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REASSESSMENT OF ^{239}PU ON PLANCHETS FROM HUMAN URINE SAMPLES AT ULTRA-TRACE LEVELS USING ARIDUS-ICP-SFMS AND AMS

Héctor Hernández-Mendoza[1], Elena Chamizo[2,*], Antonio Delgado[1], Manuel García-León[3] and Abel Yllera[1]
[1]Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Av. Complutense 22, 28040 Madrid, Spain
[2]Centro Nacional de Aceleradores (CNA), Av. Thomas Alba Edison, 41092 Sevilla, Spain
[3]Departamento de Física Atómica, Molecular y Nuclear, Universidad de Sevilla, 41012 Seville, Spain

*Corresponding author: echamizo@us.es

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New analytical methods developed at the facilities here, based on two ultra-sensitive mass spectrometry (MS) techniques, inductively coupled plasma sector field mass spectrometer with a desolvator system (Aridus-ICP-SFMS) and accelerator MS (AMS), have been applied in this work for the reassessment of ^{239}Pu in alpha spectrometry (AS) planchets corresponding to spiked human urine samples. The obtained ^{239}Pu minimum detectable activities (MDAs) values by Aridus-ICP-SFMS and AMS were 3 fg (∼6.92 μBq) and 0.4 fg (∼0.92 μBq), respectively, per sample, which are much better than those attainable by AS [50 fg (∼115.3 μBq) of ^{239}Pu per sample, approximately]. Therefore, it is demonstrated that the MS techniques employed in this work are very powerful tools for internal dosimetry studies in human urine samples, giving excellent results when the reassessment of AS planchets is needed (samples with a Pu concentration below or at the MDA levels measurable by AS). This work is the continuation of an article published in J. Anal. At. Spectrom. 25 (1410–1415) 2010.

INTRODUCTION

The successful measurement and assessment of internal exposure to radioactivity in dosimetry studies are highly dependent on the instrumental capabilities for measuring radionuclides in biological samples (urine, feces, blood or other secretions)[1, 2]. Normally, during the Pu bioassay of human urine samples, it is mandatory to preconcentrate and purify the Pu fraction. In the case of mass spectrometry (MS) techniques, it is usually important to prevent the presence of ^{238}U in the sample, because it can interfere with the signal of the major Pu isotope ^{39}Pu ($T_{1/2}$=24 110 y), and also to avoid matrix effects. For these purposes, ion-exchange or solid-phase extraction chromatography is extensively used in worldwide laboratories[3–8].

Alpha spectrometry (AS) is the most commonly used radioanalytical technique for the determination of Pu in routine bioassay studies, due to its simplicity and low cost. However, this method is very time-consuming and it cannot resolve the ^{239}Pu and ^{240}Pu peaks because of their very similar energies (5.15 and 5.16 MeV). Analytical results from AS are therefore expressed as the sum of the ^{239}Pu and ^{240}Pu activity concentration (i.e. $^{239+240}$Pu). Additionally, this technique shows some sensitivity shortcomings when the involved $^{239+240}$Pu activity levels are below 0.3 mBq per sample (∼1.3 pg of ^{239}Pu per sample), due to the noise associated with the detector and the poor statistics[9]. On the other hand, several parameters, such as counting efficiency, chemical yield, sample counting time, tracer activity used and background condition the precision and accuracy of the results for low-level samples and, therefore, the minimum detectable activity (MDA) of AS[10–12].

Because of its excellent detection sensitivity, MS techniques are useful tools for measuring ^{239}Pu at sub-fg levels, and also ^{240}Pu/^{239}Pu atomic ratios, which would be impossible to measure using conventional radioactive decay counting techniques. Due to the requirements imposed by the International Commission on Radiological Protection (ICRP), techniques capable of measuring $^{239/240/241}$Pu isotopes at concentrations of ∼1 fg l^{-1} in urine samples are becoming mandatory[13, 14].

Different MS techniques, such as inductively coupled plasma (ICP) MS[3–6], Thermal ionisation MS (TIMS)[15, 16] and accelerator MS (AMS)[14, 17, 18], are good candidates for the dosimetric control of the population exposed to ionising radiation, opening up the possibility of identifying and quantifying small amounts of different radionuclides in a sample, and also offering isotopic composition unattainable by radioactive counting techniques[19–22].

ICP-MS is one of the most suitable methods for the analysis of actinides at ultratrace levels, in particular ^{239}Pu, due to its high sensitivity, good

accuracy and precision and generally simple sample preparation procedure versus AS[3]. However, the accurate determination of Pu isotopes by ICP-MS is hampered by both spectral and non-spectral interferences. For the analysis of Pu, the most common interferences are $^{238}UH^+$ and $^{238}UH_2^+$, which interfere with the ^{239}Pu and ^{240}Pu isotopes, respectively, due to the presence of U. To avoid these problems, two complementary solutions are usually applied: the preconcentration and purification of the Pu fraction using ion-chromatography resins[4, 5], and/or the reduction of uranium hydride formation using special sample introduction systems, such as micronebulizers with desolvator system[6].

On the other hand, AMS has recently been demonstrated to be a competitive technique for the precise and accurate determination of Pu at sub-fg levels in urine bioassay samples. It features a high sensitivity with virtually no matrix effects (high rejection of molecular isobaric interferences), allowing the identification of abnormal activities of Pu with no special chemical requirements[7].

The aim of this study was to develop and validate an analytical method for the reassessment of ^{239}Pu in AS planchets containing small amounts of ^{239}Pu (from 8 to 40 fg per sample), using the Aridus desolvator coupled with an ICP-SFMS, and a 1-MV compact AMS system. This is specially interesting for the authors' research centre, CIEMAT (Research Center of Environment and Energy and Technology), where there is a big stock of Pu electrodeposits from human urine samples from the population of Palomares (Almeria, Spain), affected by a nuclear accident in 1966, and from professionally exposed people.

MATERIALS AND REAGENTS

Instrumentation

Spectrophotometry and AS

Creatinine determination was carried out by using a spectrophotometer Zuzi, Model 4211/20 (Auxilab S.L., Spain). AS measurements were performed with an Alpha Analyst Integrated Alpha Spectrometer (Canberra, TECNASA S.L., Spain) equipped with Passivated Implanted Planar Silicon detectors. These detectors have an active area of 450 mm^2 and their nominal alpha-peak energy resolution, expressed as full-width at half-maximum, is 18 keV. The planchets (Pu sources) were placed at 1.5 mm from the detector surface. For the evaluation of the data, the Genie 2000 v.2.2 software (Canberra) was used.

HR-ICP-MS instrumentation

Pu quantification was carried out with an Element XR Mass Spectrometer (Thermo Fisher Scientific, Bremen, Germany). The sample introduction system employed was an Aridus desolvator (CETAC Technologies, Inc., USA) with a Microflow nebulizer PFA-100 (Elemental Scientific Inc., USA). Aqueous samples were introduced to the desolvator in the continuous flow mode by using an auto sampler CETAC ASX-520 (CETAC Technologies, Inc., USA). The ICP torch was shielded with a grounded platinum electrode (GuardElectrodeTM, Thermo Scientific, Germany).

Accelerator MS

The measurements of ^{239}Pu were performed using the 1-MV compact AMS system set up at the Centro Nacional de Aceleradores (CNA, Seville, Spain). The system was designed and manufactured by High Voltage Engineering Europa (HVEE, Amersfoort, Holland).

Materials and reagents

^{239}Pu and ^{242}Pu standards were obtained from National Physical Laboratory (NPL, UK). Standards were diluted with 2 M HNO_3 to obtain stock solutions with a concentration of 20.3 mBq ml^{-1} (140.4 ng l^{-1}) of ^{242}Pu and 7.9 mBq ml^{-1} (3.4 ng l^{-1}) of ^{239}Pu. ^{237}Np (chosen as external standard for ICP-SFMS measurements) was obtained from Amersham International plc (UK). This standard was diluted with 0.1 M HCl to obtain a stock solution with a concentration of 3.256 mBq ml^{-1} (123 ng l^{-1}). For ICP-SFMS mass calibration, a certified multi-element solution XXIII (Ba, B, Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Y, Tl and U) from Merck (Germany) was used. The rest of the salts and solutions were prepared using analytical grade reagents from Merck. High-purity water (>18 MΩ cm^{-1}) was obtained from a Milli-Q Element A10 Century (Millipore Ibérica, Spain). Nitric acid was purified by sub-boiling distillation (Duopur, Milestone S.r.l., Italy). Certified Ar gas (99.999 %) was supplied by Air Liquide (Spain). Certipur® iron ICP standard (Merck, Germany) and 500-mesh pure aluminium powder (Alfa-Aesar, UK) were employed for preparation of the AMS cathodes. AG1X2 anion-exchange chromatography resins (Bio-Rad Laboratories S.A., Spain) were used for Pu purification. The ICP-SFMS measurements were carried out in a clean room (ISO 6 class) at 24 ± 1°C.

Experimental

The different features of the method for the extraction and purification of ^{239}Pu in human urine samples and the reassessment of AS planchets for ICP-SFMS and AMS determinations are shown in the diagram in Figure 1.

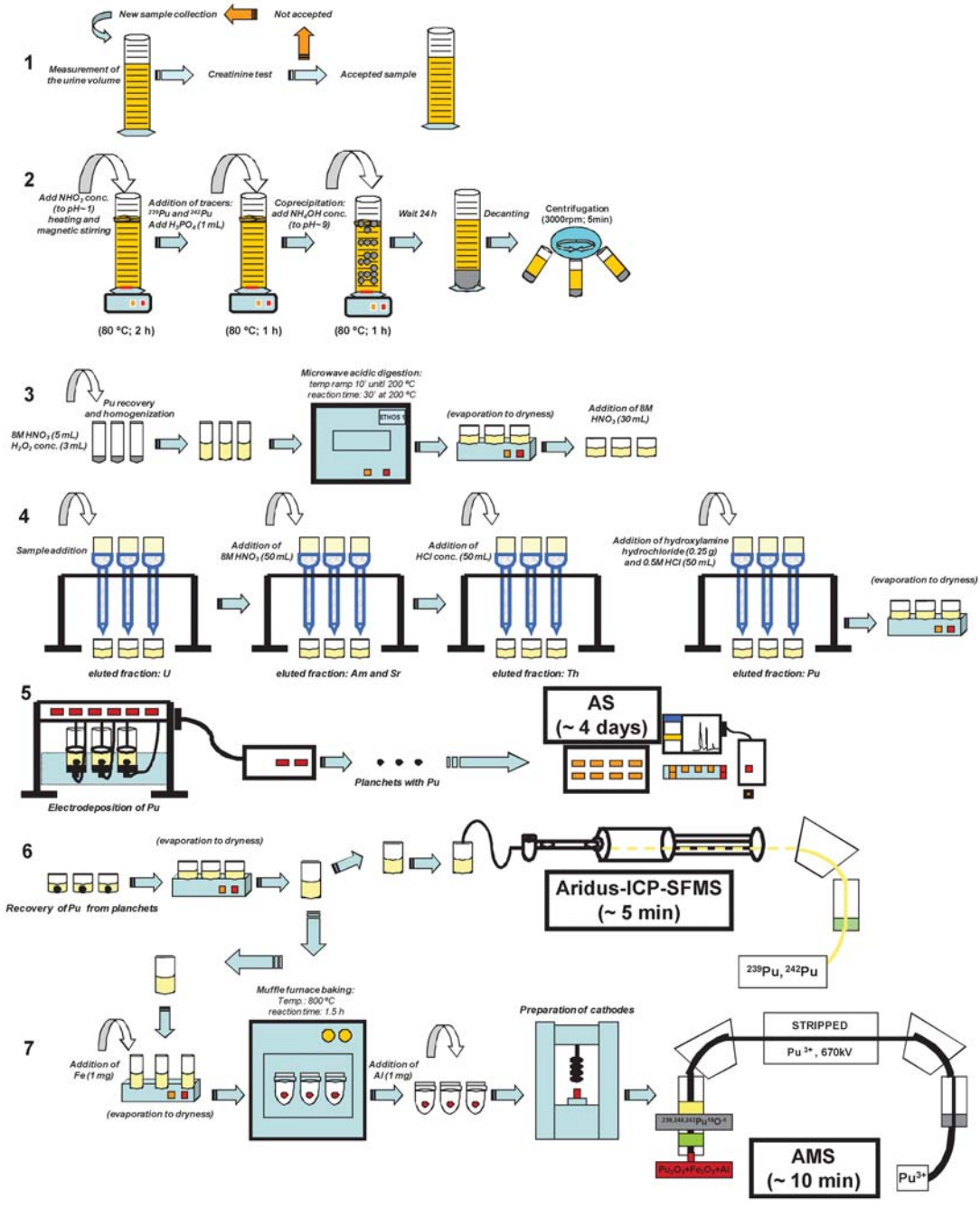

Figure 1. Schematic diagram for the preparation procedure of urine samples and measurements of Pu by AS, Aridus-ICP-SFMS and AMS: (1) collection of sample (time: 24 h); (2) co-precipitation (~24 h); (3) Mineralisation (~2 h); (4) radiochemistry (~3 h); (5) electrodeposition (~2 h); (6) recovery of Pu from planchets (~24 h) and (7) preparation of the cathodes for AMS (~3 h) and reassessment of ^{239}Pu by Aridus-ICP-SFMS and AMS. This figure appears in colour in the online version of *Radiation Protection Dosimetry*.

Creatinine measurements

Measurements of creatinine concentrations in urine have been commonly used in the laboratory to estimate 24 h excretion of radionuclides from urine samples collected in a day, then 14 samples of 24 h human urine ($V_{sample}=1725\pm114$ ml) were collected from several healthy adult male volunteers. The analytical procedure was initiated the same day of the collection by the determination of creatinine content in the urine samples, in order to check whether those met the requirements needed previous to bioassay. The method is based on the Jaffé reaction: addition of sodium picrate into the urine and formation of a red-coluored complex (sodium picramate)[23]. The colour intensity is directly proportional to the concentration of creatinine at a specific wavelength (520 nm), which is measured with a spectrophotometer[24].

Co-precipitation

The method carried out for co-precipitation is described in Kuwabara and Noguchi[8] and Robredo *et al.*[9] The 24 h urine samples were transferred into respective graduated cylinders, acidified with concentrated HNO_3 to pH=1, and heated in a hot plate with magnetic stirring at 80°C during 2 h. Then, the hot samples were spiked with known amounts of ^{242}Pu (8.4 pg) as internal standard, and ^{239}Pu (from 8 to 40 fg, see Table 1). Next, 1 ml of concentrated orthophosphoric acid was added, continuing the heating and the stirring for a further 1 h. Then, the Pu was co-precipitated by the addition of concentrated ammonium hydroxide until pH=9, keeping the same conditions for 1 h. The precipitate was allowed to settle overnight and then separated by decanting and centrifugation. The supernatant was discarded, and the graduated cylinder was washed several times with 0.5 M HNO_3. The washings were also transferred into the centrifuge tube, and the precipitate was dissolved with 5 ml^{-1} of 8 M HNO_3 plus slow addition 3 ml of concentrated H_2O_2. The procedural blanks (unspiked urine samples) were processed in the same way.

Mineralisation, radiochemistry, electrodeposition and preparation of the cathodes for AMS

A summary of the processes involved in this section is given in Figure 1. A detailed description has been provided in previous studies[25].

Recovery of Pu for planchets reassessment

In order to determine the radiochemical yield during Pu purification, the samples were previously measured by AS. After that, the extraction of the electrodeposits was carried out by dipping the planchets into 20 ml of 5 % HNO_3 overnight. Next, the planchets were rinsed with 5 % HNO_3 and the resulting solutions were heated to dryness, diluted to 10 ml of the same acid in volumetric flasks, and divided in two twin aliquots for the Aridus-ICP-SFMS and the AMS determinations. In the case of the ICP-SFMS aliquots, 4.4 fg of ^{237}Np were also added as an external standard.

RESULTS AND DISCUSSION

Creatinine test

The Pu is a long-lived radionuclide that is excreted from the human body in very small amounts, which cannot always be easily detected by AS. The recommendations for good routine analysis of Pu in urine establish that the sample must contain the creatinine equivalent of, at least, of 24 h excretion[26]. This contributes to minimise the uncertainty of the results normalised to 24 h excretion, specially when analysing spot urine samples[7, 13, 27]. Therefore, the determination of creatinine in urine is essential for monitoring the excretion of long-lived radionuclides and it is also a decisive test for accepting or rejecting the sample[28]. In this work, the average creatinine concentration was 1.1 ± 0.13 g l^{-1} ($n=15$), which is in agreement with the ICRP-89 recommendations for accepting urine samples for dosimetry studies[10].

Treatment of sample and purification of Pu

The co-precipitation of Pu with calcium phosphate in ammonia medium was performed to pre-concentrate it, because it is adequate to perform in human urine at a sub-pg/l concentration level of Pu.

Normally, the routine bioassay of long-lived radionuclides requires mineralisation of the sample, which is usually carried out by wet ashing of the precipitate followed by muffle furnace incineration[9]. This process is very time-consuming and tedious. Therefore, in this work, the mineralisation was performed by microwave-assisted acidic digestion (8 M HNO_3 and concentrated H_2O_2) of the calcium phosphate precipitate, which accelerates the preparation of the sample.

When using MS and radiochemistry techniques for Pu quantification in low-level samples, the elimination of matrix elements contained in the sample is a must. In this work, this was achieved using anion-exchange resins (BioRad AG1X2). The purification of Pu using AG1X2 resin does not present significant drawbacks in contrast to other Pu purification processes which, in principle, are faster[5]. In case, the necessary time for processing 10 samples was 2–4 h. Moreover, as measured by AS, AG1X2

resin offers an excellent chemical recovery of the Pu fraction in urine samples (Table 1).

Optimisation of Aridus-ICP-SFMS parameters

The instrumental settings were optimised for the quantification of ^{237}Np ^{239}Pu and ^{242}Pu. Optimisation was performed in three steps:

(1) Tuning the parameters of Aridus (argon and nitrogen flow) to obtain the maximum intensities for ^{115}In and ^{238}U isotopes, using a dilution (1:10) of the certified multielement solution in low resolution mode. The signal intensity for these isotopes was about 7.0×10^5 cps and 1.0×10^6 cps, respectively, and the ^{238}U oxides content in the plasma was ~0.6 %.
(2) Optimisation of maximum ion intensity for ^{242}Pu and minimum background at m/z=239 using a ^{242}Pu standard solution of 0.4 pg l^{-1}. The background signal obtained during this step was 0.3 ± 0.1 cps to m/z=239. Additionally, a stability test was also performed for monitoring the signal of ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu and ^{242}Pu isotopes (10, 0.1, 32, 2.7 and 42 pg l^{-1}, respectively) in standard samples of these isotopes during 15 min.
(3) Optimisation of the method for the measurement of ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu and ^{242}Pu isotopes. Instrumental operation conditions are summarised in Table 2.

Reassessment of the Pu by MS techniques

The main problem when measuring ^{239}Pu by ICP-SFMS appears when U is present in the sample (molecular isobaric interference due to the formation of $^{238}U^1H^+$ in the plasma), and also from the tailing effect of the ^{238}U peak, which leads to an increase in the background signal at m/z=239. Some alternatives have been considered in the literature in order to avoid these problems: one option consists in using a low-flow micronebulizer coupled with a membrane desolvator as sample introduction system (Aridus)[6], and the second option consists in using deuterated water as sample solvent[29]. In this work, the influence of ^{238}U on the background signal at m/z=239 was investigated using the Aridus-ICP-SFMS. Thus, a certified standard solution of 0.1 ppb of ^{238}U in HNO_3 5 % [(^{238}U)≈ $10^5\times$(^{239}Pu)samples] was measured, obtaining a background signal at m/z=239 of 1.0 ± 0.3 cps (n=10). The background signal obtained with HNO_3 5 % blanks at m/z=239 was 0.3 ± 0.1 cps, indicating that the contribution of ^{238}U to the ^{239}Pu signal is negligible in these conditions. These results are in good agreement with other works for the analysis of Pu in urine samples[3].

External calibration was employed during the reassessment of ^{239}Pu and ^{242}Pu in AS planchets for Aridus-ICP-SFMS analysis (Figure 2). All the solutions (blanks, standards and samples) were spiked with ^{237}Np as an external standard, to monitor the instrument stability during the measurements (Figure 3).

The results indicate the excellent chemical recovery achieved with the proposed extraction process for the reassessment of Pu from AS planchets

Table 1. Results of radiochemical yield for Pu (measured by AS). All the samples were initially spiked with 8.4 pg of ^{242}Pu.

Sample	^{239}Pu added (fg)[a]	^{242}Pu measured (pg)	Recovery yield of ^{242}Pu (%)
1	8	6.49 ± 0.43	78
2	10	6.82 ± 0.58	82
3	10	6.24 ± 0.50	75
4	17	6.74 ± 0.43	81
5	20	6.49 ± 0.70	78
6	26	6.74 ± 0.67	81
7	32	6.24 ± 0.67	75
8	35	8.07 ± 0.80	97
9	40	6.07 ± 0.66	73

[a]239+240Pu measured is below the MDA.

Table 2. Instrumental conditions optimised for the measurement of Pu from planchets by Aridus-ICP-SFMS.

Solution uptake rate	0.1 ml min^{-1}
RF power	1300 W
Cool gas flow rate	16.0 l min^{-1}
Auxiliary gas flow rate	0.70 l min^{-1}
Nebulizer gas flow rate	1.194 l min^{-1}
Ion extraction lens potential	−2000 V
Mass resolution ($m/\Delta m$)	300
Isotope	^{237}Np; ^{238}U; ^{239}Pu; ^{240}Pu; ^{242}Pu
Samples per peak	100
Settling time	10 ms
Sample time	10 ms
Points per width	10
Peak shift	1.0
Mass window	100 %
Integration window	20 %
Scan type	E-Scan
Detection mode	Triple (ion counting, analogue and Faraday)
Total analysis time per sample	3 min
Sampler/skimmer cone	Nickel
Aridus desolvator	Sweep gas (Ar): 4.57 ml min^{-1} Nitrogen flow: 6 ml min^{-1}
Nebulizer	Microflow nebulizer PFA-100

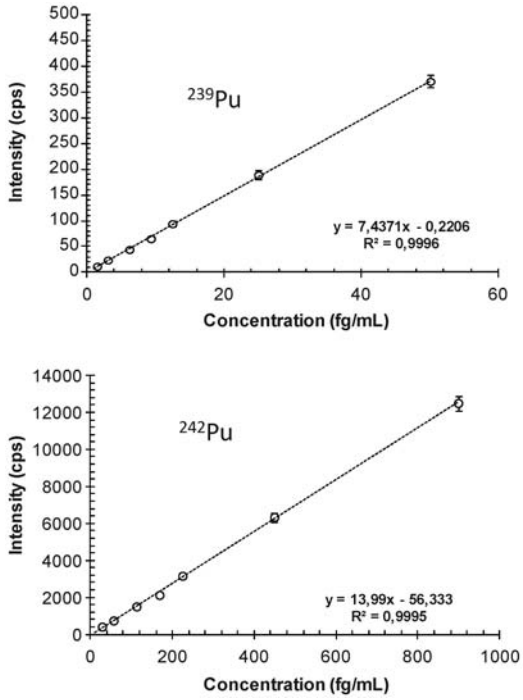

Figure 2. Calibration curves for ^{239}Pu and ^{242}Pu measured by Aridus-ICP-SFMS.

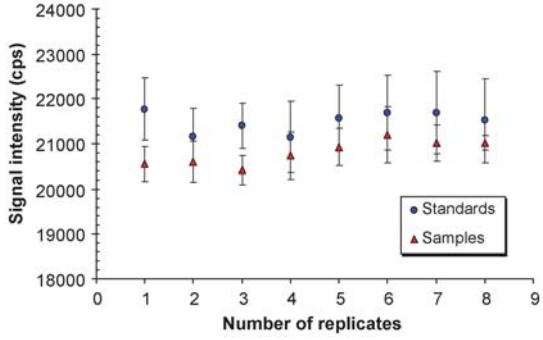

Figure 3. Instrumental stability of the Aridus-ICP-SFMS, monitored during the analyses using ^{237}Np as external standard.

(Table 3). However, it must be pointed out that, in the case of AMS measurements, the presence of milligrams of iron coming from the planchet (due to corrosion) can affect the sensitivity of the analysis due to a dilution effect on the sample[7].

The calculation of the ^{239}Pu content in the initial urine samples was performed by the isotope dilution method, considering the ^{239}Pu/^{242}Pu isotopic ratio measured by Aridus-ICP-SF-MS in the Pu fraction

Table 3. Reassessment of ^{239}Pu on planchets by Aridus-ICP-SFMS and AMS.

Sample	Aridus-ICP-SFMS		AMS
	^{239}Pu (fg)[a]	^{239}Pu (fg)[b]	^{239}Pu (fg)[b]
1	5.4 ± 0.9	8.1 ± 1.7	8.2 ± 0.8
2	6.5 ± 0.8	10.1 ± 1.7	9.8 ± 0.6
3	7.2 ± 0.5	10.0 ± 1.2	10.3 ± 0.8
4	13.7 ± 0.7	17.1 ± 1.7	17.4 ± 0.9
5	13.9 ± 0.8	20.0 ± 2.1	19.5 ± 0.9
6	19.3 ± 1.2	27.1 ± 3.0	25.8 ± 1.4
7	22.4 ± 1.2	32.3 ± 3.4	31.6 ± 1.6
8	30.6 ± 1.4	36.1 ± 3.4	34.8 ± 1.3
9	27.6 ± 1.4	40.1 ± 4.0	38.3 ± 1.8

[a]Result obtained of ^{239}Pu with external calibration by Aridus-ICP-SFMS.
[b]Calculated mass of ^{239}Pu used method of isotope dilution method, considering the ^{239}Pu/^{242}Pu isotopic ratio measured.

leached from the planchets (~90 %) and the amount of spike initially added to the samples; these results are shown in Table 3, column two and the results were confirmed by AMS. The levels of ^{239}Pu concentration by both methods no showed significant difference in results.

Limit of detection (LOD) and MDA for ^{239}Pu using Aridus-ICP-SFMS were calculated from the analysis of a series of 10 procedural blanks, and compared with those reported in previous publications by AS, AMS and conventional ICP-SFMS (Table 4)[25].

The obtained results with the new set up are about one order of magnitude lower than those reported by conventional ICP-SFMS, and compares with those obtained by AMS. LOD for Pu by AS was calculated using the Currie criterion[30] and, then, MDA was calculated considering the LOD, the average chemical yield for Pu (80 ± 7 %) and the total volume of urine (1725 ± 114 ml). In the case of Aridus-ICP-SFMS and AMS, the LOD and AMD calculations were made as described in a previous work[7, 25].

Accordingly with[8], and assuming an acute intake by inhalation of a type S substance, an excretion of 2.3×10^{-6} (Bq of Pu/Bq intake) is predicted at the first day of the intake[13]. Therefore, considering the MDA levels for Pu reported here (7.4×10^{-6} Bq per sample for Aridus-ICP-SFMS, and 1.0×10^{-6} Bq per sample for AMS), it can be concluded that the method developed in this paper provides enough sensitivity to perform the reassessment of planchets when AS is unable to give any information during internal dosimetric controls. Minimum detectable doses can be then calculated at given days after

Table 4. Results obtained in the LODs and AMDs of Pu in human urine samples by AS, Aridus-ICP-SFMS and AMS.

Method	LOD ^{239}Pu (fg/sample)	MDA ^{239}Pu (fg/sample)
AS	20.2 ± 2.2	51.1 ± 5.2
HR-ICP-MS[a]	4.87 ± 0.09	23.43 ± 0.94
Aridus-HR-ICP-MS	0.81 ± 0.03	3.23 ± 0.12
AMS[a,b]	0.20 ± 0.08	0.44 ± 0.16

[a]These data correspond to a previous work[25].
[b]Data of LOD for Pu by AMS corresponds to the 'critical level' as defined by Currie[30] as criteria level=$2.33(\sigma_B 1/2)$, where σ_B correspond to the standard deviation of blank samples.

intake from the MDA of the method, urinary excretion rate (24 h urine samples) and dose coefficient. If the urine is collected on the first day of acute intake of type S ^{239}Pu after an accident, the minimum detectable dose of the method is 0.03 mSv for Aridus-ICP-SFMS, and 0.004 mSv for AMS. One year after the intake, the minimum detectable dose of this method is lower than 0.5 mSv for both techniques.

CONCLUSIONS

Different analytical methods for quantifying ^{239}Pu in urine with MS techniques have been optimised and evaluated in this paper. The results indicate that they are suitable for dosimetric monitoring of the staff occupationally exposed to Pu. The analytical techniques employed (Aridus-ICP-SFMS and AMS) have shown success in these kinds of controls, exhibiting excellent sensitivity for Pu analysis, and a remarkable increase of productivity when compared with AS. This opens the possibility of giving support to the internal dosimetry service for routine analysis in those cases where the Pu content is below the MDA achieved by AS, both in urine samples and in the reassessment of planchets.

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