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A highly sensitive method for the reassessment and quantification of ^{239}Pu in urine samples based on a 1 MV accelerator mass spectrometry system

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Received 3rd February 2010, Accepted 30th April 2010
First published as an Advance Article on the web 27th May 2010
DOI: 10.1039/c002420a

Published on 27 May 2010. Downloaded by Gral Universidad Sevilla on 26/02/2015 13:22:28.

A new and highly sensitive method for the determination of ^{239}Pu in human urine has been developed permitting the reassessment of planchets initially prepared for alpha spectrometry (AS) analysis in the context of internal dosimetry. A set of urine samples (volume: 500 mL) was spiked with known quantities of ^{239}Pu, ranging from 2 to 120 fg (4.6 μBq–0.3 mBq), employing 14 pg (2.05 mBq) of ^{242}Pu as internal standard. The Pu was purified by ion-chromatography using BioRad AG1X2 anion-exchange resins (Bio-Rad Laboratories Inc.). The chemical yield was determined by alpha-spectrometry, being about 80%. Afterwards, the planchets so obtained were leached with diluted HNO_3 and the dissolved plutonium was determined by Accelerator Mass Spectrometry (AMS) at the Centro Nacional de Aceleradores (CNA) in Seville, Spain. The minimum detectable activity (MDA) for the AMS measurements was determined through the study of a set of procedural blanks, giving figures of about 0.44 fg (~1 μBq) per sample. This contrasts with the MDA obtained by AS for the same set of samples, of about 50 fg (~0.1 mBq). The results now presented helps to demonstrate that the routine measurement of ^{239}Pu at ultra trace levels in human urine samples is possible with the new-generation of compact AMS systems, offering a highly sensitive method for the reassessing of planchets prepared for bioassay purposes.

Introduction

Plutonium (Pu) comprises fifteen isotopes[1] of which the ^{239}Pu (half-life: 24110 years) is the most important, being widely used in civil and military applications due to its fissile nature. Monitoring of occupationally exposed workers to risk of radioactive contamination is based on workplace and individual monitoring. Individual monitoring can be achieved through *in vivo* and *in vitro* measurements. Internal exposure to Pu is principally assessed from *in vitro* measurements of the element excreted in urine, feces, blood or biological secretions.[2] The most common method is the bioassay of urine samples, which involves the processing of very large volumes of urine (typically 1.5–2 L), in order to obtain a concentrated and purified fraction of Pu that can be quantified by either Alpha-Spectrometry (AS) or Mass Spectrometry (MS) techniques.

AS is the most widely used radioanalytical technique for the determination of Pu isotopes in dosimetry studies.[3,4] Its main disadvantage is the relatively long counting time (from days to weeks, depending on the precision required) that is necessary for the final quantification of the plutonium, usually electrodeposited onto stainless-steel planchets.

Another drawback is the impossibility of obtaining information on the ^{240}Pu/^{239}Pu isotopic ratio, as the difference between the alpha-energy emissions of both isotopes—^{240}Pu: $T_{1/2} = 6564$ y, E_α (keV)= 5168 (76%) and ^{239}Pu: $T_{1/2} = 24110$ y, E_α (keV)= 5157 (73.3%)—is smaller than the energy resolution of conventional Passivated Implanted Planar Silicon (PIPS) detectors. This ratio offers very useful information on the origin of the plutonium. The typical Minimum Detectable Activity (MDA) for ^{239}Pu obtained by AS is about 50 fg of ^{239}Pu/sample, or 0.1 mBq/sample. This is about two orders of magnitude higher than the ^{239}Pu activity excreted by a person per litre of urine from the general population,[5] which can be taken as the reference value to determine the existence of additional intakes. The convenient reduction of the MDA can be achieved by MS techniques, such as TIMS (Thermal Ionization Mass Spectrometry), ICP-MS (Inductively-Coupled Plasma Mass Spectrometry), RIMS (Resonance Ionization Mass Spectrometry) and AMS (Accelerator Mass Spectrometry).

TIMS and ICP-MS are widely employed for routine analysis of Pu, providing accurate and precise results at very low concentrations.[6,7] However, sample preparation protocols for TIMS analysis are very time-consuming in comparison with ICP-MS. Currently, the most widely used technique for the determination of actinides remains AS. However, ICP-MS has been gaining ground in this area due to its multi-elemental analytical capability, speed of analysis and increasingly lower limit of detection (LOD). More recently, the employ of high resolution instruments (sector-field ICP-MS) coupled with innovative feeding systems for sample introduction has provided better sensitivity and accuracy in the determination of Pu isotopes at femtogram levels.[6,8–11] The major disadvantage in high resolution ICP-MS analysis for ^{239}Pu appears when there is also U in the sample, due to the formation of $^{238}U^1H^+$ polyatomic ions in the plasma during the ionization process, which would demand a resolution of $m/\Delta m \sim 37000$ for resolving the peaks. Therefore,

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a very efficient chemical procedure is necessary to extract and purify the plutonium fraction from the sample, usually based on ion-chromatography methods.

In the last ten years, conventional AMS systems, based on 3 to 12 MV electrostatic tandem accelerators, have been increasingly used for the precise and accurate determination of Pu isotope ratios at ultra-trace levels. Among the different MS techniques, AMS is the best tool for interference discrimination, making it possible to measure plutonium isotopes with almost any matrix effect. A detailed description of AMS systems can be found in Chamizo[12] and the references therein. Shortly, almost all AMS facilities can be understood as two mass spectrometers (called "injector" and "analyzer") linked with a tandem accelerator. The radionuclide of interest is first prepared as a solid target, and then injected into the system as a negative ion by ion sputtering (using a Cs^+ primary ion source). The sputtered negative ions that pass the first cinematic filters are injected into the tandem accelerator, where they experience the so-called stripping process, *i.e.*, two or more electrons are removed from each ion following the collision of the beam with, usually, argon gas. That way, the molecules are dissociated. The resulting positive atomic ions are then accelerated back to ground potential in the high energy part of the accelerator. Finally, the accelerated beam is mass and charge analyzed through, usually a sector magnet and an electrostatic deflector. The ions of interest are finally counted on a detector, usually a multianode gas ionization chamber (Hellborg and Skog[13]). Recently, compact AMS systems, working with terminal voltages lower than 1 MV, have demonstrated their applicability for Pu isotope determination at ultra-trace levels, making AMS a cost-effective and a competitive technique compared to other MS facilities in this field.[14] In the Table 1, a comparison between the MDA, the sample preparation time, and the time devoted per analysis for the different MS techniques is shown, and also compared against AS.

In this paper, we demonstrate the capabilities of the 1 MV AMS system at the CNA, the second compact AMS in the world with the potential to measure actinides, for the measurement of ^{239}Pu in urine samples at ultra-trace levels. The experimental details and the obtained results are discussed in the following sections.

Experimental

Standards, reagents and resins

The ^{239}Pu and ^{242}Pu spikes were obtained from two certified solutions supplied by the National Physical Laboratory (NPL, England). They were diluted with 2 M HNO_3 to obtain stock solutions with a concentration of 20.3 mBq mL^{-1} (140.4 pg mL^{-1}) of ^{242}Pu and 7.9 mBq mL^{-1} (3.4 pg mL^{-1}) of ^{239}Pu. All reagents (salts and solutions) were prepared using analytical grade reagents from Merck and high purity Milli-Q water (Millipore Ibérica). Certipur® iron ICP standard (Merck) and 500 mesh pure aluminium powder (Alfa-Aesar) were employed for preparation of the AMS cathodes. AG-1X2 ion-chromatography resin (Bio-Rad Laboratories) was used for the purification of the plutonium.

Samples

The 24 h urine samples were collected from several healthy adult volunteers. The samples were divided in aliquots of 500 mL and spiked with known amounts of ^{242}Pu (~14 pg, used as internal reference) and ^{239}Pu (in the range from 2 to 120 fg) at the moment of the collection. The sample preparation procedure is shown in the diagram of Fig. 1 and is explained in the following paragraphs.

Sample mineralization and chemical separation of Pu

Samples were mineralized by microwave digestion (Milestone, Model ETHOS-1) in Teflon closed vessels using 15 mL of 8 M HNO_3 and 5 mL of H_2O_2 per sample. A temperature programme was selected: the final set value, 200 °C was reached in 10 min and maintained for 30 min. Once cooled, the resulting residue was dissolved with 30 mL of 8 M HNO_3, being ready for the radiochemical purification.

Ion-exchange resins were prepared as follows: aliquots of 10 g of Bio-Rad AG1X2 resin were introduced into a 50 mL chromatography glass column and washed with 100 mL of Milli-Q water and 200 mL of 8 M HNO_3 to condition the matrix to the nitrate form. The sample (30 mL in 8 M HNO_3 matrix) was then loaded into the column, and the eluted fraction (corresponding to U) was discarded. Then, sequential steps were followed for purification: elution with 50 mL of 8 M HNO_3 to strip the Am and Sr fractions; elution of Th with 50 mL of concentrated HCl and, finally, addition of 0.20 g of hydroxylamine hydrochloride and plutonium elution with 50 mL of 0.5 M HCl.

Electrodeposition

All the samples were prepared according to the Hallstadius method.[15] Firstly, the purified solution with the Pu fraction was

Table 1 Comparative MDA and time needed for sample preparation and determination of ^{239}Pu in human urine using mass spectrometric and radiometric techniques

Analytical Method	Sample Preparation time	Analysis time	MDA (fg/μBq)	Reference (Instrument)
AS	2–3 days	4 days	87–130/200-300	Ref. 21
TIMS	3–4 days	20–30 min.	0.53/1.2	Ref. 7
			1.7/3.8	Ref. 23
ICP-MS	12 h	5–10 min.	130/300	Ref. 24 (Agilent HP-4500)
SF-ICP-MS	1–2 days	5–10 min.	16/37	Ref. 9 (Element-2/APEX nebulizer)
			1/2.3	Ref. 6 (Element-2/DIHEN nebulizer)
AMS	1–2 days	30–40 min.	0.35/0.82	Ref. 26 (6.5 MV tandem accelerator)
			0.22/0.51	Ref. 25 (10 MV tandem accelerator)
			1/2.3	Ref. 14 (0.6 MV tandem accelerator)

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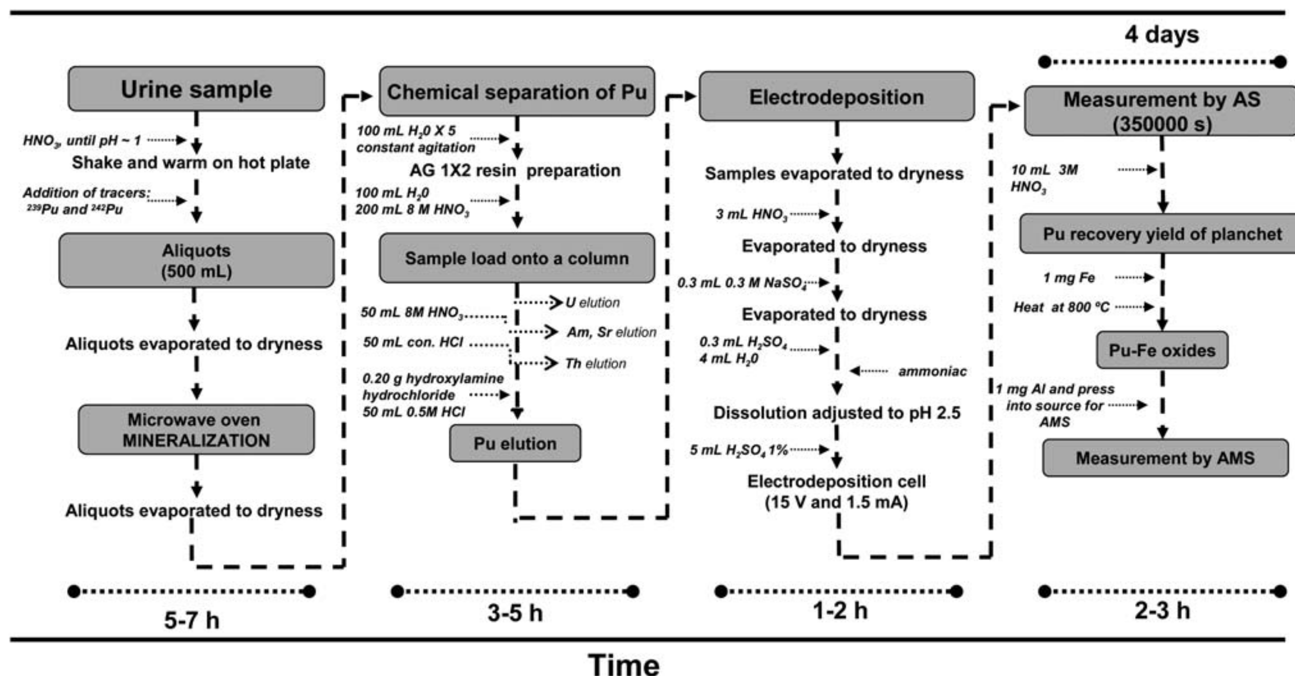

Fig. 1 Schematic diagram of the urine samples preparation procedure and the time required for every process.

evaporated to dryness. Wet-ashing of the residue was carried out by adding 3 mL of concentrated HNO_3 and baking to dryness. Then, 1 mL of 0.3 M sodium sulfite was added. The resulting solution was then evaporated to dryness and 0.3 mL of concentrated sulfuric acid and 4 mL of Milli-Q grade water were added. The solution was then adjusted to pH = 2.5 with concentrated ammonium hydroxide and 5 mL of 1% sulfuric acid were added to the sample to avoid the eventual adsorption of the actinides onto the electrodeposition cell-walls. The pH of the electrolyte was adjusted to 2.1–2.5 with ammonium hydroxide.

In our experimental set-up, the electrodeposition was performed onto mirror polished stainless steel disks (2.5 cm diameter, 1 mm thickness), which acts as cathode of the electrolysis cell, while the anode was a platinum wire. During the procedure, a density current of 0.52 A cm^{-2} was set and the electrodes were kept at 7 mm distance. This resulted in a deposit covering an area of approximately 2.2 cm diameter.[16]

Recovery of Pu from planchets and preparation of samples for AMS

Once the samples were measured by AS, every planchet was submerged in 10 mL of 3 M HNO_3 overnight in order to recover the electrodeposited Pu. After that, the resulting solution was evaporated to dryness and dissolved with 2 mL of 8 M HNO_3 to proceed with the AMS sample preparation. Firstly, the former solution was transferred to 30 mL centrifuge Teflon tubes. After the addition of 1 mg of Fe^{3+}, which acts as the final carrier for the plutonium, the solution was once again evaporated to dryness, and the residue was transferred to 5 mL crucibles as shown in Fig. 2. Then, the sample was baked at 800 °C in a muffle furnace (Milestone, Model PYRO) for 3 h, to transform the plutonium and iron to oxides (Pu_3O_8, Fe_2O_3). Finally, 1 mg of 500 mesh pure aluminium powder was properly homogenized with the oxides and the resulting mixture was pressed into a 1.3 mm diameter aluminium cathode. That way, the samples were ready to be measured by AMS.[17]

Analysis

Alpha spectrometry. Alpha spectrometry was performed with PIPS detectors. These detectors have an active area of 450 mm^2 and the nominal alpha-peak energy resolution, expressed as full width at half-maximum (FWHM), is 18 keV. The planchets (Pu sources) were placed at 1.5 mm from the detector surface. For the evaluation of the spectra, the Genie 2000 v.2.2 software (Canberra) was used.

Accelerator mass spectrometry. The AMS determinations were performed at the 1 MV compact AMS facility at the Centro Nacional de Aceleradores (CNA) in Seville, Spain (Fig. 3). Details about the technique can be found in Chamizo *et al.*[18]

Briefly, the plutonium isotopes are extracted from the sample as PuO^- in the Cs^+ sputter ion source; mass analyzed with a 90° sector magnet; stripped to Pu^{3+} in an Argon gas stripper with 0.1 μg cm^{-2} mass thickness in the terminal of the accelerator, working at 670 kV; and finally charged, energy, and mass analyzed with a 90° sector magnet and a 120° electrostatic deflector with spherical electrodes. The ions of interest are counted from the total energy signal provided by the detector, a gas ionization chamber with a 30 nm thickness silicon nitride window. The spectrum so obtained is displayed in Fig. 3, together with the different measurement details. Pulsing times of 5 s for ^{242}Pu and 15 s for ^{239}Pu are used, adding up to 20 min of analysis per sample. On the whole, about 11% of the plutonium ions extracted from source are transmitted to the detector. A sample containing 1 pg of plutonium produces a typical count rate of 100 cps for about 30–40 min. The $^{239}Pu/^{238}U$ mass suppression

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Fig. 2 Pictures showing the steps involved in the AMS cathode preparation process: (a) dry iron residue obtained after the evaporation of the purified plutonium solution with 1 mg of iron; (b) iron oxide obtained after baking at 800 °C the former residue; (c) images of the cathode where the final iron oxide plus aluminium mixture is pressed.

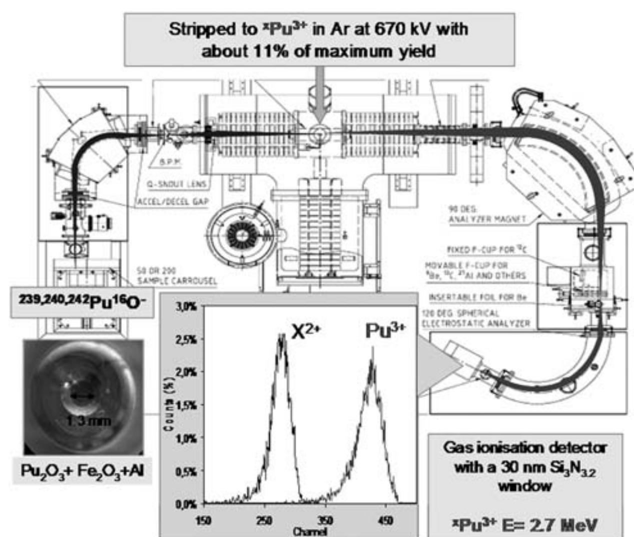

Fig. 3 Diagram of the 1 MV AMS facility SARA at the CNA, together with the Pu isotopes measurement details. In the final spectrum, X^{2+} represents the molecular fragments in the 2+ charge state with the same M/q as the ions of interest. They pass the cinematic filters, but can be discriminated in terms of their total energy in the detector.

factor is about 10^{-9}, which means that a sample containing 1 μg of ^{238}U produces a typical ^{239}Pu background of 1 fg.

Results and discussion

Optimization of the treatment and radiochemical separation

The volume of urine for the analysis of Pu has been optimized as described in previous studies,[19,20] which were carried out as an alternative to the classic methods using 24 h excretion. In this work, a maximum volume of 500 mL of urine was employed because it was optimal to evaporate, mineralize (by microwave digestion) and finally to perform the Pu measurements in a reasonably short time (500 mL corresponds to the volume of the first excretion in the morning, more or less). The improvements obtained when compared with the routine procedures used for the analysis of plutonium isotopes, are basically the reduction of the time needed for the sample preparation. The preparation process including microwave digestion lasted between 5 and 7 h (Fig. 1). Regarding to the radiochemical separation of Pu, the purification with AG1X2 resin is a standard method, which is commonly used for the internal dosimetry monitoring of occupationally exposed workers. This method has been largely verified in several intercomparison exercises, with good results concerning to Pu separation and recovery.[21] The main advantage of this method is the fast and effective separation of Pu from other radioisotopes (Am, Sr, Th, and U). In our case the time necessary to complete the Pu purification was about 3 h.

Alpha measurements

Table 2 summarizes MDA and LOD for ^{239}Pu and ^{242}Pu obtained from the analysis of a set of 50 blank urine samples measured by AS. LODs were calculated using the Currie criteria,[22] and the evaluation of MDA was achieved by applying the following the formula:

$$\mathrm{MDA} = \frac{4.65 \times \sigma_B + 3}{T} \times \frac{100}{\varepsilon} \times \frac{100}{R} \times \frac{1000}{V}$$

where: MDA= minimum detectable activity (Bq/sample), T = counting time (s), ϵ = counting efficiency (%), R = mean value of the chemical recovery yield (%), σ_B= standard deviation of the blank counts, V = analyzed volume of urine (mL).

Then, the LODs were translated into MDAs taking into account that the counting efficiency was 33.9 ± 1.4%, the background ranges were between 0 and 3 counts for a counting time of 350 000 s, and a radiochemical yield of 82 ± 5%.

An example of alpha spectrum for a urine sample processed with this method is presented in the Fig. 4.

Reassessing of planchets by AMS

Some of the planchets, previously measured by AS, were chosen for reassessing. The selection criteria used was to measure those samples corresponding to the activity range below or near the LOD for AS. It is also important to remark that the AMS measurements were performed as a blind test.

Two different processes were tested to recover the Pu from the planchets to re-evaluate it by AMS. In the first one, the extraction of Pu was attempted by dipping the planchets in 20 mL of an acidic mixture (HNO_3 2.5% v/v, and HCl 2.5% v/v) overnight. Then, the planchet was rinsed with HNO_3 2.5% v/v, the extract was heated to dryness and, finally, the residue was used for preparing the AMS cathodes. This residue contained a high amount of iron oxide coming from the planchet (between 6 and 15 mg), so the samples were diluted at least six times more than

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Table 2 LODs and MDAs for ^{239}Pu and ^{242}Pu in sample blanks and urine

		LOD		MDA	
		^{239}Pu	^{242}Pu	^{239}Pu	^{242}Pu
AS	μBq/sample	44.8 ± 5.0	56.8 ± 11.9	117.3 ± 12.8	134.5 ± 18.7
	fg/sample	19.4 ± 2.2	387.6 ± 81.2	50.9 ± 5.6	918.1 ± 127.8
AMS[a]	μBq/sample	0.57 ± 0.23	0.150 ± 0.059	1.25 ± 0.46	0.32 ± 0.12
	fg/sample	0.20 ± 0.08	0.830 ± 0.033	0.44 ± 0.16	1.76 ± 0.66

[a] Data given in the LOD columns for Pu by AMS corresponds to the "critical level" as defined by Currie[22] as LC = 2.33($\sigma_B^{1/2}$).

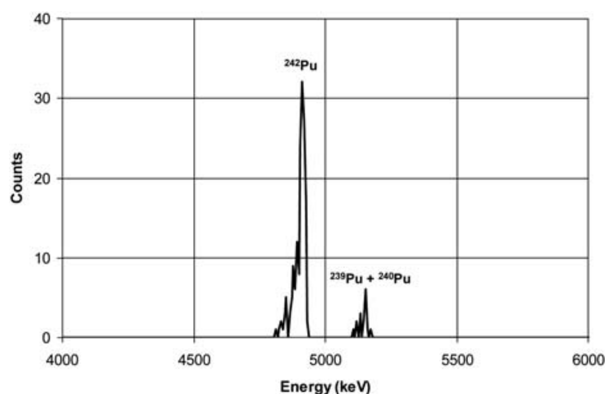

Fig. 4 Alpha spectrum obtained from a urine sample (S8* in the Table 3), spiked with ^{242}Pu and ^{239}Pu.

usual. Therefore, the obtained ^{239}Pu and ^{242}Pu count rates were significantly reduced. This explains the poorer accuracy obtained for samples marked with an asterisk in the Table 3.

In the second process, the planchets were treated with 20 mL of HNO_3 5% v/v (HCl was not used), in the same way as described above. In this case, almost any iron was extracted from the planchets, and the samples produced the expected count-rates. Therefore, for reassessing purposes using AMS, the use of HCl must be avoided.

Fourteen unspiked urine samples (procedural blanks) were prepared and ^{239}Pu and ^{242}Pu were measured by AMS (see Table 2). The corresponding LOD's were calculated from the obtained count rates considering as well the statistical criterium given in Currie,[22] and they were traduced into ^{239}Pu and ^{242}Pu mass in the sample considering the efficiency of the measurement. This efficiency, which strongly depends on the experimental set-up, was estimated measuring a set of three samples spiked with well-known amounts of ^{239}Pu and ^{242}Pu during the same experiment. On average, a sample containing 1 pg of plutonium produced about 100 ± 10 cps in the detector. Finally, these LOD's were traduced into MDA's considering the yield of the chemical procedure, as determined by alpha-spectrometry (R), and the measurement time (T = 20 min), according to the following formula:

$$\mathrm{MDA} = \frac{4.65 \times \sigma_B + 3}{T} \times \frac{1pg(Pu)}{100cps} \times \frac{100}{R}$$

where MDA= minimum detectable activity (pg/sample) and σ_B is the square root of the total number of counts produced by the procedural blanks for any isotope during the measurement. The obtained MDA's are displayed in Table 3.

It is interesting to mention that the procedural blanks produced the same ^{239}Pu and ^{242}Pu count-rates as the instrumental blanks (high-purity iron-oxide mixed with aluminium), which means that any additional Pu was introduced during the sample processing. The main limitation in this case was the background introduced by the ion source due to cross contamination effects, with a contribution factor of about 10^{-3} between neighboring samples. During our experiments, this background was introduced by the standards (samples with a certified Pu isotopic composition), which have to be measured every half an hour to control the stability and reliability of the measurements.

Conclusions

The possibility of reassess the ^{239}Pu in urine samples by AMS starting from electrodeposited planchets, initially prepared for

Table 3 Experimental results for AS and AMS measurements. Accuracy is expressed as 2σ

Samples	Spiked ^{239}Pu/μBq	Spiked ^{239}Pu/fg	Recovery yield ^{242}Pu (%)	Measured ^{239}Pu by AS (fg)	Planchet reassessing of ^{239}Pu by AMS (fg)
S1	4.9	2.0	80	below LOD	2.2 ± 1.2
S2	9.9	3.9	76	below LOD	4.1 ± 0.8
S3	14.8	5.9	83	below LOD	6.2 ± 1.4
S3[a]	14.8	5.9	93	below LOD	5.4 ± 2.8
S4	19.7	7.8	79	below LOD	8.7 ± 1.2
S5	29.6	11.8	82	below LOD	14.6 ± 2.8
S6	39.5	15.7	77	below LOD	17.7 ± 2.2
S6[a]	39.5	15.7	77	below LOD	15.4 ± 4.2
S7[a]	98.6	39.2	83	35.3 ± 8.1	41.6 ± 7.8
S8[a]	295.9	117.6	89	114.8 ± 14.6	92.7 ± 8.4

[a] Samples affected by the high Fe content from planchet corrosion during acid attack with HNO_3/HCl.

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AS measurement, has been studied in this work. The results obtained demonstrate the feasibility of such reassessment with very good sensitivity and reliability: the reported MDA for AMS reassessment being 0.44 ± 0.16 fg/sample, far lower than for AS, which is of the order of 50.9 ± 5.6 fg/sample. The work was undertaken after the good results obtained by using AMS for the quantification of ^{239}Pu in urine samples obtained in a previous work.[20] AMS is an extremely sensitive technique which makes feasible to handle smaller volumes of urine, thereby significantly reducing both the time of preparation as well as the time required for measurement of Pu content in the sample. The possibility of reassessing planchets that could not be quantified by conventional AS, because the activity of Pu is lower than the MDA of this radioanalytical technique, is a new and exciting possibility for the proper quantification of Pu incorporation in humans.

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