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Determination of Pu in urine at ultratrace level by sector field inductively coupled plasma mass spectrometry

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Abstract

A new analytical procedure has been developed for the determination of Pu in urine at the low ag ml^{-1} concentration level by double-focusing sector field inductively coupled plasma mass spectrometry (ICP-SFMS). One liter of urine doped with 4 pg ^{242}Pu was analyzed after co-precipitation with $Ca_3(PO_4)_2$ followed by extraction chromatography on TEVA resin in order to enrich the Pu and remove uranium and matrix elements. Figures of merit of ICP-SFMS for the determination of Pu were studied using two nebulizers, PFA-100 and direct injection high-efficiency nebulizer (DIHEN), for solution introduction with uptake rates of 0.58 and 0.06 ml min^{-1}, respectively. The sensitivity for Pu in ICP-SFMS was determined to be 2000 and 1380 MHz ppm^{-1} for the PFA-100 and DIHEN nebulizers, respectively. Due to the low solution uptake rate of DIHEN the absolute sensitivity was about seven times better and yielded 1380 counts fg^{-1} in comparison to 207 counts fg^{-1} measured with the PFA-100 nebulizer. Recovery using ^{242}Pu tracer was about 70%. The limits of detection for ^{239}Pu in 1 l of urine, based on an enrichment factor of 100 for PFA-100 nebulizer and 1000 for DIHEN, were 9×10^{-18} and 1.02×10^{-18} g ml^{-1}, respectively.

Measurements of $^{240}Pu/^{239}Pu$ isotopic ratio in synthetically prepared urine standard solution yielded a precision of 1.8 and 1.9% and accuracy of 1.5 and 1.8% for the PFA-100 and DIHEN nebulizers, respectively.
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1. Introduction

Determination of the concentration and isotope ratios of actinides is required in environmental monitoring of nuclear contamination in nuclear safeguards and nuclear forensic studies [1,2]. In particular, plutonium isotopes are used for this purpose so that knowledge of their natural and artificial isotopic composition is of great interest for evaluating the source of contamination (nuclear power plant accidents [3,4], nuclear weapon tests [5] or weapons with depleted uranium [6,7]). The $^{240}Pu/^{239}Pu$ isotopic ratio distribution of plutonium in moss samples collected from a bog in the eastern Italian Alps was recently studied in our laboratory [8]. It was demonstrated that the environment at the sites analyzed had been contaminated with artificial transuranium elements, and the probable Pu contamination source was the global fallout after nuclear weapons tests in the 1960s.

In addition, plutonium is considered to be the most radiotoxic element [9]. Determination of its concentration in body fluids, especially in urine and faeces, is of increasing interest in order to investigate the potential health impact on military personnel [10,11] and occupational exposure [2,12,13]. Studies of plutonium in humans [14] suggest that the expected Pu concentration in the human body is above 10^{-14} g g^{-1} and therefore the determination of its concentration is extremely important.

The most widely used analytical techniques for the determination of Pu isotopes are radioanalytical techniques, such as α-spectrometry or liquid scintillation radiometry [5,15]. However, with respect to α-spectrometry determination very large sample volumes, typically 10–25 l, are processed, and for the final measurement step plutonium in the concentrate is electrodeposited onto stainless steel disks prior to counting, which is time-consuming and labor-intensive. A major disadvantage of α-spectrometry relates to the counting pe-

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riod, which can take from days to several weeks depending on the sensitivity and precision required [8]. In addition, ^{239}Pu and ^{240}Pu isotopes are difficult to analyze due to the similar α energies of ^{239}Pu and ^{240}Pu (5.24 and 5.25 MeV, respectively). Implanted passivated junction silicon detectors and special spectra deconvolution software were proposed two decades ago to improve α-spectrometry resolution [16]. However, this method did not find wide application for the measurement of ^{240}Pu/^{239}Pu activity ratios because of its complexity.

Accelerator mass spectrometry (AMS) [17,18] and thermal ionization mass spectrometry (TIMS) [19,20] have been used as ultrasensitive mass spectrometric techniques for Pu isotope analysis in different samples. However, AMS is very expensive and is not widely used. As an alternative to AMS, high-selective resonance ionization mass spectrometry (RIMS) was also established for determination of Pu at ultratrace level [21–23], but at present RIMS instruments are not available on the analytical market.

Inductively coupled plasma mass spectrometry is one of the most suitable methods for the ultratrace isotope analysis of actinides, in particular Pu, due to its high sensitivity, good accuracy and precision, and generally simple sample preparation procedure [24,25]. A number of papers devoted to the determination of Pu by ICP-MS in different samples have been published in recent years [4,26–29] that prove the capability of ICP-MS for the study of Pu at ultratrace concentration level. However, uranium hydride ion formation ($^{238}U^1H^+$) and peak tailing from ^{238}U are the limiting factors for the determination of Pu at a very low concentration level. Moreover, depending on the matrix of the analyzed sample, other molecular ions, e.g., lead or rare earth elements, which can be expected in the actinide mass range (see Table 1), will disturb the accurate determination of Pu. Therefore, special solution introduction systems, such as a micronebulizer with desolvator, are necessary to reduce molecular ions formation and improve the limits of detection for actinide isotopes [30,31]. Laser ablation ICP-MS (LA-ICP-MS) has also been studied for the determination of Pu at the ultratrace level [8,32]. For the solid sample, where the uranium concentration is usually significantly higher than that of plutonium by more than 7 orders of magnitude, this method has the advantage for Pu analysis of direct analysis without sample digestion. This, therefore, leads to a significant decrease in the formation of $^{238}U^1H^+$ molecular ions, and a limit of detection for ^{239}Pu in the sub-fg g^{-1} range can be achieved [8]. However, inhomogeneous distribution of analyte on the investigated sample, instability of the laser ablation rate and lack of certified materials restrict the widespread usage of LA-ICP-MS for Pu analysis in solid samples.

Table 1
Possible interferences for Pu isotopes and required mass resolution on ICP-SFMS

Nuclide	Molecular ions	Required mass resolution, $m/\Delta m$
^{238}Pu	$^{238}U^+$	193665
	$^{206}Pb^{16}O^{14}N^1H_2^+$	3874
	$^{208}Pb^{16}O^1H_2{}^{12}C^+$	3818
	$^{208}Pb^{14}N_2{}^1H_2^+$	4654
^{239}Pu	$^{238}U^1H^+$	36885
	$^{207}Pb^{16}O^{14}N^1H_2^+$	3817
	$^{208}Pb^{16}O^{14}N^1H^+$	3430
^{240}Pu	$^{238}U^1H_2^+$	19116
	$^{208}Pb^{16}O^{14}N^1H_2^+$	3774
^{241}Pu	$^{207}Pb^{16}O_2{}^1H_2^+$	3193
^{242}Pu	$^{208}Pb^{16}O_2{}^1H_2^+$	3159
^{244}Pu	$^{206}Pb^{12}C_3{}^1H_2^+$	3293
	$^{207}Pb^{12}O_3{}^1H^+$	3031

For Pu determination in urine, seawater, waste water samples, etc., mostly chemical separation of ultratrace plutonium from U as well as matrix elements has been proposed. Ion-exchange and extraction chromatography on the resin have been widely used in different labs for this purpose [5,8,33]. Muramatsu et al. [34] investigated ^{239}Pu and ^{240}Pu in environmental samples using Dowex 1 × 8 and Eichrom's TEVA chromatographic resins for the separation of Pu. A decontamination factor of up to 10^4 for many matrix elements, including U, was observed for both resins.

In urine, where the concentration of actinides is usually lower than in the human body, further enrichment of Pu in the sample is required for accurate analysis. Recently, a combination of co-precipitation with extraction chromatography separation has been successfully established in order to concentrate and separate Pu prior to analysis by α-spectrometry [35–37] or by ICP-MS [29] in different samples.

The aim of the present work is to develop an analytical technique for ultrasensitive Pu determination in urine and Pu isotope analysis at the ultratrace level by ICP-SFMS after co-precipitation and trace matrix separation.

2. Experimental

2.1. ICP-MS instrumentation

A double-focusing sector-field ICP-MS (ICP-SFMS, ELEMENT, Finnigan MAT, Bremen, Germany) was used for the determination of Pu and the plutonium isotopic ratio in urine samples. The ICP torch was shielded with a grounded platinum electrode (GuardElectrode™, Finnigan MAT). Solution introduction into the ICP-SFMS was performed using a Microflow nebulizer PFA-100 (Elemental Scientific, Inc., Omaha, NE, USA) and a direct injection high-efficiency nebulizer (DIHEN, JE, Meinhard Associates, Inc., Santa Ana, CA, USA). Samples were introduced in the continuous flow mode using a peristaltic pump (Perimax 12, Spetec GmbH, Erding, Germany) and high-precision syringe pump (CMA-100, Carnegie Medicine, Solna, Sweden) for the PFA-100 and DIHEN nebulizers, respectively.

2.2. Quality control materials

Because of the lack of certified plutonium isotopic standards with urine matrix three quality control test solutions were prepared to evaluate the precision, accuracy and limit of detection (LOD) of the new analytical method. Firstly, fresh urine was subjected to the same co-precipitation and separation steps as the samples in order to obtain the solution for the blank values of Pu in urine (called "blank urine" solution in the following). Then, $10 \pm 1\,\mathrm{pg\,ml^{-1}}$ ^{242}Pu (Pu-1) and $100 \pm 11\,\mathrm{fg\,ml^{-1}}$ ^{239}Pu (Pu-2) were prepared by volumetric dilutions of ^{242}Pu (SRM 4334F) from NIST (Gaithersburg, MD, USA) and aqueous solution with known plutonium isotopic ratio ($^{240}\mathrm{Pu}/^{239}\mathrm{Pu} = 0.014230 \pm 0.0003$) respectively, that were added to the "blank urine" solution. ^{242}Pu isotopic standard (SRM 4334F) was also used for optimization of the experimental parameters and to control the recovery of the developed procedure.

Calibration standards were prepared by dilution of $1\,\mathrm{ng\,ml^{-1}}$ aqueous ^{242}Pu into "blank urine" solution. Five urine laboratory standards solutions were prepared at the following concentrations of ^{242}Pu: 50, 100, 200, 500 and $1000\,\mathrm{fg\,ml^{-1}}$.

In order to study the uranium hydride formation rate $\mathrm{UH^+/U}$ and peak tailing effect from $^{238}\mathrm{U^+}$ a stock solution of U with natural isotopic composition was used.

All acids used were of supragrade (Merck, Darmstadt, Germany). Nitric acid was further purified by subboiling distillation. High-purity deionized water (18 MΩ) was obtained from a millipore Milli-Q-Plus water purifier (Millipore Bedford, MA, USA).

2.3. Samples and sample preparation

The urine sample was collected from healthy adult volunteers in containers previously washed repeatedly with 2% (v/v) nitric acid in 18 MΩ cm water. A schematic diagram of the sample preparation procedure is shown in Fig. 1.

2.4. Co-precipitation Pu with $Ca_3(PO_4)_2$

The 1 l of fresh urine was acidified with nitric acid to pH 2. In order to determine the recovery procedure the urine was spiked with 4 pg of ^{242}Pu and thoroughly mixed. 0.5 ml of 1.25 M $Ca(NO_3)_2$ and 0.2 ml of 3.2 M $(NH_4)_2HPO_4$ was added and the urine was heated to a temperature of approximately 40–50 °C. After that concentrated NH_4OH was added (very slowly) up to the point where the formation of $Ca_3(PO_4)_2$ precipitate was observed. The sample was then stirred with a glass rod, heated for 20 min and allowed to settle overnight. After settling the precipitate was transferred to a centrifuge tube and centrifuged for approximately 10 min at 4000 rpm. The supernatant was decanted and discarded to waste, the precipitate was filtered by gravity over the filter paper.

2.5. Chemical separation of plutonium

Plutonium was separated from the $Ca_3(PO_4)_2$ precipitate by extraction chromatography using Eichrom's TEVA resin (particle size 50–100 μm, active component: aliphatic quaternary amine). The residue of the filtrate was redissolved in 25 ml of 3 M HNO_3. To be retained on TEVA resin Pu must be present in a Pu(IV) form so that 1 ml 3 M $NaNO_2$ was added, mixed well and left to stand for 5 min to ensure that Pu(III) and Pu(VI) are converted to Pu(IV). After that 4 ml of 0.5 M $Al(NO_3)_3$ and 0.2 g of TEVA resin were added to the sample. The sample was shaken for 120 min at a rotational speed of $300\,\mathrm{min^{-1}}$ and loaded into the appropriate cartridge tubes. After rinsing the resin with 3×10 ml 3 M HNO_3 plutonium was eluted with 3×5 ml 0.05 M HF + 0.05 M HNO_3 into a Teflon beaker. The separated sample was then evaporated to a volume of 10 ml and divided into two equal parts (2×5 ml). The first 5 ml was applied for measurements of Pu concentration by ICP-SFMS using the PFA-100 nebulizer. The second 5 ml was further evaporated to a volume of 0.5 ml and introduced into ICP-SFMS via the DIHEN nebulizer.

2.6. Optimization of experimental parameters in ICP-MS and measurement procedure

Optimization of the experimental parameters of ICP-MS instruments was performed with respect to the maximum ion intensity of $^{242}\mathrm{Pu^+}$ and minimum background at m/z 239 u using a ^{242}Pu standard solution. Instrument operation conditions are summarized in Table 2. Further details about the instrumentation and measurement procedure are described elsewhere [38,39]. The measured plutonium ion intensity was corrected taking into account the dead time of the ion detector that was found to be 45 ns using 1, 2 and $10\,\mathrm{ng\,ml^{-1}}$ solutions of NIST U020 standard reference ma-

Table 2
Optimized operation conditions of double-focusing ICP-SFMS for determination of Pu in urine samples using PFA-100 and DIHEN nebulizers for solution introduction

	PFA-100	DIHEN
Solution uptake rate, $\mathrm{ml\,min^{-1}}$	0.58	0.06
RF power, W	1199	1199
Cooling gas flow rate, $\mathrm{l\,min^{-1}}$	18	18
Auxiliary gas flow rate, $\mathrm{l\,min^{-1}}$	0.75	1.07
Nebulizer gas flow rate, $\mathrm{l\,min^{-1}}$	0.935	0.2
Extraction lens potential, V	2000	
Sampler cone	Nickel, 1.1 mm orifice diameter	
Skimmer cone	Nickel, 0.9 mm orifice diameter	
Mass window, %	20	
Runs	7	
Passes	100	
Scanning mode	Peak hopping	
Mass resolution, $m/\Delta m$	300	

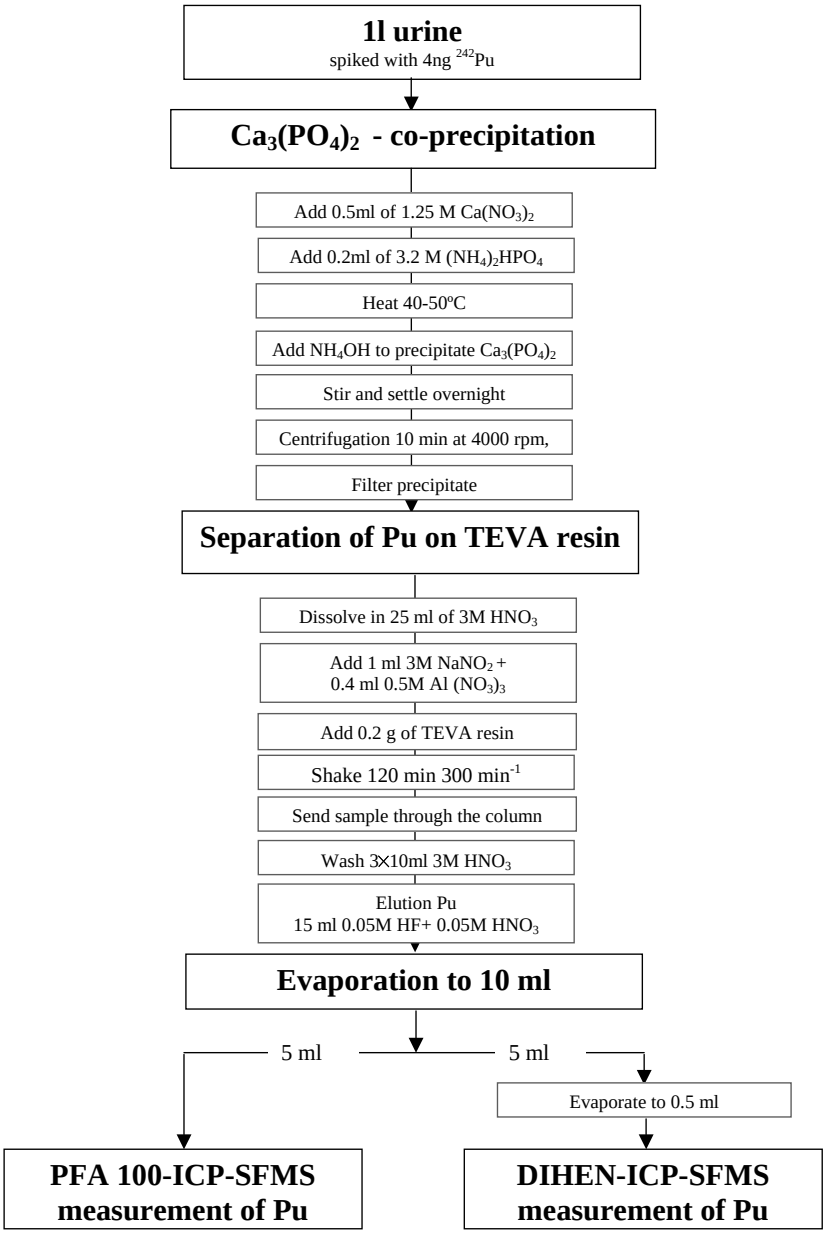

Fig. 1. Sample preparation procedure for Pu separation from urine.

terial. Because the uranium concentration after the separation of the sample on TEVA resin did not exceed 5 pg ml^{-1}, the influences of hydride uranium molecular ions as well as of the peak tailing effect from ^{238}U on the background of m/z 239 u were considered negligible.

3. Results and discussion

3.1. Precision and accuracy of Pu measurement

Precision and accuracy of the developed method was studied on "blank urine" solution spiked with ^{239}Pu (Pu-2). A precision assessment was based on 10 repeated measurements of this synthetically prepared standard with a concentration of ^{239}Pu 100 fg ml^{-1}, achieving an accuracy of 2.5%. Short-term stability ($n = 10$) of this measurement (Fig. 2) was determined to be 7% (R.S.D.). For further proof of the accuracy of the developed analytical method, measurements of the "blank urine" solution spiked with ^{242}Pu isotopic standard (Pu-1) were performed. For the 10 pg ml^{-1} of ^{242}Pu the accuracy was determined to be 1.1%. The calibration curve for ^{242}Pu at the ultratrace level, measured using prepared calibration standards, is shown in Fig. 3 (correlation coefficient: 0.9985). ^{240}Pu/^{239}Pu isotopic ratio measurements in urine using the new method were studied in ICP-SFMS with PFA-100 and DIHEN nebulizers. The results of these measurements (see Table 3) show good agreement between the

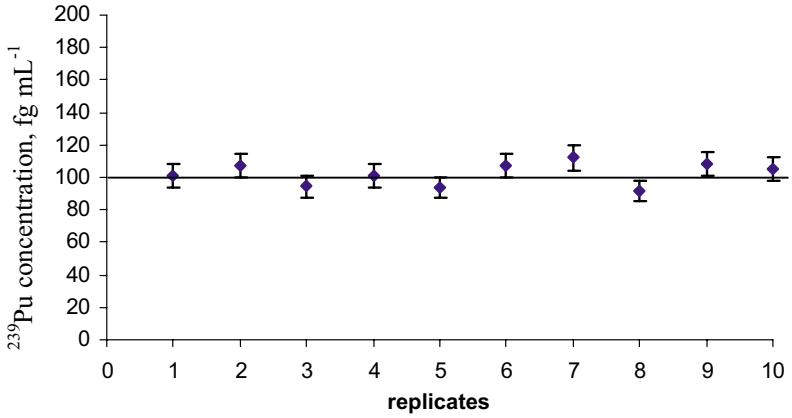

Fig. 2. Short-term stability of ^{239}Pu in synthetically prepared standard solution.

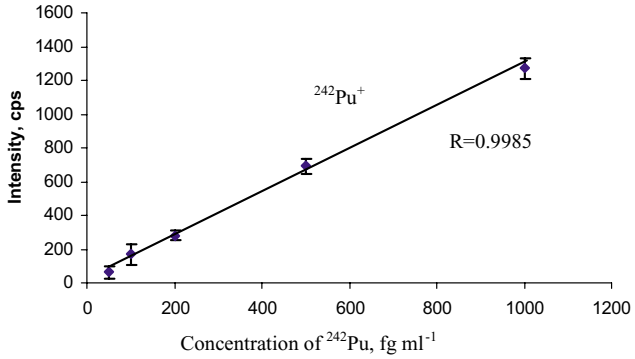

Fig. 3. Calibration curve for $^{242}Pu^{+}$ measured by ICP-SFMS.

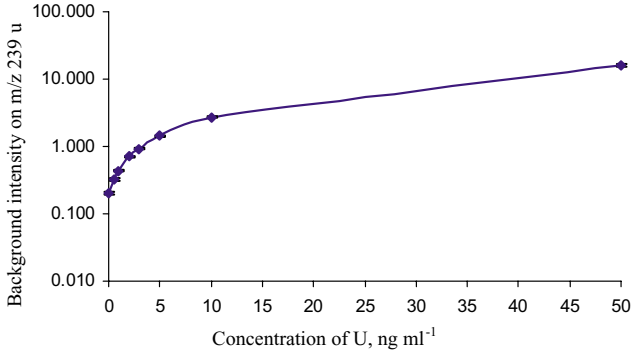

Fig. 4. Influence of U concentration on the background signal on *m*/*z* 239 u.

expected and measured values of $^{240}Pu/^{239}Pu$ isotopic ratio in the synthetically prepared urine standard solution. A precision (R.S.D.%, $n = 10$) of 1.8 and 1.9% and an accuracy of 1.5 and 1.8% were determined for the PFA-100 and DIHEN nebulizers, respectively.

3.2. Co-precipitation and separation of plutonium

^{242}Pu tracer was used to indicate the efficiency of the co-precipitation and separation of the plutonium in the new method. A concentration of dissolved plutonium in 1 l of mixed urine was estimated to be approximately 4 fg ml^{-1}. Recently reported LODs for ^{239}Pu were in the sub-fg ml^{-1} range (e.g., 30 fg ml^{-1}, measured in high-purity deionized water by MC-ICP-MS [40]). Ting et al. [13] studied ^{239}Pu in urine using ICP-SFMS and a microconcentric nebulizer with desolvator "Aridus" for sample introduction. An LOD for ^{239}Pu in urine of 4.7 fg ml^{-1} was achieved. For the determination of Pu at lower concentrations a further preconcentration step is required, in which the matrix elements were removed, thus avoiding clogging effects of the solution introduction system and cones, matrix effects, etc.

A co-precipitation procedure based on $Ca_3(PO_4)_2$ and originally utilized for α-spectrometry was adapted for ICP-MS (schematic, see Fig. 1), where enrichment factors of 100 and 1000 were achieved for measurements with the PFA-100 and DIHEN nebulizer, respectively. The main problem in the determination of ^{239}Pu by ICP-MS is the presence of U in the analyzed sample, due to interferences from $^{238}U^{1}H^{+}$ ion formation and the peak tailing effect from $^{238}U^{+}$ that lead to an increase in the background signal of *m*/*z* 239 u (see Fig. 4). In the present work, concentration

Table 3
$^{240}Pu/^{239}Pu$ isotopic ratio measurements in synthetically prepared urine laboratory standard solution using PFA-100 and DIHEN nebulizers for solution introduction into double focusing ICP-SFMS

Nebulizer	$^{240}Pu/^{239}Pu$ isotopic ratio		Precision, %	Accuracy, %
	Measured	Expected		
PFA-100	0.1445 ± 0.004	0.1423 ± 0.0003	1.85	1.55
DIHEN	0.1448 ± 0.004		1.78	1.78

Table 4
Concentration of minor matrix elements and uranium in urine before calcium phosphate co-precipitation and after separation on TEVA resin

Element	Concentration, $\mu g\,ml^{-1}$		
	Before co-precipitation	After separation	Decontamination factor
Na	38.2 ± 1.9	0.72 ± 0.1	53
Mg	31 ± 1.4	0.75 ± 0.5	41
K	163 ± 28	2.6 ± 0.1	63
Ca	770 ± 70	1.24 ± 0.05	620
Fe	0.222 ± 0.002	0.09 ± 0.01	2.5
U	$(4.1 \pm 0.1) \pm 10^{-5}$	$(0.2 \pm 0.05) \pm 10^{-6}$	200

Table 5
Figures of merit of double-focusing ICP-SFMS for Pu determination using PFA-100 and DIHEN nebulizers for sample introduction

Nebulizer	Solution uptake rate, $ml\,min^{-1}$	Sensitivity for Pu, $MHz\,ppm^{-1}$	Absolute sensitivity for Pu, $counts\,fg^{-1}$	Uranium hydride formation rate, UH^+/U^+	Abundance sensitivity $(m+1)/m$	LOD (3σ), $10^{-18}\,g\,ml^{-1}$	
						^{239}Pu	^{242}Pu
PFA-100	0.58	2000	207	1.3×10^{-4}	2.01×10^{-5}	9	8
DIHEN[a]	0.06	1380	1380	1.2×10^{-4}	2.02×10^{-5}	1.02	0.9

[a] Calculated LODs for ^{239}Pu and ^{242}Pu assumed concentration of the sample after evaporation from 5 to 0.5 ml.

of U in the precipitate was about $40\,pg\,ml^{-1}$, therefore, necessitating the removal of U from the analyzed sample.

To further separate plutonium from the uranium and matrix element of the precipitate (mainly Ca, and Na) extraction chromatography by means of Eichrom's TEVA resin was applied.

The efficiency of the co-precipitation and separation procedure in terms of the removal of matrix ions, as well as U, is shown in Table 4. The concentrations of minor elements in the sample after pre-concentration and separation were significantly lower (2 orders order of magnitude) than in the original urine. U concentration was determined to be $0.2\,pg\,ml^{-1}$, and, no increase of the background on *m/z* 239 u was observed.

3.3. Figures of merits of ICP-MS

Sensitivity, abundance sensitivity and limit of detection in ICP-SFMS for Pu determination were studied using the PFA-100 and DIHEN nebulizers for sample introduction. A slightly higher sensitivity (1.4-fold) was observed with the PFA-100 nebulizer in comparison to the DIHEN nebulizer, whereas the absolute sensitivity was 6.6-fold better with the DIHEN nebulizer (see Table 5) and thus demonstrating the significance of applying this nebulizer for small or hazardous samples. The uranium hydride formation rate and abundance sensitivity remained the same for two selected nebulizers, hence ensuring a negligible increase of the background on *m/z* 239 u.

3.4. Pu recovery by the method developed and Pu measurements

In order to investigate the Pu recovery of the method developed, comparative measurements of 5 ml of the separated sample and 5 ml of the spiked "blank urine" using the PFA-100 and DIHEN nebulizers were performed. All the data from the measurements are summarized in Table 6. Because the solution uptake rate of the DIHEN nebulizer ($0.06\,ml\,min^{-1}$) is about 10 times lower than in the PFA-100 nebulizer ($0.58\,ml\,min^{-1}$) for the DIHEN measurements 5 ml of the analyzed sample was evaporated to the volume of 0.5 ml. By applying this approach, the analysis time of the measurements with the PFA-100 and DIHEN

Table 6
Intensities measured by ICP-SFMS in spiked urine and "blank urine" solution on *m/z* 238, *m/z* 239 and *m/z* 242

	Intensities, cps			Recovery, %
	m/z 238	*m/z* 239	*m/z* 242	
PFA-100				
"Blank urine" solution	484 ± 16	0.5 ± 0.4	761.1 ± 31	70.8
Urine	451 ± 26	0.6 ± 0.5	533.8 ± 29	
DIHEN				
"Blank urine" solution	3760 ± 42	0.6 ± 0.3	5120 ± 92	71.5
Urine	3741 ± 53	0.7 ± 0.4	3662 ± 80	

For measurements with DIHEN 5 ml of analyzed sample was evaporated to a volume of 0.5 ml. 1 l of urine and "blank urine" solution were spiked with $4\,pg\,ml^{-1}$ of ^{242}Pu before and after the co-precipitation/separation steps, respectively.

nebulizers as well as the consumption of the original sample remained the same. The recovery of ^{242}Pu by the new method was about 71% for both nebulizers.

Using the intensity values on the *m*/*z* 239 u and *m*/*z* 242 u measured in "blank urine" solution and the sensitivity for Pu in ICP-SFMS, the LODs (3σ-criterion) for ^{239}Pu and ^{242}Pu in urine were calculated for two selected nebulizers (see Table 5). In the case of the DIHEN nebulizer, the calculation assumed the 10-fold concentration of the sample due to evaporation. Limits of detection for ^{239}Pu in urine with the PFA-100 and DIHEN nebulizers were 9×10^{-18} and 1.02×10^{-18} g ml^{-1}, respectively, whereby for ^{242}Pu values of 8×10^{-18} and 0.9×10^{-18} g ml^{-1} were achieved.

4. Conclusion

This study demonstrates that ICP-SFMS, combined with co-precipitation and extraction chromatography, represents a useful analytical technique suitable for the analysis of plutonium in urine at the low ag ml^{-1} level. Disturbing interferences affecting accurate determination of the Pu that arise from the presence of U in the analyzed sample as well as matrix elements were successfully removed by means of co-precipitation and separation of the sample on Eichrom's TEVA resin. Recovery of Pu in the new method was 70%. In comparison to α-spectrometry, ICP mass spectrometry offers significant advantages, including isotopic information (as distinct from ^{239}Pu and ^{240}Pu), short analysis time and substantial reduction in sample size. The last becomes more significant if the DIHEN nebulizer is applied for sample introduction into ICP-MS. In this case, separation of the sample from the matrix, additional increase of the LOD (1 order of magnitude in comparison to the nebulizers with solution uptake rate $\geq$0.6 ml min^{-1} and sensitivity about 2 GHz ppm^{-1}) can be achieved by concentrating the sample (e.g., by evaporation) and introducing it into the plasma via the DIHEN nebulizer. Using the method presented in this study, the limit of detection for ^{239}Pu in 1 l of urine obtained on the ICP-SFMS with the DIHEN nebulizer was 1.02×10^{-18} g ml^{-1}.

Measurements of the ^{240}Pu/^{239}Pu isotopic ratio in synthetically prepared urine standard solution yielded a good precision and accuracy that, therefore, proves that it is possible to assess the source of contamination in urine samples in the case of ultra-low concentrations of Pu by determining the ^{240}Pu/^{239}Pu isotopic ratio using the method developed by us.

In future work, the application of multiple collector ICP mass spectrometry with multi-ion counters for Pu isotope ratio measurements at the ultratrace level in urine would be of interest. Further improvement of the LODs for Pu isotopes in urine is expected due to the better abundance sensitivity of available MC-ICP-MS instruments. In addition, because of the simultaneous determination of several Pu isotopes by MC-ICP-MS, a high precision of isotopic ratio measurements would be possible.

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