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Articles

Urinary bioassay for the measurement of actinides by alpha spectrometry for rapid response after radiation emergency

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In response to an internal contamination accident of five workers at a plutonium (Pu) fuel research facility of Japan Atomic Energy Agency's Oarai Research and Development Center in 2017, different sample pretreatment and chromatographic purification techniques were compared to obtain a feasible and rapid method to measure U, Pu, and Am in urine samples. The combination of complete organic matter decomposition, iron hydroxide co-precipitation, and chromatographic separation/ purification using the TEVA and DGA resin cartridges followed by anion exchange Dowex 1x8 resin column was selected prior to one day counting using alpha spectrometer. This urinary bioassay demonstrated stable and high (~ 80%) yields, and low detection limit (approximately 0.5 mBq using 500 mL urine sample) for U, Pu, and Am. The turnaround time of 38.5 h allows us to perform urgent response to a radiological/nuclear emergency. The proposed method was finally validated in the international comparison program (PROCORAD 2018), with satisfactory results for U, Pu, and Am analysis with all |Z-score| ≤2.

Keywords: *Internal contamination accident; Urinary bioassay; Actinides; Alpha spectrometry; PROCORAD 2018.*

1. Introduction

A Pu/Am internal radiation exposure accident occurred on June 6th, 2017 in Japan, in which five workers inhaled airborne Pu/Am when inspecting nuclear fuel materials at a nuclear research facility in Oarai of the Japan Atomic Energy Agency (hereafter, we call this the Oarai accident).[1] For an adult, the inhalation dose coefficients applied in the case of internal intake are much higher for alpha emitters than that for other radiation emissions: e.g., $(1.6–12) \times 10^{-5}$ Sv Bq^{-1} for ^{239}Pu or ^{240}Pu, and $(1.6–9.6) \times 10^{-5}$ Sv Bq^{-1} for ^{241}Am versus $(4.6–39) \times 10^{-9}$ Sv Bq^{-1} for ^{137}Cs (β^- and γ).[2] Therefore, internal contamination with alpha-particle emitters, such as ^{239}Pu, ^{240}Pu, ^{241}Am, is likely to bring a large radiation exposure dose to the tissues of persons even if the intake amount is small. It is thus of great importance to timely evaluate the order of magnitude of the dose to the person(s) of concern in order to provide necessary information for decision-making in radiation emergency medicine.

As the "core advanced radiation emergency medical support center" designated by the Nuclear Regulation Authority, Japan, it is one of our missions to accommodate, conduct dose assessment and medical treatment, and implement long-term monitoring for the patients accidentally exposed and/or contaminated, such as the case of the Oarai accident.[1,3] In terms of internal contamination by α particles (e.g. ^{238}U, ^{239}Pu, ^{241}Am), it would be challenging to use external monitoring techniques (e.g. whole-body counter, lung counter) to confirm low internal contamination level, since α particles will be blocked by our body.[4] In that case, rapid bioassay of urinary and fecal samples should be considered for precise dose assessment.[5-7] Although the mass spectrometric methods present advantage on the rapid measurement, it is more sensitive to measure short-lived radionuclides with high specific activities by radiometric spectrometry and presently it is of great challenge to measure ^{238}Pu using mass spectrometric methods due to the isobaric interference of ^{238}U.[8] As conventional technique, alpha spectrometric techniques are widely used for the measurement of actinides in bioassay samples.[5,9-12] However, the significant disadvantage of actinide bioassay using alpha spectrometry is that it is a significantly labor-intensive and time-consuming work.[13] Therefore, it is critical to develop rapid actinide bioassay using alpha spectrometry for emergent response after a radiological/nuclear accident.[9,12]

This work aims to develop a rapid actinide bioassay using alpha spectrometry in urine with high yield for emergent response in case of internal contamination accidents occurred in nuclear fuel-related facilities. First, we investigated the sample pretreatment of actinides in urine by wet ash and dry ash followed by calcium phosphate co-precipitation and iron hydroxide co-precipitation; and then, optimized the purification/separation procedure applicable to the measurement of actinides in urine samples, for shortening the total turnaround time. We finally validated the performance of the optimized procedure in an international inter-comparison program for bioassay analyses, the 2018 PROCORAD (Association for the PROmotion of Quality Control in RADiotoxicological Analysis) exercise.

2. Experimental

2.1. Materials and Reagents. Analytical grade reagents including HNO_3 (65%), HCl (35%), H_3PO_4 (85%), H_2O_2 (30–35%), $HClO_4$ (70%), NH_4I, $NaNO_2$, NH_4Cl, $CaCl_2$, $FeCl_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, sulfamic acid, ascorbic acid, oxalic acid, and ammonium oxalate monohydrate were purchased from Fujifilm Wako Pure Chemical Corporation (Osaka, Japan). Ammonium hydroxide (28–30%) was purchased from Kanto Chemicals (Tokyo, Japan). All the required solutions were prepared with Milli-Q water (18.2 MΩ·cm). The extraction resins of TEVA and DGA-N in 2 mL cartridges were all obtained

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from Eichrom Technologies (50–100 μm, Lyle, IL, USA). Anion exchange resins employed were Dowex^{TM} 1X8 (100–200 mesh, Cl^- form) obtained from Fujifilm Wako Pure Chemical Corporation (Osaka, Japan) and AG® 1-X4 (50–100 mesh, Cl^- form) obtained from Bio-Rad (Hercules, CA, USA). The ^{242}Pu (SRM 4334i) and ^{232}U (SRM 4324b) both obtained from the National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA), and ^{243}Am (1577–9) obtained from Eckert & Ziegler Isotope Products (Valencia, CA, USA), were diluted to approximately 80 mBq/mL and used for the measurements as yield tracers. Microwave digestion and dry ash for urine samples were performed using Discover® SP-D microwave digestion system and microwave muffle furnace of Phoenix, respectively (CEM Corporation, Matthews, NC, USA).

2.2. Procedure of alpha spectrometric analysis. As shown in Figure 1, after spiking approx. 40 mBq of ^{242}Pu, ^{243}Am, and ^{232}U into each 500-mL urine sample as yield tracers, 100 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2 were added to the urine sample, followed by wet ash at 300°C until dryness. The residue added with 10 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2 was then heated to dryness at 300°C. This process was performed more than one time as necessary to obtain completely white residue. The remaining residue was dissolved in 20 mL of 8 M HNO_3 and then diluted to 350 mL with Milli-Q water. After adding 150 mg sulfamic acid, the solution was heated to boiling for 5 min and then cooled for 5 min. After that, iron hydroxide co-precipitation was processed by adding 1 g of NH_4Cl and 20 mg of Fe^{3+}, followed by pH adjustment to ~9.0 with concentrated $NH_3{\cdot}H_2O$. After aging for 1 h and then centrifugation at 3,000 rpm for 15 min, the precipitate was dissolved in 15 mL of 8 M HNO_3 followed by the addition of 5 mL of 1 M $Al(NO_3)_3$-8 M HNO_3 to minimize the influence of phosphate naturally existing in urine for the next extraction chromatographic separation process.[9] After adding 70 mg of sulfamic acid with stirring at 40°C for 5 min, the valence adjustments of Fe to Fe(II) and Pu to Pu (III) were performed by adding 300 mg of ascorbic acid with stirring at 40°C for 5 min, and Pu to Pu(IV) by adding 500 mg of $NaNO_2$ with stirring at 80°C for 30 min.[9] The valence adjustment of Pu to Pu(IV) was then performed again by adding 500 mg $NaNO_2$ with stirring at 80°C for 10 min. The sample solution was then passed through a 0.45-μm membrane filter prior to chromatographic separation/purification with stacked TEVA and DGA resin cartridges. After the sample solution was loaded, the resin cartridges were rinsed with 25 mL of 8 M HNO_3. At this stage, Th and Pu were retained in the TEVA resin, whereas U and Am were retained in the DGA resin. After the stacked TEVA and DGA cartridges were split, Pu was eluted with 45 mL of 0.1 M NH_4I-8 M HCl from the TEVA cartridge, after Th removal with rising 40 mL of 9.5 M HCl. In addition, U and Am in the DGA resin were separately eluted by 30 mL of 0.2 M HNO_3 and 30 mL of 0.01 M HCl, respectively. The U fraction was further evaporated to dryness and dissolved in 10 mL of 0.5 M HCl. It was then loaded onto a 4-mL Dowex 1X8 resin column to remove trace ^{210}Po naturally existing in urine. Finally, U was collected with the combination of drain solution of loading and elution solution using 30 mL of 0.5 M HCl.

After the above separation procedures, the solutions of each element fraction (Pu, Am, and U) were evaporated, and the decomposition of the residual organic matters mainly from resin was achieved using wet ash with 2 mL of concentrated HNO_3 and 0.2 mL of concentrated $HClO_4$. After redissolving the residual in 10 mL 0.9 M H_2SO_4 by heating to boiling, pH was adjusted into the range of 1.2–2.8 by a buffer system of 0.9 M H_2SO_4 and 15% ammonia solution with Thymol blue indicator. Next, electrodeposition (1.0 A, 2 h) was performed to prepare samples for alpha spectrometry with the use of a

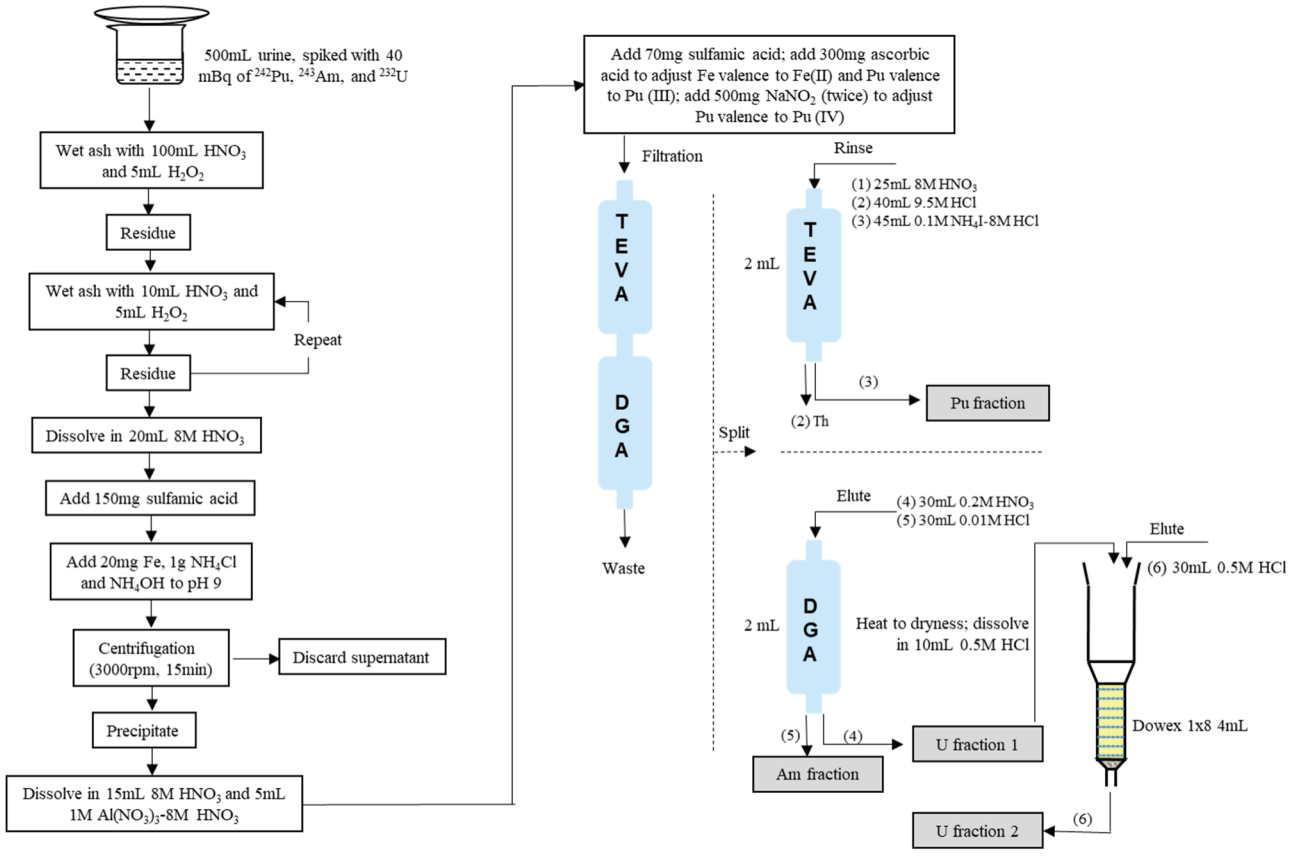

Figure 1. Rapid bioassay method for the measurement of actinides in urine samples by alpha spectrometry.

TABLE 1: The recoveries of U, Pu, and Am in urine measured by alpha spectrometry after different digestion processes and the required time of different pretreatment and separation/purification processes.

Digestion	Recovery (%)			Required time
	^{242}Pu	^{243}Am	^{232}U	
a) Fast digestion	53±27 (n=7)	66±16 (n=7)	58±6 (n=7)	7.5 h
b) One-time wet ash	77±5 (n=31)	75±8 (n=31)	73±9 (n=6)	9.0 h
c) Three-time wet ash	77±7 (n=31)	78±5 (n=31)	79±5 (n=17)	10.5 h

spectrometer (Ensemble 8, ORTEC, Oak Ridge, TN, USA) with Si detectors with an active area of 450 mm^2 (AMETEK, Oak Ridge, TN, USA). The counting time for each electrodeposited sample was normally set at 86,400 s (1 day); however, it could be shortened depending on the radioactivity in urine samples.

3. Results and discussion

Prior to chromatographic purification/separation, it is critical to decompose the organic matter and remove matrix as much as possible to avoid the influence of separation efficiency of radionuclides.[14-17] In the present study, we investigated and compared the recovery yields and required times of different sample pretreatments, chromatographic separation/purifications for the determination of actinides in urine in order to select the optimal procedure for the rapid emergency bioassay program.

3.1. Sample pretreatment. Figure S1 presents the comparison of the sample pretreatment methods tested in this study. Calcium phosphate and iron hydroxide were used as the co-precipitation reagents (Figure S1, b-d). Details on each method are described below.

As shown in Figure S1a, urine samples were evaporated to dryness at 300°C, after adding 100 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2.[13] Digestion was performed by repeatedly adding 20 mL of concentrated HNO_3 for complete decomposition of organic matters until only white residue was left. This residue was then dissolved by 35 mL of 8 M HNO_3 and allowed to stay overnight to precipitate extra minerals, which were then removed using MF^{TM} Membrane Filters with a 0.45μm pore size (Merk Millipore Ltd., Irland).

In terms of the calcium phosphate precipitation methods (Figure S1, b and c), after adding 100 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2, the urine sample was evaporated at 300°C until the volume was reduced to approximately 200 mL. To obtain calcium phosphate precipitation, 160 mg of Ca^{2+} and 125 μL of concentrated H_3PO_4 were then added to the urine sample followed with pH adjustment by concentrated $NH_3{\cdot}H_2O$ (pH 9–10). After centrifugation (3000 rpm, 30 min), the precipitate was kept for subsequent procedure. The following procedures were different between the methods b and c. In the method b, the produced precipitate was processed through two times' wet ash by adding 10 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2, and then the residue was dry ashed (at 150°C for 30 min, 300°C for 60 min, and 450°C for 120 min). In the method c, additional microwave digestion was performed after dissolving the precipitate with 17 mL of concentrated HNO_3. After evaporation of the digested solution in a beaker, wet ash was performed twice in the same manner as the method b. The well decomposed urine samples (left as white residues) from these two methods were dissolved by 20 mL of 8M HCl prepared for the subsequent separation procedure.

In terms of the iron hydroxide co-precipitation method (Figure 1d), details were described in the section 2.2.

Table S1 summarizes the required time for each pretreatment method prior to chromatographic purification/purification (Figure S1). As shown, the time of 18 h for the calcium phosphate precipitation method (Figure S1b) was much shorter than that for the presently recommended method (28 h) (Figure S1a). The former method could be further shortened to 9 h by applying microwave digestion (Figure S1c). The fastest method was found to be the iron hydroxide co-precipitation method requiring only about 7 h (Figure S1d). The iron hydroxide co-precipitation method (Figure S1d) has an advantage over the third method (Figure S1c) which requires additional sample transfer for the microwave digestion procedure. With the advantage of less time consumed and much easier operation, the pretreatment using iron hydroxide co-precipitation was thus selected as the optimal technique for the matrix removal after organic matter decomposition and prior to chromatographic separation/purification.

Prior to co-precipitation for preconcentration of actinides, it is also of importance to decompose organics naturally exiting in human urine.[15] In the present study, we attempted to examine whether further speed-up could be achieved by rough digestion, as shown in Figure S2. Table 1 provides a comparison of the performance among the fast digestion without wet ash, the one-time wet ash, and the three-time wet ash. The one-time wet ash resulted in large amount of carbonized residues (Figure S3a), and the two-time wet ash resulted in less carbonized residues (Figure S3b). After the three-time wet ash, the white residues indicated complete organic matter decomposition (Figure S3c). In addition, the fast digestion showed lower and unstable yields compared to other two methods, although the turnaround time was shortened by 3 h and the operations were easier (Table 1). The one-time wet ash had a small advantage only on the required time over the three-time wet ash. Complete decomposition of organic matters was also beneficial to avoid low flow rate even clogging during the chromatographic separation/purification step. Therefore, the three-time wet ash was considered to be the best way for complete organic matter decomposition prior to the iron hydroxide co-precipitation (Figure S1d).

3.2. Chromatographic separation/purification procedures. Several chromatographic separation/purification methods for U, Pu, and Am were tested in this study using extraction chromatography resins and anion exchange resins (Figure S4). Figure S4a shows the presently recommended separation method using anion exchange resins in Japan,[13] whereas Figure S4b and S4c show the rapid separation methods using extraction chromatography resins and/or anion exchange resins. A flow rate was adjusted to be 1–2 mL/min for all separation processes in these methods. Details on each method are described below.

In terms of the presently recommended separation method (Figure S4a), 500 mg of $NaNO_2$ was added to adjust Pu valence to Pu(IV) prior to separation/purification with 7 mL of AG 1-X4 resin column. The drain solution of loading and elution solution with extra rinse with 80 mL of 8 M HNO_3 were then collected for the following Am and U separation

processes. After that, Th (trapped by the resins together with Pu) was removed by washing with 60 mL of 8M HCl.[18] After that, Pu was eluted with 50 mL of 0.1 M NH_4I-8 M HCl solution from the resin. The Am and U fraction was evaporated to dryness, and dissolved in 30 mL of 8M HCl solution. The filtration was also conducted if there were precipitates for the subsequent processes. Subsequently, the sample solution was then loaded onto 7 mL of Dowex 1X8 resin column. The drain solution of loading and elution solution with 50 mL of 8M HCl, were then used for the following Am separation processes. After that, U trapped in the resin was eluted with 50 mL of 0.2 M HNO_3. The Am fraction was then evaporated to dryness and dissolved by 50 mL of 8 M HNO_3. After dilution with milli-Q water to a volume of 300 mL, co-precipitation was performed by adding 10 g of oxalic acid, 10 g of ammonium oxalate monohydrate, and 500 mg of Ca^{2+} followed by pH adjustment using concentrated $NH_3{\cdot}H_2O$ (to pH 1.8). The produced precipitate was filtered with membrane filter paper with a pore size of 3 μm and the precipitate was further processed for dry ash in a furnace with increasing temperature (at 150°C for 30 min, 450°C for 60 min and 600°C for 360 min). The residual was dissolved by 30 mL of 8 M HCl and then diluted to 200 mL with milli-Q water. Followed by adding 20 mg of Fe^{3+} and 1 g of NH_4Cl, the iron hydroxide co-precipitation was performed through the pH adjustment (pH ~9) using concentrated $NH_3{\cdot}H_2O$. After aging for 1 h and then centrifugation at 3,000 rpm for 15 min, the precipitate was then dissolved in 20 mL of 8 M HCl and loaded onto 7 mL of Dowex 1X8 resin column to remove iron. The combination of drain solution from the loading and elution solution with the rinse of additional 50 mL of 8 M HCl were then evaporated to dryness and dissolved by 20 mL of 8 M HNO_3, followed by loading onto another 7 mL of Dowex 1X8 resin column to remove any interfering isotopes such as ^{210}Po. Finally, Am was collected with the drain solution of loading and elution solution with 50 mL of 8 M HNO_3. The final fractions (containing Am, Pu, and U, respectively) were used for the following process for alpha source preparation.

In the first rapid separation/purification method (Figure S4b), the anion exchange Dowex 1x8 resin column and the extraction DGA resin cartridge were used. Pu in the pretreated sample solution was adjusted to Pu(IV) by adding 500 mg of $NaNO_2$, and the solution was loaded onto 7 mL of Dowex 1x8 resin column. The drain solution from the loading and elution solution with the rinse of 50 mL of 8 M HCl were collected for the following Am separation processes. Subsequently, the U fraction was eluted by using 50 mL of 0.5 M HNO_3, following eluting the Pu fraction by using 50 mL of 0.1 M NH_4I- 8 M HCl. The Am fraction was evaporated to approximately 5 mL and dissolved in 20 mL of 8 M HCl, then loaded onto 2 mL of DGA resin column. After rinse with 25 mL of 8 M HCl, Am was eluted by 35 mL of 0.01 M HCl.

In terms of the second rapid separation/purification method (Figure S4c) using the stacked TEVA and DGA resin cartridges combined with anion exchange Dowex 1x8 resin column for the separation of U, Pu and Am, details were described in the section 2.2.

Table S2 summarizes the required time for each chromatographic separation method (Figure S4). The presently recommended method (Figure S4a) required more than 1 day (37 h), whereas the rapid separation/purification method using anion-exchange and DGA resin columns significantly shortened the required time to 6.5 h (Figure S4b). Using the stacked TEVA and DGA resin cartridges followed by anion exchange Dowex 1x8 resin column enabled to further shorten the required time to 3.5 h (Figure S4c).

With the combination of three-time wet ash, iron hydroxide co-precipitation, and separation/purification using stacked TEVA and DGA resin cartridges followed by anion exchange Dowex 1x8 resin column, stable and sufficient chemical yields (nearly 80%) for U, Pu and Am could be obtained, as shown in Table 1. Based on the above results, we considered that this combination, as shown in Figure 1, was the best bioassay method available at our laboratory for the rapid measurement of actinides in urine using alpha spectrometry in emergency situations. This method was characterized by low detection limits of approximately 0.5 mBq for U, Pu, and Am analysis in 500 mL urine, in the case of a counting time of 86,400 s by alpha spectrometry. The required time for the pretreatment and separation/purification (Pu, Am and U) was 10.5 h in total, and 14.5 h including the sample preparation of electrodeposition for alpha spectrometric analys

3.3. Method validation and application. Finally, the developed actinide bioassay was validated by participating 2018 PROCORAD international comparison, and our results are demonstrated in Table 2 (actinides in urine) and Table 3 (U in urine). This exercise offers various test samples containing various radionuclides, such as actinides, and participants can select samples that one wants to test.

Exploitation of results and performance evaluation are conducted in accordance with ISO standard 13528 and IUPAC 2006.[19,20] In the PROCORAD program, the performance index of Z-score was used to check the performance of the laboratories if the number of participants were ≥ 7, and the equation was listed as follows:

TABLE 2: Actinide results in urine during 2018 PROCORAD program.

Sample	Recovery (%)	Isotope	Concentration (mBq/sample)	Assigned value (mBq/sample)	Z-score	Bias (%)
	76±6	^{238}Pu	2.07±0.71	2.23±0.13	-0.5	-7
18ACTUA	76±6	^{239}Pu	1.93±0.67	2.24±0.13	-1.0	-14
	79±7	^{241}Am	ND	ND		
	76±6	^{238}Pu	4.70±0.11	4.96±0.23	-0.4	-5
18ACTUB	76±6	^{239}Pu	5.01±1.09	4.98±0.23	0.0	1
	85±8	^{241}Am	9.38±1.50	8.82±0.42	0.4	6
	73±6	^{238}Pu	ND	ND		
18ACTUC	73±6	^{239}Pu	ND	ND		
	85±8	^{241}Am	ND	ND		

ND: not detected.

TABLE 3: Uranium results in urine during 2018 PROCORAD program.

Sample	Recovery (%)	Isotope	Concentration (mBq/sample)	Assigned value (mBq/sample)	Z-score	Bias (%)
18UA	87±7	^{234}U	140±13	143±11	-0.2	-2
		^{235}U	6.71±1.62	6.87±0.54	-0.1	-2
		^{238}U	147±13	142±9	0.4	4
18UB	82±6	^{234}U	35.2±4.3	37.1±3.7	-0.5	-5
		^{235}U	1.22±0.64	1.81±0.18	-1.9	-33
		^{238}U	39.5±4.7	36.7±3.3	1.0	8
18UC	76±6	^{234}U	584±48	527±18	1.4	11
		^{235}U	11.8±2.3	12.6±1.4	-0.3	-6
		^{238}U	ND	2.92±2.17		

ND: not detected.

$$Z\text{-score} = \frac{X_{lab} - X}{S^*} \quad (1)$$

where X_{lab} is the laboratory's result; X is the assigned value; S* is the robust standard deviation calculated from the results of participants. |Z-score| ≤2 indicates satisfactory performance; 2< |Z-score| ≤3 indicates questionable result with warning; |Z-score| >3 indicates unsatisfactory performance, requiring corrective action.

In the 2018 exercise, we obtained satisfied results with all |Z-score| ≤2, as shown in Table 2 and Table 3. In terms of bias (Bias = $\frac{X_{lab} - X}{X}$), all data were within the relative bias of 15% for all tested items excluding ^{235}U (-33% compared to the assigned values) in the 18UB and ^{238}U (not be detected) in the 18UC. The relatively large discrepancy for ^{235}U in the 18UB was turned out to be due to a miscalculation of the overlapped peak affected by the peak tailing from ^{234}U. The recalculation improved the result for ^{235}U (only -6% bias). In terms of the ^{238}U in the 18UC, even the assigned value was 2.92±2.17 mBq/sample (500 mL/sample), with a relative standard deviation of 74%. The ^{238}U assigned value in the 18UC was corresponding to be 0.469±0.349 μg L^{-1}, which were in the range of those in the occupationally unexposed persons (0.0008−3.70 μg L^{-1}).[21] All these results mentioned above indicated that the developed urinary bioassay method could be applied to the actinide measurement in urine.

4. Conclusions

A new rapid bioassay method to determine actinides in urine samples using alpha spectrometry was developed in this work. By performing acid digestion and iron hydroxide co-precipitation, 28 h process time for the pretreatment of urine samples in the presently recommended method was reduced to 7 h. In the chromatographic separation/purification process, by optimizing the use of extraction resin cartridges followed by anion exchange resin column, the required time was reduced to 3.5 h compared to the presently recommended method which took 37 h. The whole turnaround time for this new method, including alpha source preparation process (about 4 h) and measurement time (24 h), was approximately 38.5 h. The significant reductions in time required allow us to provide timely information for decision-making in radiation emergency medicine. The average recoveries of Pu, Am and U were approximately 80% and the detection limit was approximately 0.5 mBq using 500 mL urine sample with a counting time of 86,400 s. The application of the new rapid bioassay method demonstrated satisfactory performance in the international comparison program (PROCORAD 2018).

5. Conflict of interest

The authors declare that they have no conflict of interest.

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Supporting Information

TABLE S1. The required times of the pretreatments for urine samples.

Pretreatment	Required time
a) Presently recommended method	28 h
b) Calcium phosphate co-precipitation	18 h
c) Calcium phosphate co-precipitation with microwave digestion	9 h
d) Iron hydroxide co-precipitation	7 h

TABLE S2. The required times for the chromatographic purification/separation of U, Pu, and Am in urine.

Chromatographic purification	Required time
a) Presently recommended method	37 h
b) Anion exchange resin column and DGA-N resin cartridge	6.5 h
c) TEVA and DGA-N resin cartridge, and Dowex 1X8 column	3.5 h

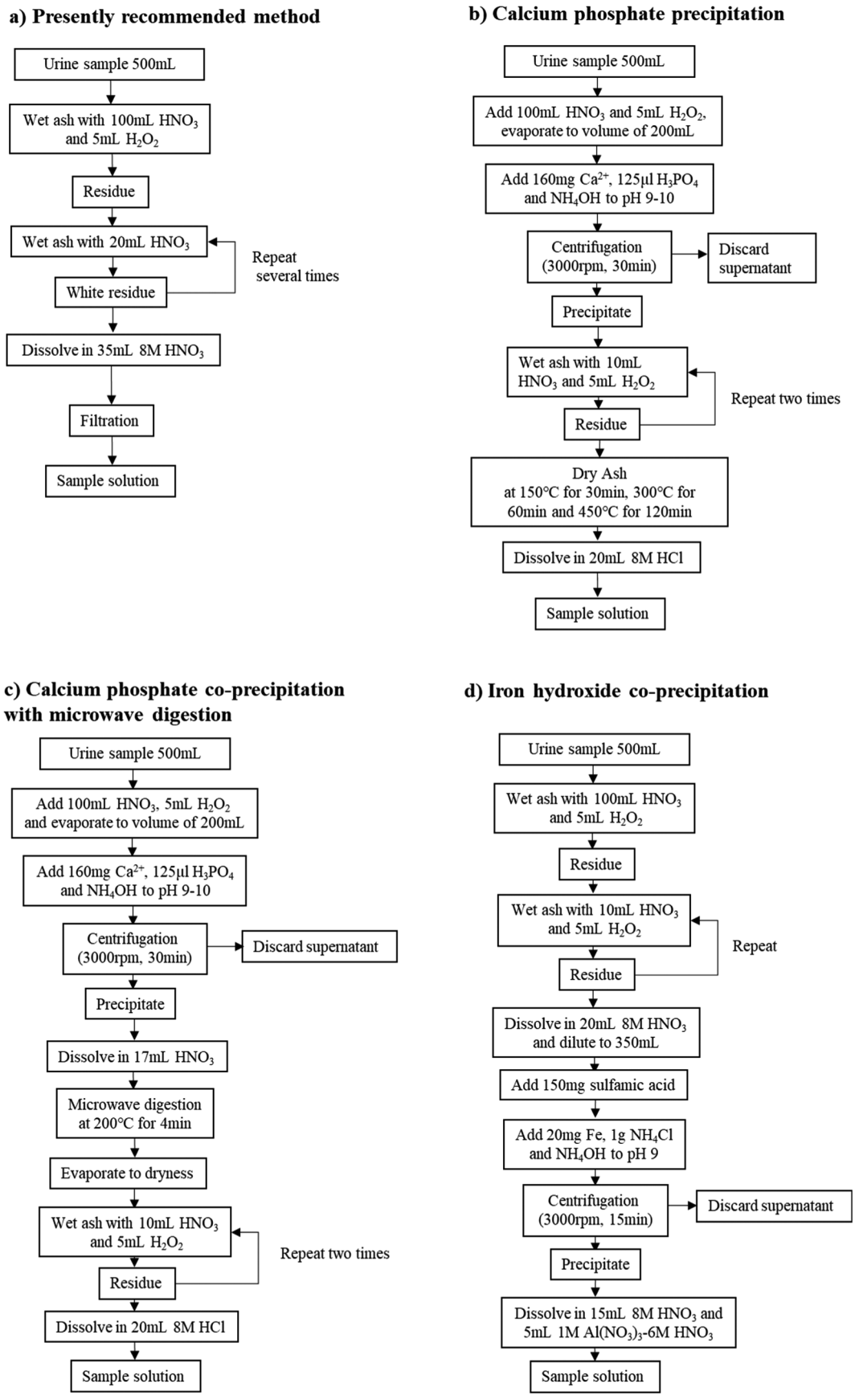

Figure S1. Comparison of the digestion methods for the measurement of actinides in urine samples.

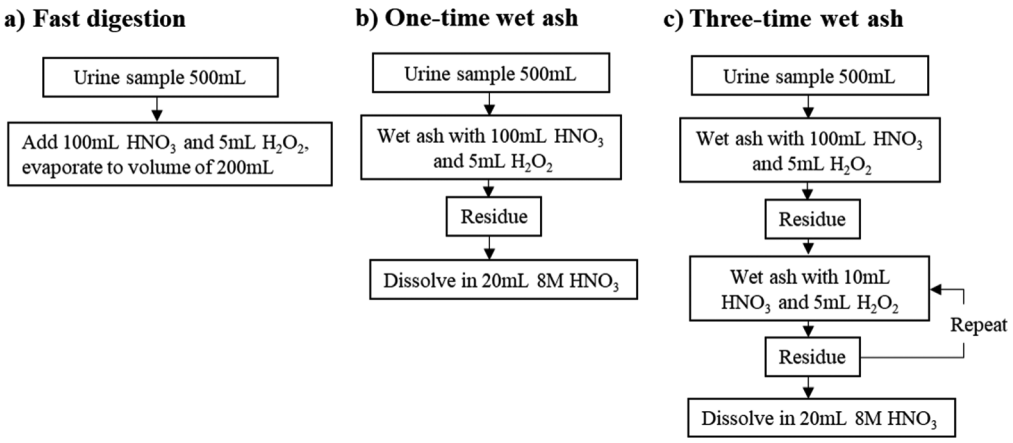

Figure S2. Comparison of the digestion methods for the measurement of actinides in urine samples.

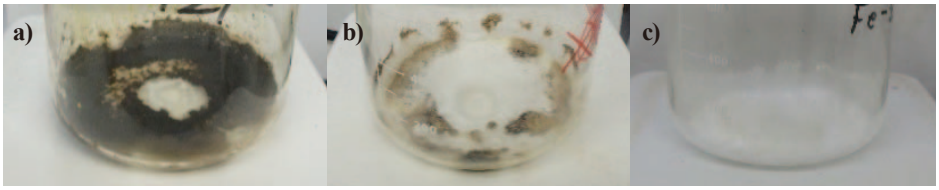

Figure S3. a), b): Urine samples with carbonized residues, c): Urine sample with complete organic matter decomposition.

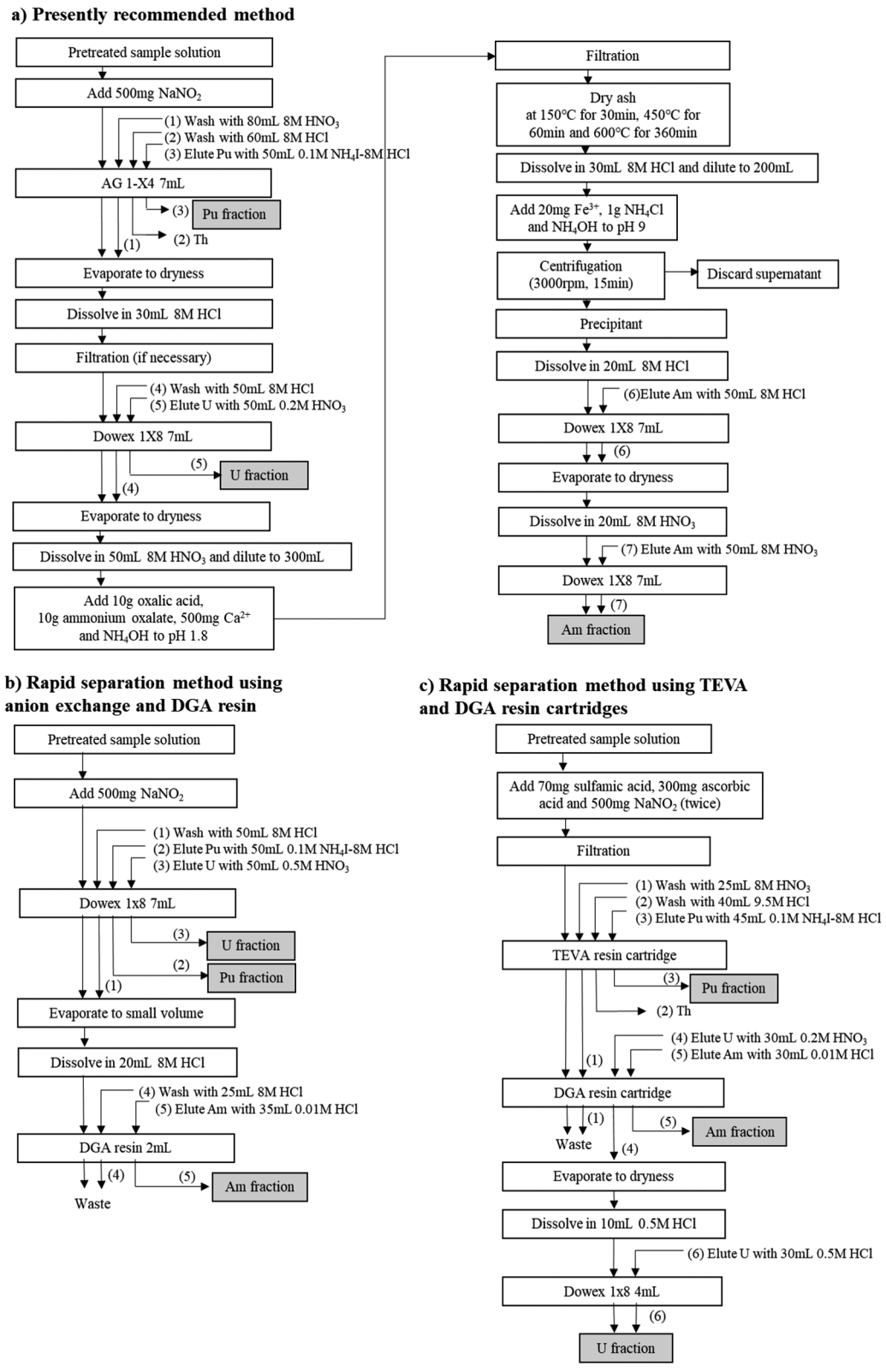

Figure S4. Comparison of chromatographic purification/separations for the measurement of actinides in urine samples.