RADIOANALYTICAL DETERMINATION OF $^{239+240}$Pu AND ^{241}Am IN BIOASSAY SAMPLES BY ANION EXCHANGE AND EXTRACTION CHROMATOGRAPHY: PRELIMINARY CONSIDERATIONS ABOUT THE TWO METHODS

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During the radiation protection surveillance of exposed workers samples of urine and faeces were collected. Anion exchange chromatography was used for the separation of Pu. We investigated a technique to purify and separate Pu and Am isotopes using extraction chromatography with TRU resin. We tested different procedures to dissolve organic matter and eliminate interferences for chromatographic elution. At the end of the process we have succeeded in electroplating the two radionuclides separately. We have also studied extraction chromatography with UTEVA resin to purify Pu isotopes and separate it from natural uranium radioisotopes, present in some biological samples. We validated a method for the determination of Pu in biological samples and a rather constant chemical yield and resolved peaks were obtained. The preliminary studies on TRU resin have indicated that it is possible to combine extraction and anion-exchange chromatography for analysing separately Pu and Am isotopes from the same sample aliquote.

1 Introduction

During the radiation protection surveillance of the workers, involved in decommissioning activities of a reprocessing nuclear plant, radiotoxicological analyses on excreta were carried on in order to determine a possible internal contamination by $^{239+240}$Pu. Actinides normally have not a sufficient γ-emission to be detected by *in-vivo* measurements. Usually excreta monitoring programmes plan analyses of urine, because there is not a big daily fluctuation in 24 h representative sample and collection for routine monitoring is rather simple. Anyway faecal analyses can be required when the element is preferentially excreted via faeces (like in the case of inhaled or ingested Am) or to evaluate Type-S material clearance from the respiratory tract [1].

Due to its extremely high radiotoxicity and because of the great difficulty to detect it at very low levels, Pu is an element which requires great attention [2]. The decommissioning activities of the workers monitored in our surveillance programme expose them mainly to internal contamination risk. We decided to investigate a method for determining simultaneously Am in excreta to offer a more accurate radiation protection surveillance service, because Pu contamination often goes with Am contamination [2,3]. For this

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purpose we tried to separate both radionuclides from the same sample. To improve both the chemical recovery and the decontamination factor two different chromatographic techniques before electroplating were used: anion-exchange with chloride form AG 1-X2 resin chromatography and extraction chromatography with TRU resin. We tested different molecular species to find the best reducing agent for Pu and we considered the possibility to use UTEVA resin to retain uranium avoiding its deposition during the electroplating process.

2 Experimental

All commercial chemicals were of analytical-reagent grade and were used with no further purification. ^{242}Pu was used to spike all the samples; further tests have been performed using both ^{242}Pu and ^{243}Am. The standard solutions of ^{242}Pu and ^{243}Am were supplied by Amersham (UK). The standard solution of ^{242}Pu was diluted to obtain a specific activity of 53.5 mBq L^{-1} in 2M HNO_3, ^{243}Am standard solution was diluted to 10.7 mBq L^{-1} in 2M HNO_3.

The anion-exchange resin used in this work was the chloride form of AG 1-X2 resin (50-100 mesh, Bio-Rad). The resin was first conditioned in a glass column (20 mL volume, internal ∅ 9 mm, h = 80 mm) with HNO_3 8 M (*ca*. 100 mL). For the extraction chromatography we used TRU and UTEVA columns, purchased from Eichrom Technologies. AG 1-X2 resin shows a high affinity for tetravalent species [4], while TRU resin has a high retention for trivalent and tetravalent species of actinides [5]. On the other hand these tetravalent and hexavalent species have high value of distribution coefficients for UTEVA resin. Lower pH reduces the affinity for tetravalent and hexavalent actinides [6,7]. Demineralised water by an OSMODEMI water purification system was used (BICASA, Milan, Italy).

1 L of urine sample was placed in a Pyrex beaker, spiked with 0.0107 Bq of ^{242}Pu and mineralized with concentrated HNO_3 (150 mL) to decompose organic matter. After introduction of 1 mL of 1.25 M $Ca(NO_3)_2$, it was heated under magnetic stirring for 3 hours at *ca*. 100 °C on hot plate; if abundant foam was observed some drops of 2-ethyl-1-hexanol were added, for its antifoam action. After the sample had cooled down (*ca.* 2 hours), 0.5 mL of 3.2 M $(NH_4)_2HPO_4$ were added and under magnetic stirring the solution pH was slowly adjusted to *ca.* 9 with ammonium hydroxide (generally 200 – 250 mL of NH_4OH were added dropwise). In conditions of basic pH calcium and phosphate ions precipitate and, since calcium is an isodimorphous carrier for actinides, these elements precipitate. The sample was left overnight, then the supernatant was discarded and the precipitate was centrifuged. The supernatant was discarded and washed with H_2O and centrifuged. This operation was repeated twice. The precipitate was dissolved in 5 mL of concentrated HNO_3 in a quartz beaker. Both the original Pyrex beaker and the centrifuge tube were rinsed two times with 5 mL of concentrated HNO_3 and the rinse was transferred to the quartz beaker. 2 mL of H_2O_2 were added to oxidize the remaining organics in the sample and evaporated to dryness. To ensure a complete elimination of organic material 5 mL of concentrated HNO_3 and 5 mL of H_2O_2 were alternatively added to the sample, which was digested and evaporated to dryness until a white residue appeared.

The residue was dissolved in 30 mL of 8 M HNO_3 or in 20 mL of 3 M HNO_3– 1 M $Al(NO_3)_3$ depending on the chromatographic technique chosen for elution.

Faeces samples, whose weight was various depending on the individual excretion, were calcined at 600 °C with a gradual increase of temperature. After cooling, each sample was transferred in a quartz beaker and approximately 50 mL of concentrated HNO_3 were added. Then it was spiked by 0.0107 Bq of ^{242}Pu and 0.0107 Bq of ^{243}Am and it was digested and evaporated to dryness. The procedure was repeated 5 times. The residue was dissolved in a mixture of 20 mL of concentrated HCl:HNO_3 3:1 and evaporated to dryness. This operation was repeated until a light yellow residue appeared, which was dissolved in 30 mL of 8 M HNO_3.

Anion-exchange chromatography

To the urine or faeces sample in 8 M HNO_3 a large excess of $NaNO_2$ was added to oxidize plutonium to valence state IV. Approximately 5 g of chloride form AG 1-X2 resin in H_2O (*ca.* 20 mL) were introduced in a glass column and conditioned with 100 mL of 8 M HNO_3. The sample was eluted after being filtered by a Whatman 41 paper filter. The beaker was rinsed with 20 mL of 8 M HNO_3 and each rinse after filtration was loaded on the column. The collected eluate was discarded as waste if ^{243}Am was not introduced as internal spike; otherwise it was conserved for further analyses. Three increments of 20 mL of 10 M HCl were added to wash the bulk of the sample out of the column. Hydroxylamine hydrochloride (0.25 g) was dissolved in 15 mL of 0.5 M HCl and loaded on the column to reduce Pu(IV) to Pu(III) and to elute it. The rinse with 15 mL of 0.5 M HCl was repeated two times and all the eluates were collected in the same quartz beaker. The sample was evaporated to dryness. The residue was mineralized and evaporated to dryness adding 4 times a mixture of 20 mL of concentrated HCl:HNO_3 3:1 and then two times 3 mL of concentrated HCl. The residue was electroplated according to the procedure suggested by Eichrom Technologies [5] and the electroplated source was measured by alpha spectrometry.

Extraction chromatography

The urine sample dissolved in 20 mL of 3 M HNO_3 – 1 M $Al(NO_3)_3$ was filtered by a Whatman 41 paper filter and 4 mL of a solution of 0.6 M ferrous sulfamate, prepared daily, were added to the filtrate to reduce Pu(IV) to Pu(III). A drop of solution of 1 M NH_4SCN indicated the presence of Fe(III). Fe(III) could interfere in the chromatographic procedure so it was reduced to valence state II by adding 0.2 g of ascorbic acid. To the TRU column 5 mL of 2 M HNO_3 were added and the sample was loaded on the column. The beaker was rinsed with 5 mL of 2 M HNO_3 and the rinse was loaded on the column. 5 mL of 0.5 M HNO_3 were loaded to the column and allowed to drain. The eluate was discarded as waste. 3 mL of 9 M HCl were added to convert to chloride form and 5 ml of a solution of 4 M HCl - hydroxylamine hydrochloride 8 g/L were added to ensure reduction of Pu(IV) to Pu(III). 5 and 15 mL of 4 M HCl were added sequentially. The eluate containing plutonium was collected in a quartz beaker and evaporated to dryness.

The residue was mineralized as in the anion-exchange chromatographic technique with a mineralization mixture of 2 mL of concentrated $HClO_4$:HNO_3 1:1 before the last mineralization with 20 mL of concentrated HCl:HNO_3 3:1. The residue was electroplated and measured by alpha spectrometry.

3 Results and Discussion

Alternative reductants instead of ferrous sulfamate were tested to avoid the presence of Fe(III), which has a negative effect on the absorption of Am(III) on the TRU column [8]. Moreover, Fe(III) can be absorbed by the TRU column [9] and if it is electroplated it can inhibit the deposition of actinides [10]. Using $NH_2OH{\cdot}HCl$, good recoveries of plutonium were obtained and we confirmed that hydroxylamine can adequately reduce Pu(IV) to Pu(III). Introducing $NH_2OH{\cdot}HCl$ (0.30 g), $FeCl_3{\cdot}6H_2O$ (0.45 g) and NH_4SCN in a solution of 20 mL of 3 M HNO_3– 1 M $Al(NO_3)_3$, the capability of $NH_2OH{\cdot}HCl$ to reduce Fe(III) to Fe(II) was tested in order to eliminate interferences from iron naturally present in faeces.

Using TRU resin we observed that Pu was present in the Am fraction. The use of anion-exchange chromatography with chloride form AG 1-X2 resin yielded a better separation of the two actinides: in fact with this method Pu was not detected in Am fraction, like Am was not detected in Pu fraction. We observed that separation using TRU resin did not completely eliminate ^{228}Th and natural uranium normally present in human excreta, from the plutonium fraction. The ^{228}Th peak at 5423 keV can interfere with the ^{238}Pu peak at 5499 keV and the ^{234}U peak at 4774 keV can interfere with an enlarged peak of ^{242}Pu at 4901 keV in case of bad resolution. To avoid this problem it is possible to follow the procedure suggested by Eichrom Technologies, according to which extraction chromatography with UTEVA column precedes TRU column elution, in order to retain the uranium isotopes [11]. We had to introduce another column in the procedure but we noticed that in Pu separation using AG 1-X2 resin neither thorium nor uranium interferences were detected. AG 1-X2 resin retains U and Th isotopes and both Pu and Am eluate fractions are U and Th free. Therefore we suppose that U and Th isotopes either are eluted during the washing bulk with 10 M HCl or are retained by the resin. Further tests are necessary to investigate this aspect.

We decided to use anion-exchange chromatography to separate plutonium from other actinides. If the separation of Am is needed also, the eluate from the AG 1-X2 resin was further loaded in TRU column [11]. In Figs 1 and 2 we can observe the separation of plutonium and americium from the same sample (F1). Moreover, if the Am determination is not needed, Pu determination can be performed without uranium using only one column and we eliminate also the overlap of the ^{228}Th and ^{238}Pu peaks, as one can see comparing a sample spectrum obtained by chloride form AG 1-X2 resin (Fig. 3) with a sample spectrum obtained by the TRU column (Fig. 4). In Fig. 4 we observed also the presence of ^{224}Ra, which is a decay product of ^{228}Th.

We have calculated the *Minimun Detectable Activity (MDA)* for ^{238}Pu, $^{239+240}$Pu and ^{241}Am in the bioassay samples (Table 1).

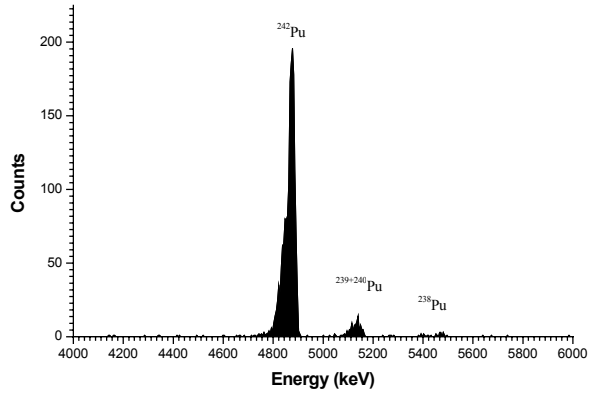

Fig. 1. Spectrum of a faecal sample (F1) obtained by separating and purifying plutonium using anion-exchange chromatography with chloride form AG 1-X2 resin.

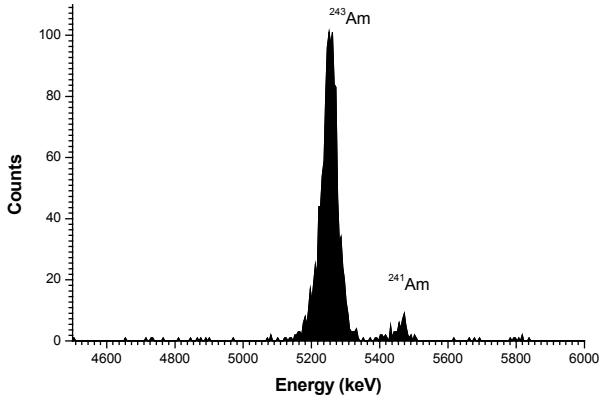

Fig. 2. Spectrum of a faecal sample (F1) obtained by separating and purifying americium using a TRU column.

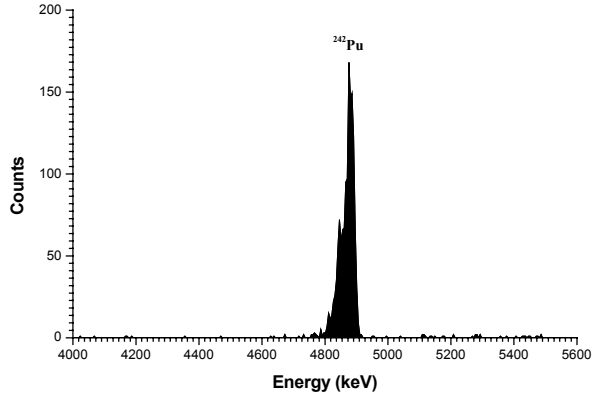

Fig. 3. Spectrum of a urine sample obtained by separating and purifying plutonium by anion-exchange chromatography with chloride form AG 1-X2 resin.

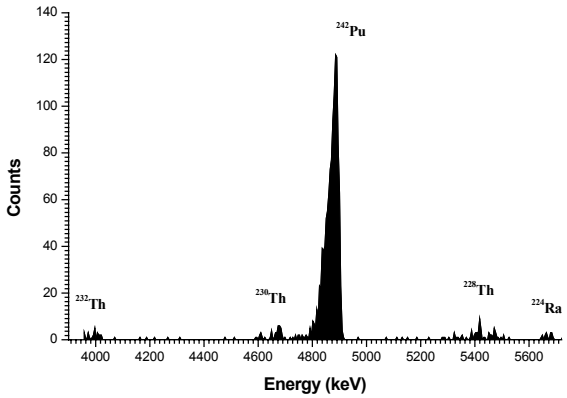

Fig. 4. Spectrum of a urine sample obtained by separating and purifying plutonium by extraction chromatography with a TRU column.

Table 1. *MDA* and chemical yield calculated for ^{238}Pu, $^{239+240}$Pu and ^{241}Am according to the type of bioassay sample and the technique of the chromatographic separation

Isotope	*MDA* (mBq)			Yield (%)		
	Urine		Faeces	Urine		Faeces
	AG 1-X2 resin	TRU resin	AG 1-X2 resin	AG 1-X2 resin	TRU resin	AG 1-X2 resin
^{238}Pu	0.16	–	0.59	70-82	60-70	71-84
$^{239+240}$Pu	0.17	0.19	0.44	70-82	60-70	71-84
^{241}Am	–	–	0.45	–	–	70-79

4 Conclusions

Hydroxylamine chloride proved its effectiveness for reducing Pu(IV) to Pu(III) and separating it from Am(III), with no necessity to be daily prepared as ferrous sulfamate solution. The use of $NH_2OH{\cdot}HCl$ in a HNO_3 solution did not affect the chromatographic separation. Moreover, it is also possible to reduce Fe(III) to Fe(II), thus eliminating any interference in electroplating.

We have managed to find an efficient procedure to determine $^{239+240}$Pu in bioassay samples, with a rather constant chemical yield and good resolved peaks. The preliminary studies on TRU resin have led us to hypothesize that it is possible to associate extraction chromatography and anion-exchange chromatography for analysing sequentially $^{239+240}$Pu and ^{241}Am from the same sample. The use of anion-exchange chromatography with AG 1-X2 eliminates the interferences from uranium without need for the use of UTEVA resin for further purification.

The results obtained in this work lead us to investigate more in detail the role of the anion-exchange chromatography in separating plutonium retaining thorium and uranium isotopes. We hope to optimise the procedure for improving the chemical yield (reported in Table 1). In fact this parameter is a warrantee of the sensitivity of the analyses, for the *MDA*, to which it is necessary to refer to evaluate internal contamination, is lower as the yield is higher.

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