness. The residue is treated with the addition of 5 ml conc. HNO_3 to expel the fluoride and evaporated to dryness. This process is repeated with small amounts of conc. HCl acid and evaporated to dryness twice.

Finally, the residues obtained in the previous steps (preparation of urine or faecal sample) are dissolved in 80 ml of 8M HCl (Solution A).

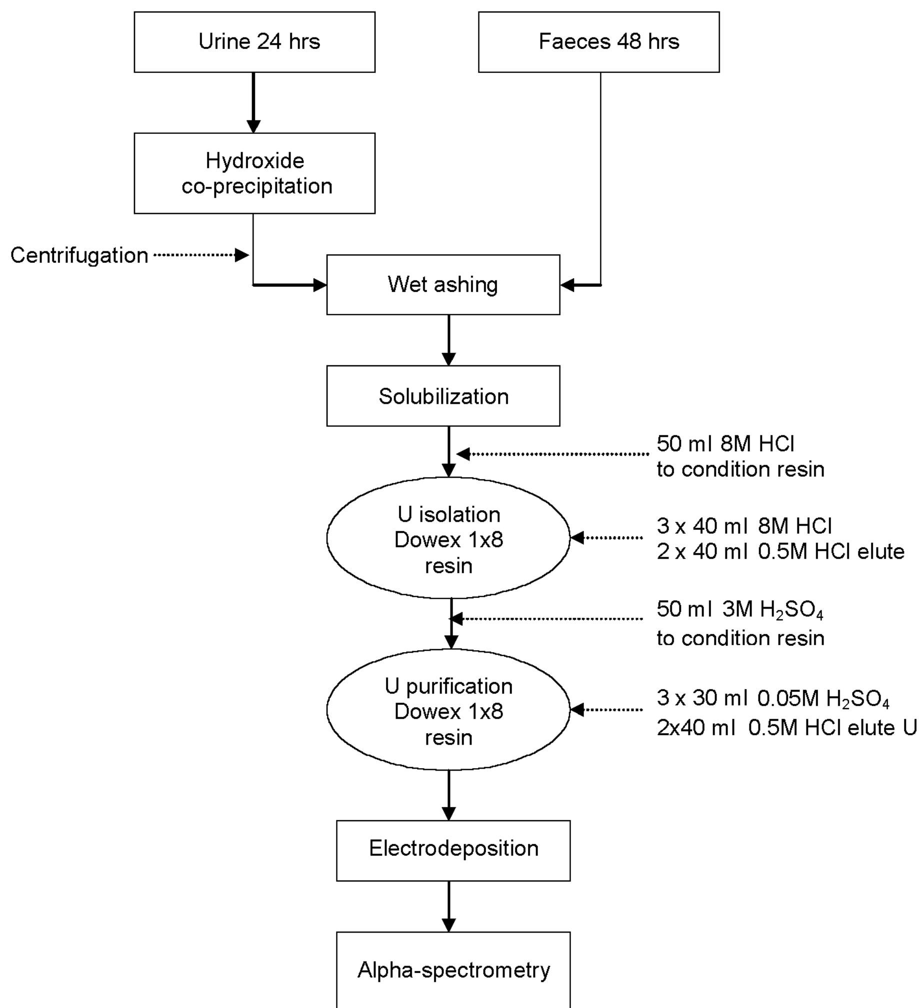

Fig. 1. Flow chart of the analytical procedure for the measurement of uranium in excreta samples

Radiochemical separation

The uranium separation and purification, is performed by anion-exchange using Dowex 1X8. An amount of 10 g of resin, suspended in H_2O, is transferred into a glass column and rinsed with 50 ml of 8M HCl. The sample (Solution A) is loaded and the resin is washed with three fractions of 40 ml each of 8M HCl. The effluent is collected if thorium is to be determined otherwise it is discarded. The uranium is eluted from the resin with two fractions of 40 ml 0.5M HCl solution (Solution B), dried and the residue is re-dissolved in 100 ml 0.05M H_2SO_4. The Solution B is again percolated through 10 ml of ion-exchange resin (Dowex 1x8) preconditioned with 50 ml of 3M H_2SO_4. The impurities are eluted with 0.05M H_2SO_4 and the retained uranium is eluted with two fractions of 40 ml each of 0.5M HCl. The uranium solution (Solution C) is evaporated to dryness on a low temperature hotplate. Wet-ashing of the residue is carried out with 5 ml of conc. HNO_3. This procedure is repeated 3 times.

Electrodeposition

Source preparation for alpha-particle counting is performed by electrodeposition following the procedure described by TADDEI et al.[4,5] In this case, 3 ml of 0.8M ammonium sulphate and drops of 3M sulphuric acid is added to the residue from the previous step. The solution is warmed and after cooling it is transferred to an assembled plating cell with 5 ml of 0.8M ammonium sulphate. The pH is adjusted to 2.0 with ammonium hydroxide, using thymol-blue as an indicator. The cell is placed in an electrodeposition device with a platinum electrode at 5 mm of the stainless steel disc. Electrodeposition is carried out at 1.2 A during 1 hour. At the end of this period 1 ml of conc. NH_4OH is added to the cell before switching off the current. The cell is disassembled and the disc is washed with water and then methanol.

Alpha-spectrometry

The alpha-spectrometry is carried out using semiconductor surface barrier detector with an area of 450 mm^2, Canberra alpha analyst model, with a detection time of 200,000 seconds.

Results and discussion

Examples of α-spectrum for uranium isotopes in urine and faecal ash samples processed with this method are presented in Fig. 2a and Fig. 2b, respectively, where the ^{232}U peak is due to the added tracer.

The uranium spectrum showed good resolution since the full width at half maximum (FWHM) was approximately 100 keV (~1.9%) at 5.32 MeV (Figs 2a and 2b). However, such resolution is highly dependent on the well-polished surface of the stainless steel discs, on the total elimination of organic matter from the electrodeposition solution and on careful pH adjustment just before electrodeposition. The ^{232}U tracer recovery, both for urine and faeces samples was in the range 80 to 95%, pointing to the efficiency and selectiveness of the method. These values are in the range reported in literature.[6]

The activity concentration of ^{238}U and ^{234}U in faeces samples ranged from 2.0 to 4.8 $Bq \cdot kg^{-1}$ as can be seen in Table 1. The results obtained showed radioactive equilibrium between these radionuclides. Such values of uranium in faeces samples are an indication of small intakes of this element, as in the case of the people living in a region with high natural radioactivity.[4] The activity concentration of ^{238}U and ^{234}U in urine samples is showed in Table 2 for workers occupationally exposed.

The quality control of radiochemical analysis for uranium in urine and faeces samples has been performed with participation in 2004 International Intercomparison exercises organized by Procorad (Association for the Promotion of Quality Control in Radiotoxicological Bioassays).[7]

The results obtained for uranium in urine and faecal samples were always within the 95% confidence level (2σ), and the differences with the reference values were not statistically significant, as shown in Table 3.

The great contribution of uranium alpha-spectroscopy for to the occupational monitoring programme is to determine all the alpha-emitters with low detection limits. The detection of uranium isotopes at very low levels requires extensive sample preparation or pre-concentration and also very long counting times with very low background equipment. This technique focuses on the radiochemical toxicity of uranium, which is our main concern. The fluorimetry technique is also applied in routine monitoring programme and the target is the chemical toxicity of uranium.

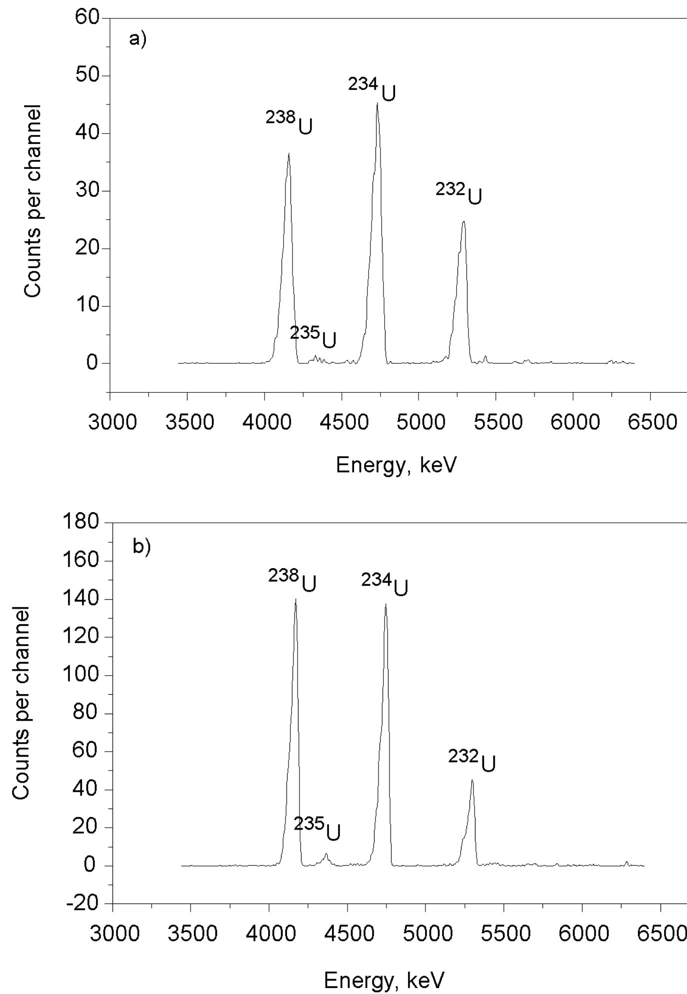

Fig. 2. Alpha-spectrum of uranium isotopes in a faeces sample (a) and in a urine sample (b)

Table 1. Activity concentration of ^{238}U and ^{234}U in faeces samples

Sample	^{232}U recovery, %	Activity concentration,* Bq·kg^{-1}	
		^{238}U	^{234}U
Faeces 01	90	3.2 ± 0.2	3.4 ± 0.2
Faeces 02	80	4.5 ± 0.3	4.8 ± 0.3
Faeces 03	93	3.8 ± 0.3	3.5 ± 0.3
Faeces 04	95	2.0 ± 0.2	2.3 ± 0.2

* The total uncertainty was determined for a confidence level of 95% (2σ).

Table 2. Activity concentration of ^{238}U and ^{234}U in urine samples

Sample	^{232}U recovery, %	Activity concentration,* Bq·kg^{-1}	
		^{238}U	^{234}U
Urine 01	87	1.98 ± 0.41	2.02 ± 0.37
Urine 02	85	2.01 ± 0.32	2.08 ± 0.30
Urine 03	84	10.95 ± 0.96	15.98 ± 1.12
Urine 04	82	8.96 ± 0.65	25.55 ±1.22

* The total uncertainty was determined for a confidence level of 95% (2σ).

Table 3. Uranium by activity in urine measurements. Uranium reference value and measured values in 2004 Intercomparison Exercises organized by Procorad

Sample	Nuclide	Reference value	Measured value*
		Bq/sample	
A	^{234}U	$1.25 \cdot 10^{-1} \pm 2.73 \cdot 10^{-3}$	$1.12 \cdot 10^{-1} \pm 4.68 \cdot 10^{-3}$
	^{238}U	$1.30 \cdot 10^{-1} \pm 2.84 \cdot 10^{-3}$	$1.12 \cdot 10^{-1} \pm 4.68 \cdot 10^{-3}$
	^{235}U	$6.00 \cdot 10^{-3} \pm 1.34 \cdot 10^{-4}$	$5.13 \cdot 10^{-3} \pm 5.11 \cdot 10^{-4}$
B	^{234}U	$1.27 \cdot 10^{-2} \pm 2.77 \cdot 10^{-4}$	$1.41 \cdot 10^{-2} \pm 1.18 \cdot 10^{-4}$
	^{238}U	$1.32 \cdot 10^{-2} \pm 2.87 \cdot 10^{-4}$	$1.37 \cdot 10^{-2} \pm 1.22 \cdot 10^{-3}$
	^{235}U	$6.06 \cdot 10^{-4} \pm 1.32 \cdot 10^{-5}$	$6.28 \cdot 10^{-4} \pm 3.00 \cdot 10^{-5}$

* The total uncertainty was determined for a confidence level of 95% (2σ).

Conclusions

The participation in the inter-laboratory comparison exercises makes it possible to check the accuracy, precision and the personal variations of the techniques being utilized for the monitoring program.

The selection of the analytical techniques for the determination of uranium in excreta samples for monitoring purpose and performed at the Brazilian facility is influenced mainly by the potential for workers exposure to uranium compounds of different isotopic composition, the kind of tasks carried out by workers, and the knowledge of the workplace conditions.

In this study, the implementation of proposed methodology offers good prospects to be applied in routine monitoring programme of workers, mainly for natural and enriched uranium compounds.

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