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Rapid determination of ultra-trace plutonium isotopes (^{239}Pu, ^{240}Pu and ^{241}Pu) in small-volume human urine bioassay using sector-field inductively coupled plasma mass spectrometry

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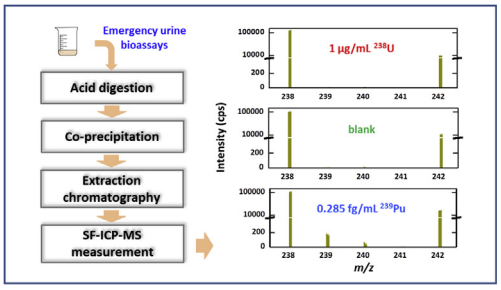
HIGHLIGHTS

- A rapid method was developed for emergency urine Pu analysis with a sample throughput of 10 samples/day.
- Small size of urine (20 mL and 100 mL) was used for accurate determination of ultra-trace level of Pu.
- High U decontamination factor ($>10^6$) was realized.
- Extremely low detection limits down to ag mL^{-1} were reached for ^{239}Pu, ^{240}Pu and ^{241}Pu with 100 mL urine bioassays.

GRAPHICAL ABSTRACT



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ABSTRACT

A rapid method with enhanced ^{238}U decontamination was developed for ultra-trace Pu analysis in small-volume urine bioassays. This method consists of acid digestion, co-precipitation, extraction chromatography and sector-field inductively coupled plasma mass spectrometry (SF-ICP-MS) measurement. Parameters that may influence the analytical performance were studied systematically. This method achieved a high ^{238}U decontamination factor (3.8×10^6) and the ^{242}Pu recovery was stable for 20 mL and 100 mL urine bioassays with an average value of 72.7 ± 5.5%. The limits of detection for ^{239}Pu, ^{240}Pu and ^{241}Pu by the method were 0.016 fg mL^{-1}, 0.016 fg mL^{-1} and 0.019 fg mL^{-1} for 20 mL urine samples and 0.003 fg mL^{-1}, 0.002 fg mL^{-1} and 0.003 fg mL^{-1} for 100 mL urine samples, respectively. Considering the small volume of urine employed in this study, the absolute detection limits of the method were comparable or even better than those measured with thermal ionization mass spectrometry and accelerator mass spectrometry. All procedures for 20 mL and 100 mL urine bioassays were completed in 9.5 h and 11 h, respectively, and analysis of 10 samples could be finished within one day. With the considerably low detection limits of Pu isotopes and high sample throughput, this method would be a promising tool for

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the quick response to radiological emergencies and for rapid screening of unexpected occupational exposures of workers involved in the future FDNPP reactor decommissioning operations.

1. Introduction

Plutonium is regarded as highly hazardous due to its chemical toxicity and the radioactivity of its main isotopes ^{239}Pu (α-decay, $T_{1/2} = 24110$ y), ^{240}Pu (α-decay, $T_{1/2} = 6563$ y) and ^{241}Pu (β-decay, $T_{1/2} = 14.4$ y). They have a strong tendency to accumulate in liver and bones and thus pose long-term health risks once introduced into the human body [1]. For example occupational exposure to Pu usually comes from inhalation [2,3]. Airborne Pu has also been reported to be released during radiological accidents and incidents [4,5]. Recently, on June 6th, 2017, five workers suffered internal radiation exposure due to inhalation of airborne Pu when inspecting nuclear fuel materials at a nuclear research facility of the Japan Atomic Energy Agency [6]. This accident once more highlighted the necessity for quick assessment of the exposure level of Pu for the purpose of radiation protection and medical intervention. While external exposure is typically assessed by biological dosimetry, internal contamination can be assessed by either in vivo or in vitro bioassay especially for alpha and beta emitters, among which urinalysis is one of the most basic and straightforward in vitro techniques [7,8]. Therefore a rapid and robust method with a low limit of detection (LOD) for urinary Pu analysis is requisite for laboratories not only for quick response to potential radiological emergencies but also for routine screening of unexpected occupational exposure; In Japan, this is especially important for ensuring the health of workers involved in the long-term reactor decommissioning operations for the Fukushima Daiichi Nuclear Power Plant (FDNPP).

Many papers have been published focusing on the determination of Pu in urine using various methodologies. A summary of typical urinary Pu analysis methods is presented in Table S1. While these methods have specific merits, there are several typical demerits which hampered their wide application for emergency response and routine monitoring. For example, conventional alpha spectrometry has relatively high LODs (generally 1 mBq L^{-1} as summarized by the ICRP) and incapability to measure beta-emitter ^{241}Pu and to provide the isotopic signature of ^{239}Pu and ^{240}Pu [8,9]. Thermal ionization mass spectrometry (TIMS) and accelerator mass spectrometry (AMS) are well-regarded for their high sensitivity and for having fewer spectra and non-spectra interferences than inductively coupled plasma mass spectrometry (ICP-MS), but the complex sample preparation steps and less accessibility to the instruments have limited their wide application to rapid radiological assessments. Urinary Pu analysis with ICP-MS has also been intensively reported, but ICP-MS suffers from higher LODs than TIMS and AMS, making it less competitive from the viewpoint of performances. However, ICP-MS benefited a lot from its operational simplicity and wide-spread accessibility to instruments, and if lower LODs could be reached, it would be even more promising.

Furthermore, many of the methods in Table S1 were developed on the basis of processing large urine sample volumes (1 L or more) with co-precipitation in order to obtain low LODs. During radiological emergencies large size urine bioassays may not always be easily conducted while small volumes of urine are more likely to be used if multiple radionuclides need to be assessed separately. Relatively long analytical times usually result from coping with large volumes of urine, which further limit sample throughput of the methods, thus posing challenges for routine monitoring among occupational populations. Additionally, the existence of organic matter and complexing reagents such as citric acid and oxalate acid in urine samples might have some influence on the co-precipitation procedure. Release of plutonium from organic compounds would be of vital importance for accurate determination of ultra-trace plutonium in urine bioassays [10].

In this study we developed a rapid method for analysis of Pu isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu) in small-volume urine bioassays (20 mL and 100 mL) using a highly sensitive SF-ICP-MS. The 100 mL sample volume was chose in order to obtain sufficiently low LOD of Pu determination while 20 mL sample volume was employed considering that only an aliquot of urine might be dispensed to conduct Pu bioassay if other radionuclides need to be analyzed immediately. Acid digestion with HNO_3-H_2O_2 in combination with CaF_2/LaF_3 co-precipitation followed by extraction chromatographic separation were employed so as to remove matrix interference elements to the fullest; stable recoveries were obtained in that way for 20 mL and 100 mL urine samples, meanwhile an enhanced decontamination factor of uranium ($>10^6$) was achieved. Extremely low LODs (down to ag mL^{-1}) were reached for ^{239}Pu, ^{240}Pu and ^{241}Pu. The whole analytical procedure could be accomplished within 1 working day, meeting the requirement of routine monitoring of unexpected occupational exposure as well as quick response during radiological emergencies.

2. Materials and methods

2.1. Reagents and materials

Analytical grade reagents including $NaNO_2$, $NH_2OH{\cdot}HCl$, $Ca(NO_3)_2{\cdot}4H_2O$, $La(NO_3)_3{\cdot}6H_2O$, H_3BO_3, ascorbic acid, ferrous sulfamate (38–42%), $TiCl_3$ (20%), HNO_3 (60–61%) and HCl (35–37%) were obtained from Kanto Chemicals (Tokyo, Japan). Ultrapure HNO_3 (68%) and HF (38%) were available from Tama Chemicals (Tokyo, Japan). All the required reagents were prepared with pure water (18.2 MΩ cm). The extraction resins TEVA, UTEVA and DGA-N resins in 2 mL cartridges were all obtained from Eichrom Technologies (Lyle, IL, USA). ^{242}Pu (CRM 130, New Brunswick Laboratory, NJ, USA) was used as a yield tracer. The mixed Pu isotope standard solution (NBS-947) with a certified ^{240}Pu/^{239}Pu atom ratio of 0.242 was employed to evaluate the trueness and precision of the method. Uranium standard solution (10 mg L^{-1}) was used for addition experiments to investigate U removal.

2.2. Sample digestion and CaF_2/LaF_3 co-precipitation

All urine samples were freshly collected and dispensed before analysis. The time between urine collection and urine analysis was generally less than 1 h. The use of freshly collected urine sample would satisfy the requirements for real emergency situations where urine bioassay needs to be conducted immediately. After urine samples were dispensed into glass beakers, 0.57 pg of ^{242}Pu was added to each sample as yield tracer. In experiments where extra U (in U standard solution) or Pu (in NBS-947) was required, they were added right before the addition of ^{242}Pu. Then samples were heated at 220 °C on a hot plate and HNO_3 was added. For the

20 mL urine sample, 2 mL concentrated HNO_3 was used, while for the 100 mL urine sample 10 mL concentrated HNO_3 was added proportionally. After boiling the mixture, 4 mL and 20 mL of 30% H_2O_2 were slowly pipetted to 20 mL and 100 mL urine samples, respectively, to decompose organic matter. After evaporating to dryness, the residual was dissolved in 4 mL concentrated HNO_3 and heating was continued until dryness. This step was repeated 3 times. Then the final residual was soaked with 10 mL concentrated HNO_3 and transferred to 50 mL centrifuge tubes. Deionized water was used to rinse the beaker and this rinse was then combined with the sample solution in the tube. Next, deionized water was added to get a sample solution volume of 35 mL. $TiCl_3$ solution (2 mL) was pipetted into the sample solution to reduce plutonium to trivalent state which undergoes co-precipitation better during the following CaF_2/LaF_3 precipitation procedure. To perform CaF_2/LaF_3 precipitation, 100 mg Ca and 100 mg La were successively added to sample solution in the form of $Ca(NO_3)_2$ and $La(NO_3)_3$ followed by addition of 7 mL concentrated HF. After mixing thoroughly, the precipitate was allowed to settle for 15–20 min for ageing. Then the precipitate was separated from the supernatant by centrifugation at 3000 rpm for 15 min. After discarding supernatant, the precipitation was dissolved in 20 mL 3 M HNO_3 with the addition of 0.5 g H_3BO_3. Finally, 0.3 g $NaNO_2$ was added to sample solution for valence adjustment of Pu to the tetravalent state by heating in a heating block at 40 °C for 30 min. This solution was ready for the following extraction chromatography separation.

2.3. Extraction chromatography separation

The extraction chromatography was performed with a combination of TEVA + UTEVA + DGA resin cartridges. We successfully employed this separation procedure in the determination of Pu in soil and sediment matrices in our previous work [11]. In brief, TEVA + UTEVA + DGA resins were preconditioned with 10 mL 3 M HNO_3. The sample solution obtained from the last step in the digestion and co-precipitation procedures was then loaded onto the TEVA resin with a 20 mL syringe tube connected above the resin cartridge, and that was followed by successive rinses: with 10 mL 3 M HNO_3 to remove Ca, Fe and rare earth elements, 40 mL 1 M HNO_3 to remove U, Pb, Tl and Pt and 10 mL 9 M HCl to remove Th, Bi and Hf. Then UTEVA and DGA resins were vertically connected to TEVA resin with DGA resin on the bottom. Next, 20 mL 3 M HNO_3-0.1 M ascorbic acid-0.02 M Fe^{2+} was used to elute Pu from TEVA resin onto DGA resin by reducing it from tetravalent state to trivalent state. In control experiments without the UTEVA resin, DGA was directly connected below TEVA resin. In both experimental and control cases, only the DGA resin was subjected to further purification with 30 mL 0.1 M HNO_3 for enhanced removal of U. Finally, Pu on the DGA resin was eluted with 20 mL 0.5 M HCl-0.1 M $NH_2OH \cdot HCl$. The sample loading and Pu elution were kept at about 0.5 mL min^{-1} flow speed while during rinsing steps faster speed (1–2 mL min^{-1}) was used. The final eluent was evaporated to dryness, soaked with 4 mL *aqua regia* and heated to dryness again. After adding 1 mL ultrapure HNO_3 and heating the mixture to near dryness, the sample residual was dissolved with 0.7 mL of 4% ultrapure HNO_3 with 0.02 ng mL^{-1} Rh as internal standard in preparation for SF-ICP-MS measurement.

2.4. SF-ICP-MS measurement

SF-ICP-MS (Element XR, Thermo Fisher Scientific, Bremen, Germany) equipped with a high efficiency sample introduction system (APEX-Q, Elemental Scientific Inc., Omaha, NE, USA) was employed in the low resolution mode for Pu measurement. The sample introduction system was operated in the self-aspiration mode to reduce the risk of contamination from the peristaltic pump tubing. The SF-ICP-MS was optimized with 0.02 ng mL^{-1} ^{238}U standard solution to provide optimum performance every time before sample analysis. We have presented detailed operation parameters and a performance evaluation of this instrument previously [12]. Typically a high sensitivity of 40 M cps per ng mL^{-1} for ^{238}U was obtained during measurements. All analytical procedures were summarized in Fig. 1.

3. Results and discussion

Due to the high salt and organic matter contents in human urine, the determination of ultra-trace level Pu with ICP-MS is susceptible to the interferences. Pappas et al. [13] observed obviously elevated counts of ^{239}Pu in diluted urine (containing 10 ng L^{-1} ^{238}U) compared with 5% HNO_3 matrix (containing 10 ng L^{-1} ^{238}U) when measured with ICP-MS, illustrating non-negligible interferences on *m/z* 239 by urine matrix. Hang et al. [14] compared the LODs of ^{239}Pu with different matrices with ICP-MS after on-line extraction chromatography purification. The LODs of ^{239}Pu for pure water, 10-fold diluted urine and raw urine were 0.06 pg mL^{-1}, 0.08 pg mL^{-1} and 0.15 pg mL^{-1}. The worse LOD for the dirty matrices might be attributed to the matrix ions and deteriorated performance of the resin [14]. For these reasons sample pretreatment is imperative before ICP-MS measurement for precise and sensitive analysis of ultra-trace Pu.

The removal of urine matrix can be realized by either acid digestion or co-precipitation followed by further chemical separation. Generally, for large urine sample volumes e.g. 1 L, co-precipitation is preferred to remove complex matrices. While for sample volumes such as tens or hundreds of milliliters, acid digestion is more efficient not only because digestion time is short, but also organic matter can be decomposed at the same time. For urinalysis it is an important issue to liberate endogenous radionuclides from organic matter associations into free ions, which ensures better reliability and repeatability than co-precipitation methods [10].

Another problem when measuring ^{239}Pu by ICP-MS is the polyatomic interference of $^{238}UH^+$ which cannot be resolved instrumentally. The typical level of uranium in human urine is 10 ng L^{-1} which may only have minor influence on the accurate determination of ^{239}Pu by ICP-MS [15,16]. Nevertheless, elevated urine uranium concentrations up to several μg L^{-1} have been reported for occupationally exposed people engaged in uranium yellow cake production [17]. In scenarios where Pu contamination occurs in the presence of high uranium content (e.g. when handling MOX fuel, in reactor decommissioning tasks at the FDNPP), elevated uranium levels may possibly occur in urine simultaneously with Pu. Therefore, enhanced decontamination of uranium during the chemical treatment makes sense in the case of extreme situations such as contamination by multiple radionuclides.

As shown in Fig. 1, after sample digestion, CaF_2/LaF_3 co-precipitation together with extraction chromatography separation was employed to concentrate and purify Pu from complex urine matrices. For the purpose of optimization, here we investigated several parameters in the pretreatment and chemical separation procedures that might influence the analytical performances such as ^{242}Pu recovery and decontamination of ^{238}U. Furthermore, we systematically evaluated the LODs of Pu isotopes, trueness and precision and sample throughput of our developed method.

3.1. Adjustment of Pu oxidation state prior to CaF_2/LaF_3 co-precipitation

Before conducting the CaF_2/LaF_3 co-precipitation, Pu isotopes

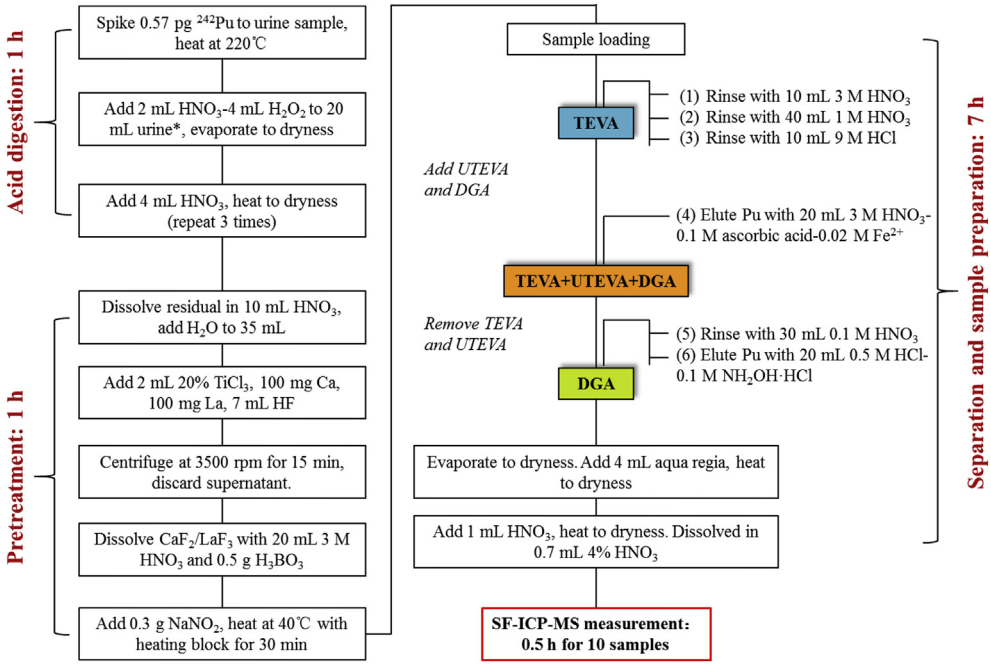

Fig. 1. Schematic diagram of rapid determination of Pu in small-volume urine bioassays. *For 100 mL urine samples, add 10 mL HNO_3-20 mL H_2O_2 proportionally.

usually need to be reduced to the trivalent state to facilitate the co-precipitation. Both $TiCl_3$ and sulfamic acid-ascorbic acid have been applied for reduction of Pu. For example, Maxwell et al. [18] employed sulfamic acid-ascorbic acid with a 3-min waiting step to reduce plutonium to Pu^{3+} before sample loading. They have also used $TiCl_3$ to reduce Pu before CaF_2/LaF_3 co-precipitation [19,20]. To compare the efficiency of these two types of commonly used reducing reagents, we used 2 mL 20% $TiCl_3$ solution and 0.5 mL 1.5 M sulfamic acid-1.25 mL 1.5 M ascorbic acid to treat urine samples before CaF_2/LaF_3 co-precipitation. Recoveries of ^{242}Pu yield tracer given as the average of 4 replicates for each condition are listed in Table 1. For 20 mL urine bioassays, recoveries for $TiCl_3$ ($74.4 \pm 3.2\%$) and sulfamic-ascorbic acid ($72.7 \pm 2.9\%$) reduction conditions showed little difference with each other (Table 1, Group 2 and 3); this indicated these two reducing reagents have similar efficiencies. Besides, stable recoveries were obtained with $TiCl_3$ reduction for both 20 mL and 100 mL urine sample volumes (Table 1, Group 1 and 2). Considering the use of $TiCl_3$ is straightforward and requires no preparation of solution, we finally chose $TiCl_3$ as the reductant.

3.2. Dissolution of CaF_2/LaF_3 precipitation

Urine is characterized by very complex matrices with high salt and organic matter contents; Ca^{2+}, PO_4^{3-}, SO_4^{2-} are among the main ionic species in human urine [21]. Direct precipitation of $Ca_3(PO_4)_2$ with endogenous Ca^{2+}, PO_4^{3-} in urine has been reported, also illustrating a non-negligible amount of phosphate exists in actual urine samples [22]. As suggested by Horwitz et al. [23], the existence of fluorides, phosphates, and sulfates in a loading solution could diminish Pu sorption on TEVA resin. Aluminum can complex with these ions and its addition might contribute to improving recoveries. For similar reasons, Maxwell et al. [19,20] added $Al(NO_3)_3$ to sample solution after dissolution of CaF_2/LaF_3 with HNO_3-H_3BO_3. We explored the influence of $Al(NO_3)_3$ on the method performance. As seen in Table 1, for Group 4 and 5, 20 mL 3 M HNO_3-1 M $Al(NO_3)_3$ was added to dissolve CaF_2/LaF_3 with the addition of H_3BO_3. Compared with Group 2 and Group 3, the use of $Al(NO_3)_3$ did not improve the recovery, on the contrary slightly lower recoveries occurred. This was probably because the concentrations of related anions were still too low to have any significant influence on the affinity of Pu onto the TEVA resin, especially after CaF_2/LaF_3 co-precipitation. Besides, the use of high concentration of $Al(NO_3)_3$ increased the matrix of the sample loading solution thus brought an extra burden to extraction resins.

3.3. Enhancement of uranium decontamination

As we noted earlier, there are possible scenarios where Pu contamination occurs in the presence of high uranium content, for example during the decommissioning tasks of nuclear reactors. Besides, difference exists between their excretion rates from urine. For example, in the case of acute intake by inhalation of type S substance (insoluble oxides), the excretion rates (Bq Bq^{-1} intake) of

Table 1
^{242}Pu recoveries under different conditions.

Group ID	Urine volume (mL)	Replicates	Reducing reagents	CaF_2/LaF_3 dissolution	Recovery (%)
1	100	4	2 mL 20 w% $TiCl_3$	0.5 g H_3BO_3 + 20 mL 3 M HNO_3	72.1 ± 0.6
2	20	4	2 mL 20 w% $TiCl_3$	0.5 g H_3BO_3 + 20 mL 3 M HNO_3	74.4 ± 3.2
3	20	4	0.5 mL 1.5 M sulfamic acid + 1.25 mL 1.5 M ascorbic acid	0.5 g H_3BO_3 + 20 mL 3 M HNO_3	72.7 ± 2.9
4	20	3	2 mL 20 w% $TiCl_3$	0.5 g H_3BO_3 + 20 mL 3 M HNO_3-1 M $Al(NO)_3$	63.5 ± 4.2
5	20	3	0.5 mL 1.5 M sulfamic acid + 1.25 mL 1.5 M ascorbic acid	0.5 g H_3BO_3 + 20 mL 3 M HNO_3-1 M $Al(NO)_3$	67.2 ± 5.4

uranium and plutonium were predicted to be 7.0×10^{-4} and 2.3×10^{-6} on the first day of the intake [9]. The about 300 times faster clearance rate of uranium is likely to cause an elevated uranium concentration in urine. As a result, it is meaningful to develop a method with enhanced decontamination of uranium in preparation for extreme situations such as contamination by multiple radionuclides.

To investigate the ability of uranium removal with our present method, we spiked 20 μg ^{238}U in 20 mL urine sample resulting in a final concentration of 1 μg mL^{-1} ^{238}U. The ^{242}Pu recoveries as well as decontamination factor (DF) of ^{238}U are presented in Table 2. At the same time, we also investigated the influence of reducing reagents used before CaF_2/LaF_3 co-precipitation on DF (U). When conducting extraction chromatography with TEVA + DGA resins, the DF (U) in the $TiCl_3$-employed situation reached 1.1×10^4, which was several times higher than that under the sulfamic acid-ascorbic acid (2.1×10^3) reduction condition. In contrast, for both $TiCl_3$ and sulfamic acid-ascorbic acid reduction cases, the combination of CaF_2/LaF_3 co-precipitation with TEVA + UTEVA + DGA resins presented enhanced ^{238}U removal. More specifically, the average DF (U) (n = 2) values in the $TiCl_3$ and sulfamic acid-ascorbic acid reduction cases were estimated to be 3.8×10^6 and 4.1×10^6, respectively. Maxwell et al. [24] employed $Ca_3(PO_4)_2$ and TEVA + UTEVA + DGA extraction chromatographic separation for the urine Pu purification. They reported DF (U) of their method to be 2.7×10^6. Our DF (U) values obtained with CaF_2/LaF_3 co-precipitation and TEVA + UTEVA + DGA separation were slightly higher than their results. Fig. 2 (a) and (b) show the ICP-MS spectra of ^{238}U spiked urine sample (20 mL urine with a ^{238}U concentration of 1 μg mL^{-1}) and operational blank (20 mL urine) after $TiCl_3$ reduction, CaF_2/LaF_3 co-precipitation and TEVA + UTEVA + DGA separation, respectively. The final ^{238}U counts for the 1 μg mL^{-1} U spiked urine were at the same level as the operational blank. For comparison, Fig. 2 (c) shows the spectrum of 20 mL urine spiked with the least amount of ^{239}Pu (with 0.285 fg mL^{-1} ^{239}Pu in urine). These results further demonstrated that the present method is capable of sufficient removal of uranium even in extreme situations where as much as 1 μg mL^{-1} U was present in 20 mL urine; additionally it is also able to determine sub-fg mL^{-1} level Pu in such small-volume urine bioassays. Regarding the specific requirements, TEVA + DGA resins could also be employed when a lower DF (U) is required. Another interesting fact is that the ^{242}Pu recoveries with TEVA + DGA separation were obviously higher than that with TEVA + UTEVA + DGA separation (Table 2, Sample 5, 6). Such results might indicate Pu loss when the eluent (3 M HNO_3-0.1 M ascorbic acid-0.02 M Fe^{2+}) containing Pu^{3+} flowed through the UTEVA resin, a future systematic investigation is needed to provide further explanations.

3.4. Detection limits of Pu isotopes

Based on the above investigations, we finally employed HNO_3-H_2O_2 digestion, $TiCl_3$ reduction of Pu, CaF_2/LaF_3 co-precipitation, and HNO_3-H_3BO_3 dissolution together with TEVA + UTEVA + DGA extraction chromatographic separation for the determination of Pu in small-volume urine bioassays. Details of the procedures are presented in Fig. 1. For 20 mL and 100 mL urine samples the ^{242}Pu recoveries were 71.2 ± 4.5% and 74.2 ± 6.0%, respectively, with an average of 72.7 ± 5.5%. We estimated the LODs of Pu isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu) based on three times the standard deviation of operational blanks as recommended by the IUPAC [25]. The LODs in both mass and radioactivity units are given in Table 3 based on 7 replicates for each urine sample volume. Owing to the high sensitivity of SF-ICP-MS and our efforts to remove matrices during the sample treatment, we achieved extremely low LODs for Pu isotopes. For 20 mL urine samples, LODs of ^{239}Pu, ^{240}Pu and ^{241}Pu were 0.016 fg mL^{-1}, 0.016 fg mL^{-1}, 0.019 fg mL^{-1}, corresponding to 0.036 mBq L^{-1}, 0.138 mBq L^{-1} and 70.9 mBq L^{-1} respectively. For 100 mL urine samples, LODs of ^{239}Pu, ^{240}Pu and ^{241}Pu were 0.003 fg mL^{-1}, 0.002 fg mL^{-1} and 0.003 fg mL^{-1}, corresponding to

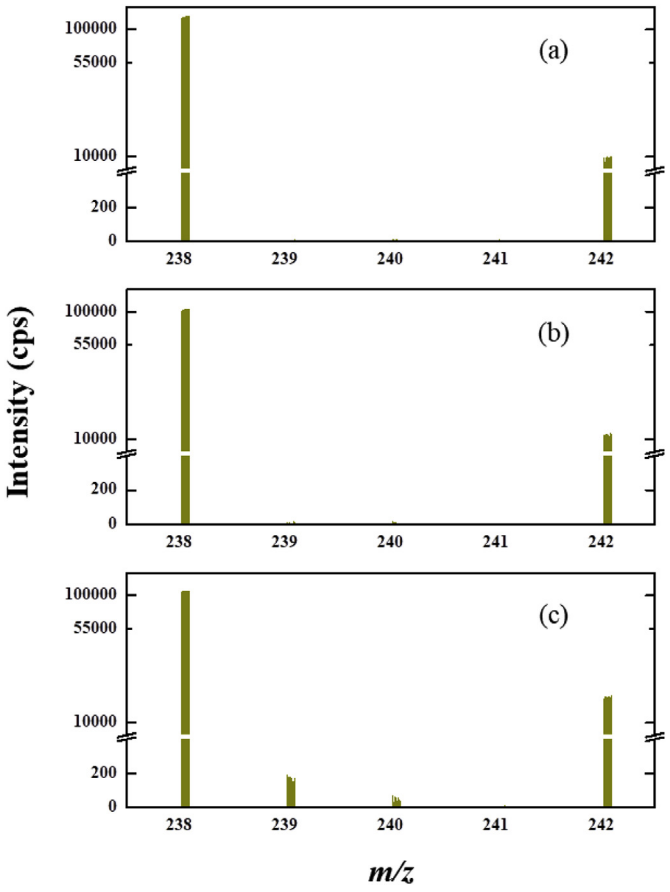

Fig. 2. ICP-MS spectra for: (a) 20 mL urine with 1 μg mL^{-1} ^{238}U; (b) operational blank of 20 mL urine; (c) 20 mL urine with 0.285 fg mL^{-1} ^{239}Pu (spiked with NBS-947).

Table 2
Comparison of ^{238}U decontamination factor with TEVA + UTEVA + DGA and TEVA + DGA resin separations.

Sample ID	Urine volume (mL)	Spiked ^{238}U (μg)	Reducing reagents	Co-precipitation	Separation	^{242}Pu recovery (%)	DF(U)
1	20	20	2 mL 20 w% $TiCl_3$	CaF_2/LaF_3	TEVA + UTEVA + DGA	75.2	2.3×10^6
2	20	20	2 mL 20 w% $TiCl_3$	CaF_2/LaF_3	TEVA + UTEVA + DGA	73.0	5.2×10^6
3	20	20	0.5 mL 1.5 M sulfamic acid+1.25 mL 1.5 M ascorbic acid	CaF_2/LaF_3	TEVA + UTEVA + DGA	75.5	4.2×10^6
4	20	20	0.5 mL 1.5 M sulfamic acid+1.25 mL 1.5 M ascorbic acid	CaF_2/LaF_3	TEVA + UTEVA + DGA	75.7	4.0×10^6
5	20	20	2 mL 20 w% $TiCl_3$	CaF_2/LaF_3	TEVA + DGA	85.2	1.1×10^4
6	20	20	0.5 mL 1.5 M sulfamic acid+1.25 mL 1.5 M ascorbic acid	CaF_2/LaF_3	TEVA + DGA	86.9	2.1×10^3

Table 3
Limit of detection (LOD) of ^{239}Pu, ^{240}Pu and ^{241}Pu (in mass unit and activity unit) for 20 mL and 100 mL urine bioassays (n = 7).

Urine volume (mL)	^{239}Pu LOD (fg mL^{-1})	^{240}Pu LOD (fg mL^{-1})	^{241}Pu LOD (fg mL^{-1})	^{239}Pu LOD (mBq L^{-1})	^{240}Pu LOD (mBq L^{-1})	^{241}Pu LOD (mBq L^{-1})
20	0.016	0.016	0.019	0.036	0.138	70.9
100	0.003	0.002	0.003	0.006	0.015	9.8

0.006 mBq L^{-1}, 0.015 mBq L^{-1} and 9.8 mBq L^{-1} respectively. The present LODs of ^{239}Pu and ^{240}Pu were more than 100 times lower than the general level of the radiometric method (1 mBq L^{-1}) as summarized by the ICRP [9]. In view of the long residence time of Pu in the human body and its slow excretion rate from urine, even in the case of a radiological accident, the Pu concentration in actual urine samples is assumed to be low. Therefore, it would undoubtedly be a common prerequisite for a method to achieve low LODs so as to accurately quantify any anomalous Pu. Li et al. [26] summarized some requirements for radiation emergency urine bioassay techniques. They calculated the required LOD (Bq L^{-1}) for 10 high risk radionuclides in urine analysis based on 0.1 Sv effective dose which was suggested by the ICRP as the maximum dose constraint in emergency situations for workers [27]. Li et al. [26] suggested an LOD of 1.1 × 10^{-3} Bq L^{-1} (i.e. 1.1 mBq L^{-1}) for ^{239}Pu was necessary in the emergency urine analysis. The LODs of ^{239}Pu of our method (0.036 mBq L^{-1} for 20 mL urine and 0.006 mBq L^{-1} for 100 mL urine samples) were much lower than that recommended by Li et al. [26], indicating our method would be useful in such emergency situations.

We summarized the typical LODs for ^{239}Pu, ^{240}Pu and ^{241}Pu for different methods in Table S1. In general, alpha spectrometry measurements are time-consuming. MDA (minimum detectable activity) of 0.8 mBq L^{-1} for ^{239}Pu was reported recently by Kumar et al. [28] with a 24-h counting time, which was more than 20 times lower than that of Dai et al. [29] with only a 4-h counting time. Methods employing ICP-MS result in lower LODs of ^{239}Pu than alpha spectrometry does for the same urine sample volume. For processing 1 L urine bioassay, 0.3 mBq L^{-1} and 0.021 mBq L^{-1} LODs of ^{239}Pu were realized by Kuwabara et al. [30] and Zoriy et al. [31] respectively. Some researchers have employed flow injection system or on-line separation chromatography to process raw urine without pretreatment. With the combination of an automated flow injection system and SF-ICP-MS, Larivière et al. [32] obtained good LODs for ^{239}Pu (0.21 mBq L^{-1}) and ^{240}Pu (0.19 mBq L^{-1}); however, in other cases, problems were sometimes encountered such as insufficient removal of matrix elements and deteriorated LOD despite of the advantage of the very short analytical time [14,33]. Recently Shi et al. [34] increased the sensitivity of SF-ICP-MS through concentrating the analytes into very small volume (300 μL) and using micro-flow injection technique. Although very low LODs of ^{239}Pu, ^{240}Pu and ^{241}Pu (equivalent to 0.046 mBq L^{-1}, 0.056 mBq L^{-1} and 19.8 mBq L^{-1}, respectively) were reached, the presence of ^{238}U higher than 30 pg in the initial urine would lead to distinct worse of LOD [34]. Some of these ^{239}Pu LODs meet the requirement for emergency urinary Pu analysis (1.1 mBq L^{-1}) as suggested by Li et al. [26], but the LODs of our method were consistently lower than them, indicating a greater potential for application in radiological incidents. The ^{239}Pu LODs are generally more than one order of magnitude lower for TIMS and AMS than for ICP-MS methods. For example, Elliot et al. [35] combined $Ca_3(PO_4)_2$ co-precipitation and ion exchange chromatography with TIMS measurement for 1.4 L urine samples. The LOD of this method was 0.00087 mBq L^{-1} for ^{239}Pu. A slightly lower ^{239}Pu LOD was achieved recently by Dai et al. [36] using high sensitivity AMS; meanwhile LODs of ^{240}Pu and ^{241}Pu which have been less referred in the literature were also reported in their work. Qiao et al. [37] innovatively combined a sequential injection system with AMS measurement for urinary Pu analysis based on the use of 1 L urine. They reported the ^{239}Pu LOD was 0.0069 mBq L^{-1} [37]. In contrast, by using SF-ICP-MS measurement, we obtained extremely low LODs of ^{239}Pu, ^{240}Pu and ^{241}Pu in small-volume urine bioassays. The LOD of ^{239}Pu, ^{240}Pu and ^{241}Pu were 0.006 mBq L^{-1}, 0.015 mBq L^{-1} and 9.8 mBq L^{-1}, respectively, for 100 mL urine sample volume. The ^{239}Pu LOD of our method was even slightly lower than that of Qiao et al. [37] although we employed a much smaller volume of urine. The corresponding absolute LODs of our method for ^{239}Pu, ^{240}Pu and ^{241}Pu were 0.0006 mBq, 0.0015 mBq and 0.98 mBq, calculated by multiplying the sample volume (L) with LODs (mBq L^{-1}). The absolute LODs of Dai et al. [36] were calculated to be 0.00087 mBq, 0.0034 mBq and 0.31 mBq respectively for ^{239}Pu, ^{240}Pu and ^{241}Pu using AMS analysis. Besides, the absolute detection limits for ^{239}Pu of Elliot et al. [35] and Qiao et al. [37] were 0.0012 mBq and 0.0069 mBq respectively. Considering the small urine sample volumes were used for our method, the absolute detection limits of our method were comparable or even better than those measured with TIMS and AMS. As large amount of Pu isotopes (8.3 × 10^{15} Bq of $^{239+240}$Pu, 7 × 10^{17} Bq of ^{241}Pu) remain in the damaged FDNPP reactors buildings, the proposed method would be a promising tool for rapid screening of unexpected occupational exposures of workers involved in the future FDNPP reactor decommissioning operations [38].

3.5. Trueness and precision of Pu measurements

A mixed Pu isotope standard solution (NBS-947) with a certified ^{240}Pu/^{239}Pu atom ratio of 0.242 was employed to evaluate the trueness and precision of our developed method. Due to the extremely low concentration (c.a. 0.4 fg L^{-1}) of Pu in normal urine, the urine samples used here were regarded as “blank” and all Pu was from the added NBS-947 [39]. Aliquots of NBS-947 containing 5.69 fg, 11.38 fg, 56.92 fg, and 113.83 fg ^{239}Pu were added respectively to individual 20 mL urine samples, resulting in final spiked ^{239}Pu concentrations of 0.285–5.692 fg mL^{-1}. Also, 11.38 fg of ^{239}Pu was added to a 100 mL urine sample to form a ^{239}Pu concentration of as low as 0.114 fg mL^{-1} in the 100 mL urine bioassay. Corresponding ^{240}Pu concentration in the spiked urine could be calculated according to the certified ^{240}Pu/^{239}Pu atom ratio.

Results on the trueness and precision of ^{239}Pu and ^{240}Pu concentrations measured with our method are summarized in Table 4. In general, the measured ^{239}Pu and ^{240}Pu concentrations corresponded very well with the calculated spiked concentrations. The trueness of the measured ^{239}Pu was from −1.81% to +0.57% over the concentration range of 0.114–5.692 fg mL^{-1}. Our method trueness was slightly better than that (2.5%) reported by Zoriy et al. [31] who used SF-ICP-MS for 10 repeated analyses of urine containing 100 fg mL^{-1} of Pu. The precision (RSD %) of our triplicate measurements of ^{239}Pu ranged from 1.01% to 2.77%. We also realized good trueness for ^{240}Pu measurement in the urine samples containing 0.028–1.383 fg mL^{-1} ^{240}Pu, which varied from −1.33% to +5.27% with precision better than 4.83%. These results illustrated that the present method is robust and reliable in accurate

Table 4
Trueness and precision of this method to determine ultra-trace level Pu in small-volume urine samples (spiked with NBS-947).

Group ID	Urine volume (mL)	^{239}Pu				^{240}Pu			
		Spiked (fg mL^{-1})	Measured (fg mL^{-1})	Trueness (%)	Precision (%)	Spiked (fg mL^{-1})	Measured (fg mL^{-1})	Trueness (%)	Precision (%)
1	100	0.114	0.114 ± 0.001(n = 3)	−0.01	1.05	0.028	0.028 ± 0.001(n = 3)	−0.15	4.53
2	20	0.285	0.280 ± 0.006(n = 3)	−1.56	2.27	0.069	0.073 ± 0.004(n = 3)	+5.27	4.83
3	20	0.569	0.559 ± 0.015(n = 3)	−1.81	2.77	0.138	0.133 ± 0.004(n = 3)	−3.68	3.08
4	20	2.846	2.862 ± 0.029(n = 3)	+0.57	1.01	0.692	0.696 ± 0.019(n = 3)	+0.68	2.78
5	20	5.692	5.610 ± 0.061(n = 3)	−1.44	1.08	1.383	1.365 ± 0.028(n = 3)	−1.33	2.04

determination of ultra-trace level Pu (down to 0.028 fg mL^{-1}) in small-volume urine bioassays.

The trueness and precision of the ^{240}Pu/^{239}Pu atom ratios obtained by our developed analytical method were evaluated with NBS-947 spiked urine samples containing different ^{239}Pu concentrations as introduced before. For each concentration 6 replicates were measured. The results are illustrated in Fig. 3. The mean determined ^{240}Pu/^{239}Pu atom ratio for the 30 samples was 0.247 ± 0.024 (k = 2) and the overall trueness and precision were 1.92% and 4.72% respectively, suggesting that the present method is capable of providing an accurate determination of ^{240}Pu/^{239}Pu in urine samples with sub-fg mL^{-1} levels of Pu. Besides, for 20 mL urine samples containing 0.285–5.692 fg mL^{-1} ^{239}Pu, the precision (RSD %, n = 6) decreased from 7.1% to 1.3% with the increase of ^{239}Pu concentration, and that suggested better precision was possible with higher ^{239}Pu concentrations. A compromised precision of 5.2% was also obtained for the 100 mL urine sample containing 0.11 fg mL^{-1} ^{239}Pu.

3.6. Analytical time and sample throughput

The whole analytical method takes 9.5 h and 11 h, respectively, to process 20 mL and 100 mL urine bioassays: 1 h and 2.5 h for acid digestion of 20 mL and 100 mL urine samples, respectively; 1 h for co-precipitation and Pu valence adjustment; 3 h for TEVA + UTEVA + DGA extraction chromatographic separation; 4 h for sample preparation; and 0.5 h for SF-ICP-MS measurement. With appropriate time arrangement, a batch of 10 samples can be analyzed within one day.

4. Conclusion

In this study we developed a rapid method for Pu isotopes (^{239}Pu, ^{240}Pu and ^{241}Pu) analysis in small-volume (20 mL and 100 mL) urine bioassays with SF-ICP-MS. Conditions that may influence the analytical performance were studied systematically. The use of $TiCl_3$ or sulfamic acid-ascorbic acid as reductants before CaF_2/LaF_3 co-precipitation showed no influence on the overall chemical recovery while the employment of $Al(NO_3)_3$ in dissolving CaF_2/LaF_3 resulted in lower ^{242}Pu recoveries than when it was not used. Decontamination factor of ^{238}U of 3.8×10^6 was achieved with this method. Regarding to specific requirements, TEVA + DGA could also be employed in place to provide a DF (U) of 1.1×10^4. ^{242}Pu recovery of this method was stable for 20 mL and 100 mL urine bioassays with an average of 72.7 ± 5.5%. The limit of detection (LOD) for ^{239}Pu, ^{240}Pu and ^{241}Pu of this method were 0.016 fg mL^{-1}, 0.016 fg mL^{-1} and 0.019 fg mL^{-1} for 20 mL urine and 0.003 fg mL^{-1}, 0.002 fg mL^{-1} and 0.003 fg mL^{-1} for 100 mL urine, respectively. Considering the small volume of urine employed in this study, the absolute detection limits of this method were comparable to those with AMS or TIMS in the literature. The trueness of ^{239}Pu and ^{240}Pu concentration was better than −1.81% and +5.27% for urine containing 0.114–5.692 fg mL^{-1} ^{239}Pu and 0.028–1.383 fg mL^{-1} ^{240}Pu. In contrast the trueness and precision of ^{240}Pu/^{239}Pu atom ratio were 1.92% and 4.72% respectively over the above concentration range. The fast analytical procedure and high sample throughput together with the considerably low LODs of Pu isotopes make this method a promising tool for quick response during radiological emergencies as well as for rapid

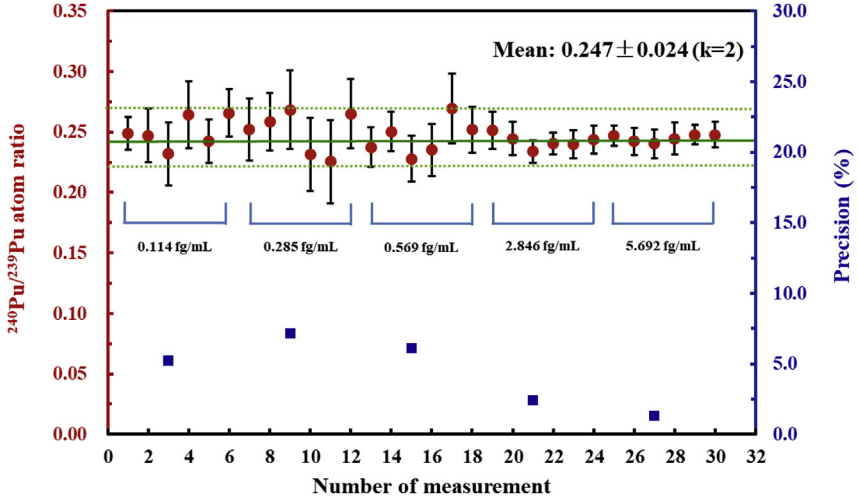

Fig. 3. Measured ^{240}Pu/^{239}Pu atom ratio in urine samples containing different concentrations of ^{239}Pu. The error bars represent the standard deviation of each measurement. The olive green solid line represents the certified ^{240}Pu/^{239}Pu atom ratio of NBS-947 (0.242). The green dashed lines represent the expanded uncertainties (k = 2) for all analyses. The violet squares represent the within-run precision (RSD%, n = 6) of ^{240}Pu/^{239}Pu atom ratio at different ^{239}Pu concentration levels. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

screening of unexpected exposures among occupational population; the latter would be especially important to ensure the health of workers involved in reactor decommissioning operations in the FDNPP.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.aca.2017.10.012.

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