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Rapid analysis for plutonium-239 in 1 ml of urine by magnetic sector inductively coupled plasma mass spectrometry with a desolvating introduction system

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The Centers for Disease Control and Prevention has a mission to protect and promote public health, which includes investigation of environmental exposures to toxic substances that could threaten health. Plutonium is an environmentally available substance that is chemically and radiologically toxic and represents a potential health threat from excessive exposure. Inductively coupled plasma mass spectrometry (ICP-MS) is a sensitive method for assessing environmental or unintentional exposure to these and other actinides. We report here a magnetic sector instrument method in which a desolvating introduction system is used to provide rapid, sensitive emergency response analysis for ^{239}Pu in only 1 mL of urine without digestion or coprecipitation. ^{239}Pu was separated from U and interfering urine organic substances by solid phase extraction. The within run limit of detection (LOD) was 0.16 fg mL^{-1} for 1 mL of urine even though originally spiked to 1018 ng L^{-1} of depleted U. A more rigorous LOD of 1.4 fg mL^{-1} ^{239}Pu was based on 3 "total" standard deviations in the presence of the same U concentration. At below 10^6 atoms of ^{239}Pu detectable in 1 mL of urine, this method is sufficiently sensitive for elevated emergency exposure assessment with high throughput. The precision for 10 duplicate samples was within 3.7% relative "total" standard deviation (RSD, within and between run) for a 9.96 fg mL^{-1} ^{239}Pu-spiked urine sample and within 2.2% for a 99.6 fg mL^{-1} ^{239}Pu-spiked urine sample. The method was demonstrated to be accurate within 2.6% of the Los Alamos National Laboratories target value at 99.6 fg mL^{-1}, to within 1.0% of target value at 9.96 fg mL^{-1} and within 1.2% at 0.996 fg mL^{-1}, just below the method LOD.

Introduction

Thorium (Th), uranium (U), and plutonium (Pu) are chemically and radiologically toxic and environmentally available natural and man-made substances that represent potential health threats from excessive exposure. Among these actinides, Pu alone is considered to be more radiologically than chemically toxic.[1] Methods to determine above average exposure to Pu are thus within the public health mission of the Centers for Disease Control and Prevention (CDC).

Quantitative analysis of Pu excreted in urine is a non-invasive way to assess levels of exposure to this toxic element. Assessment of exposure by thermal ionization mass spectrometry (TIMS),[2,3] accelerator mass spectrometry (AMS),[4,5] and resonance ionization mass spectrometry (RIMS)[5] have been established as very sensitive, faster throughput, and complimentary alternatives to alpha spectrometry for the bioassay of nuclear workers. Instrumentation for these methods is, however, not widely available. A number of quadrupole inductively coupled plasma mass spectrometry (ICP-MS) methods for the bioassay of Pu in urine have been published.[6–8] These methods have allowed further sample throughput increases with liquid introduction capabilities, although with less resolution and sensitivity than available from magnetic sector instruments.

Because of our environmental health mission, our need to measure urine Pu differs from the occupational exposure assessment goals of most laboratories. We seek to obtain reliable results with the best sensitivity possible, as would be the goal for bioassay analyses. However, higher sample throughput with smaller urine volumes than is typical for bioassay analyses is necessary to address and respond to public health emergencies such as the 2000 Cerro Grande fire, which invaded the grounds adjacent to Los Alamos National Laboratory (LANL), or to other accidental exposures to Pu. To accomplish this, it is not necessary to characterize the normal population urine ^{239}Pu levels that have been reported as approximately 10^6 atoms or 0.4 fg L^{-1} ^{239}Pu in a typical 24-hr urine.[9]

Most of the methods cited above involve time consuming sample digestions or coprecipitations as components of multi-step sample preparations. We have previously reported using a magnetic sector ICP-MS instrument for a sensitive, rapid ^{239}Pu assay requiring only 10–20 mL of urine. We achieved additional signal enhancement by using a desolvation system.[10] This method addressed the need for detecting ^{239}Pu in the urine of exposed persons, as well as eliminating urine polyatomic interference problems[10,11] by means of oxidative digestion and a desolvating introduction system. Despite decreases in $^{238}U^{1}H$ resulting from use of the desolvating introduction system, this method required a preliminary analysis for ^{238}U to assure that the urine uranium concentration was less than 20 ng L^{-1} to avoid ^{238}U peak tailing or minor $^{238}U^{1}H$ formation sufficient to significantly interfere with accurate ^{239}Pu determination.

The method reported here eliminates microwave digestion and requires only 1 mL of urine with sample preparation in one container. Separation of ^{238}U from ^{239}Pu, salt, and elimination of organic interferences[11,12] in one step eliminated the requirement for preliminary analysis of ^{238}U. In comparative terms, the limit of detection (LOD) reported for the method sample volume is comparable on a per mL basis to the measurement of normal population levels in 24 hour urine volumes for sub-femtogram to femtogram amounts of ^{239}Pu, as measured by the other established techniques described above.

Experimental

Materials and reagents

Fisher Optima nitric acid (Suwanee, GA, USA) was manufactured by Seastar Chemicals, Sidney, BC, Canada. Double

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distilled hydrofluoric acid was obtained from GFS Chemicals (Powell, OH, USA). An aqueous standard for calibration of ^{239}Pu (0.996 ± 0.0498 μg L^{-1}) and an aqueous internal and recovery standard, ^{242}Pu (0.963 ± 0.0008 μg L^{-1}) were obtained from Los Alamos National Laboratories (LANL). Depleted uranium (CRM CLU2) and iridium (CRM PLIR3) were obtained from SPEX Certiprep (Metuchen, NJ, USA). Iron(II) sulfate hydrate (99.999%) and sodium nitrite (99.99%) were obtained from Sigma–Aldrich Chemical Company (St. Louis, MO, USA). Water was polished to 18 MΩ cm^{-1} with a Milli-Q Academic system (Millipore Corp., Milford, MA, USA). Liquid argon was obtained from Matheson Gas Company (Secaucus, NJ, USA) and was "high purity" grade (99.999+ %). Falcon polypropylene centrifuge tube sample containers were obtained from Lab Depot (Alpharetta, GA, USA). TEVA resin (100–150 μm particle size) was obtained from Eichrom Technologies (Darien, IL, USA). Conical-bottomed 2 mL polystyrene sample cups were obtained from VWR (Atlanta, GA, USA).

Instrumentation

The ThermoFinnigan Element 2 ICP-MS (Thermo Finnigan MAT GmbH, Bremen, Germany) with software version 2.23 was equipped with an ASX 100 autosampler and Aridus desolvating introduction system (CETAC, Omaha, NE, USA), with an Aridus perfluoroalkoxy (PFA) spray chamber upgrade and PFA 100 μL min^{-1} microflow nebulizer (Elemental Scientific, Inc., Omaha, NE, USA) used with self aspiration at 140 μL min^{-1}.

Standards

Five calibration standard solutions were prepared by serial dilution of 0.996 ± 0.0498 μg L^{-1} aqueous ^{239}Pu into 1.4 M HF at the following final concentrations: 5.0, 25.0, 50.0, 100 and 200 fg mL^{-1} (safety precautions for handling highly toxic HF are available from the corresponding author upon request). A ^{242}Pu recovery and internal standard was prepared by dilution of 0.963 ± 0.0008 μg L^{-1} ^{242}Pu to 100 ng L^{-1} 5% v/v HNO_3. 40.0 μL of the ^{242}Pu recovery and internal standard was added per mL of the final calibration standard solution before dilution to a 250-mL volume in polypropylene volumetric flasks.

Quality control materials

Urine Pu and U quality control (QC) solutions were used directly or diluted from standards and spiked samples obtained from Oak Ridge National Laboratories (ORNL) and LANL. Base urine was collected from healthy adult volunteers and acidified to 2% v/v HNO_3. A base urine sample was spiked to 10 ng L^{-1} depleted U for comparison of the ^{239}Pu background between the urine and 10 ng L^{-1} 5% aqueous HNO_3 samples. A urine "Pu blank" was prepared by spiking 1 L of a base urine pool to 1018 ng L^{-1} depleted U to determine the LOD. A 5 year old refrigerated urine sample that had originally been characterized as containing 5.08 ± 0.25 dpm L^{-1} ^{239}Pu in urine (36.9 ± 1.8 fg mL^{-1}) was obtained from ORNL. A base urine pool spiked to 99.6 fg mL^{-1} ^{239}Pu in urine was obtained from LANL. A urine pool that was 44.81 ± 4.48 fg mL^{-1} ^{239}Pu in urine was prepared from the volumetric 1 : 2000 dilution of LANL-30378 (89.6 ± 8.96 ng L^{-1} ^{239}Pu in urine) into base urine that had been spiked to 1011 ng L^{-1} of depleted U. In addition, a LANL ^{239}Pu standard was volumetrically diluted to 0.996 and 9.96 fg mL^{-1} in separate base urine pools. Target values for Pu in the LANL and ORNL pools were determined gravimetrically and/or using alpha spectrometry after spiking with high-purity standards. The U content of each urine sample was determined after spiking as previously described.[13]

Sample preparation

100-μL urine samples for ^{239}Pu background comparison with aqueous samples were diluted with 900 μL of 50 ng L^{-1} Ir internal standard in 1% v/v HNO_3 + 1% v/v HF.[13]

Urine samples were prepared for ^{239}Pu analysis as follows. 1.000-mL samples were pipetted into 15-mL polypropylene tubes. To each sample, 40.0 μL of the ^{242}Pu recovery and internal standard was pipetted, followed by 200 μL HNO_3. Pu(VI) was reduced by the addition of 60 μL of 1.5 M iron(II) sulfate (21 °C, 30 min), followed by oxidation of Pu(III) to Pu(IV) (21 °C, 30 min) by the addition of 120 μL of 4 M sodium nitrite according to a scaled down and modified excerpt of the method of Sherrod and Fauth, with iron(II) sulfate substituted for iron(II) sulfamate.[14] Solutions were then loaded into 6-mL polypropylene solid phase extraction (SPE) columns previously packed with 0.22 g TEVA resin that had been washed with 30 mL of 1.4 M HF and equilibrated with 0.8 M HNO_3. After the solutions entered the resin bed, a 2-mL 0.8 M HNO_3 wash of the sample containers was added to the resin, followed by 2 × 6 mL of 0.8 M HNO_3 and 1 × 0.300 mL of 1.4 M HF washes of the resin. Pu was eluted with 1.000 mL of 1.4 M HF into polystyrene sample cups pre-soaked twice with 2% v/v nitric acid in 18.2 MΩ cm^{-1} water and rinsed twice with 18.2 MΩ cm^{-1} water.

A 1.0-L base urine sample was prepared for ^{239}Pu analysis by addition of 40 μL of ^{242}Pu recovery and internal standard and 250 mL of HNO_3. Pu(VI) reduction and Pu(III) oxidation were performed by addition of 1000× scaled quantities of iron(II) sulfate sodium nitrite as described above. The urine was then loaded onto a 15-mL bed volume TEVA column previously equilibrated with 0.8 M HNO_3, followed by a wash with 270 mL of 0.8 M HNO_3 and 5 mL of 1.4 M HF. Pu was eluted in the next two 1-mL fractions.

Procedure

The magnetic sector ICP-MS was mass calibrated in low resolution (400). Optimization was performed with 6 ng L^{-1} uranium in 1.4 M HF. Sample uptake times were 60 s before acquisition with 0.855 L min^{-1} sample gas, 0.76 L min^{-1} auxiliary gas, and 15 L min^{-1} plasma gas flows, 1200 W forward power, guard electrode active, with 3.50 L min^{-1} Aridus argon sweep gas and 15 mL min^{-1} nitrogen addition. The pfa spray chamber was set at 100 °C and the desolvation chamber at 160 °C. Data was acquired in "Both" (counting and analog) mode with 0.001 s settle time in "Speed" magnet cycle setting. Peaks were quantitated with signal averaging, 200 samples per peak, 0.002 s sample time, 3 runs, 50 passes, and simple linear calibration. Mass windows were 80%, 20%, and 100%, respectively, for ^{238}U, ^{239}Pu, and ^{242}Pu. Search windows were 20%, 0% and 100% for the same respective isotopes, and integration windows were set at 20%. Each standard, blank, or sample was followed by a 3-min wash with a solution of 5% v/v HNO_3 + 5% v/v HF. Total standard deviations[15] for results were calculated using a CDC SAS[16] program. Comparison between urine and aqueous ^{239}Pu background was performed with a method previously described,[13] while monitoring ^{239}Pu cps with 80% ^{239}Pu mass and integration windows and 0% search window.

Results and discussion

Calibration

Over the course of 10 runs on 10 days, simple linear regression correlation coefficients were ⩾0.999 86. Typical curves had correlation coefficients of 0.9999 or better and near zero intercepts. ^{239}Pu calibration was linear from at least 5 fg mL^{-1} (the lowest standard concentration) to 500 fg mL^{-1} (the highest concentration used in preliminary runs).

Table 1 Comparison of the accuracy and precision of ^{239}Pu pools with external target values

Spike source	^{239}Pu target (U concentration)[a]	CDC[b] ^{239}Pu analysis, mean ± total SD (RSD)	Relative error of mean to target value
CDC U spike ("Pu blank")	0.0 fg mL^{-1} Pu (1018 ng L^{-1} U)	−0.20 ± 0.45 fg mL^{-1}	NA
CDC spike from LANL[c] standard Pu001C	0.996 ± 0.005 fg mL^{-1} Pu (1.5 ng L^{-1} U)	1.08 ± 0.32 fg mL^{-1} (29.6%) (<method LOD)	+1.2%
CDC spike from LANL standard Pu010C	9.96 ± 0.05 fg mL^{-1} Pu (2.6 ng L^{-1} U)	9.86 ± 0.36 fg mL^{-1} (3.7%)	−1.0%
ORNL[d] spike (5 years old)	36.9 ± 1.8 fg mL^{-1} Pu (4.4 ng L^{-1} U)	27.7 ± 3.3 fg mL^{-1} (11.9%)	−24.9%
CDC 1/2000 dilution of LANL 30378 spike	44.8 ± 4.5 fg mL^{-1} Pu (1011 ng L^{-1} U)	47.0 ± 1.0 fg mL^{-1} (2.1%)	+4.9%
LANL spike Pu100L	99.6 ± 0.5 fg mL^{-1} Pu (3.7 ng L^{-1} U)	97.0 ± 2.2 fg mL^{-1} (2.2%)	−2.6%

[a] Centers for Disease Control and Prevention ^{239}Pu analyses are shown adjacent to target concentrations with corresponding original ^{238}U concentrations in parentheses. Standard deviations are total (within and between run). [b] Centers for Disease Control and Prevention. [c] Los Alamos National Laboratory. [d] Oak Ridge National Laboratory.

Interferences

Shen, *et al.*, have reported that polyatomic species occur in geological samples with significant organic content to cause interferences at every mass from 229 to 237.[12] We previously reported low but greater interference at mass 239 in urine matrices than in an aqueous matrix,[10] supporting the conclusion of Shen, *et al.*, that this phenomenon results from polyatomic organic species. The apparent ^{239}Pu signals resulting from 10 analyses of undigested diluted urine samples with either 1.8 ng L^{-1} or 10.0 ng L^{-1} U (acquired without desolvation because Aridus semipermeable membranes are easily clogged with organic materials from undigested urine) were 4.6 ± 2.5 and 6.7 ± 3.8 cps, respectively. In contrast, the apparent ^{239}Pu signal resulting from 10 analyses of 10.0 ng L^{-1} U in aqueous 5% v/v HNO_3 was only 1.8 ± 1.0 cps. These ion counts illustrate the mass 239 interference in a urine matrix that contains significant organic material. The false counts are significant compared with the counts that would be found at mass 239 for 1–10 fg mL^{-1} aqueous ^{239}Pu and would have interfered with accurate analyses if performed without organic separation. At U concentrations >20 ng L^{-1},[10] the ^{238}U contribution becomes more significant than the organic contributions to the 239 mass window. Oxidative digestion of urine was previously used as a solution to the organic problem, which made possible the use of the desolvation system.[10] The high urine salt concentration in the digest, however, necessitated a 1 : 10 dilution before analysis and frequent cone cleanings, which lowered the sample throughput needed in the event of a large number of samples and suppressed the ^{239}Pu signal.

As an alternative, analyses of undigested urine using TEVA anion exchange resin were performed. Separation of ^{239}Pu from ^{238}U and urine salts was desirable to decrease the signal suppression and the need for dilution, as well as to eliminate interference from tailing of the more intense ^{238}U peak into the mass range for ^{239}Pu and from formation of $^{238}U^1H^+$.[18] Separation of U from Pu was accomplished with the TEVA resin using a slightly different strategy than typically advised in Eichrom methods for U and Pu separations. Rather than using a HNO_3 concentration near the k' peak for Pu retention, 0.8 M HNO_3 was chosen. This concentration decreased the U retention k' from approximately 5 to 1.5 for faster U washout in a smaller volume, while the ^{239}Pu k' decreased from approximately 35 000 to a still highly retention-favorable 10 000.[19] HNO_3 concentrations lower than 0.8 M resulted in some loss of Pu during the U washout, whereas ⩾99% of the Pu cps were retained with 0.8 M HNO_3 as a wash solution. Pu eluted in a 1 mL volume of 1.4 M HF after a 0.3 mL 1.4 M HF wash with less than 1–3 ng L^{-1} U remaining from the original 1018 ng L^{-1} U spiked in the ^{239}Pu "blanks." The remainder of the U did not detectably interfere with Pu analyses.

The removal of interferences from U on the ^{239}Pu signal is supported by the "Pu blank" data shown in Table 1. All of the 20 "Pu blank" analyses for within run and between run ^{239}Pu LOD determinations had ^{239}Pu concentrations that were measured as less than the 1.4 fg mL^{-1} method LOD. Furthermore, only two of five ^{239}Pu spiked QCs had a positive relative error. If a urine interference resulted in significant higher ion counts relative to aqueous standards, relative errors would have been expected to be positive in all QCs.

A sample ^{242}Pu elution *versus* ^{238}U washout profile (Fig. 1) demonstrated separation of the large excess of ^{238}U from ^{242}Pu internal standard in a 1018 ng L^{-1} U "plutonium blank." Bilirubin color was apparent in the eluted resin beds but not in the final column washes or eluates, indicating that the resin apparently adsorbed poorly water soluble urine organic substances. The washes appeared to remove urine salts and soluble organic substances. The lack of false ^{239}Pu ion counts, no clogging of the semipermeable membrane in the desolvation system, and constant sweep gas flow optima over at least ten runs further supported the organic removal by SPE.

Limits of detection

Based on 3 times the standard deviation from 10 separate base urine samples, the within run LOD was 0.16 fg mL^{-1} for 1 mL

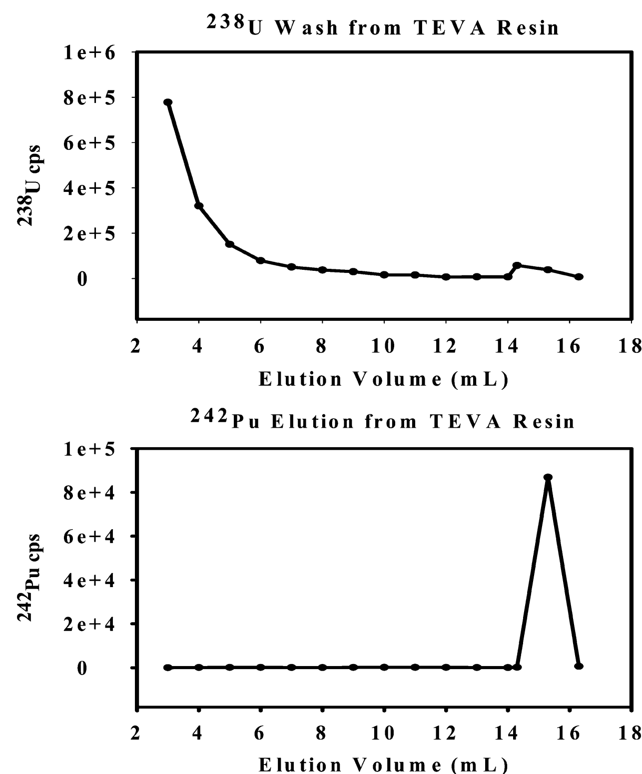

Fig. 1 Washout profile for U ion counts (upper) and elution profile for Pu ion counts (lower) from the TEVA column.

of urine spiked to 1018 ng L^{-1} depleted U. Combining the within run and between run "total" standard deviations[15] resulted in a method LOD of 1.4 fg mL^{-1} ^{239}Pu. For 2464 urine samples from the U.S. population analyzed for U in the 1999–2000 National Health and Nutrition Examination Survey (NHANES),[20] the 99th percentile (before creatinine normalization correction) for U was 123 ng L^{-1}; the 95% confidence interval on the 99th percentile was 92–206 ng L^{-1}. The practicality of the method for analysis of ^{239}Pu in urine was demonstrated by the lack of detectable interference from U spiked at over 5–11 times the population urine U 99th percentile confidence interval in blank and low ^{239}Pu concentration urine samples.

Accuracy and precision

Accuracy assessment was based on repeated analysis of the CDC-, ORNL-, and LANL-spiked urine QC materials (Table 1). Accuracy based on concentration relative error was excellent for all samples with ^{239}Pu concentrations above the method LOD (within 1.0–4.9%), with the exception of the 5-year-old ORNL sample that had never been frozen (24.9%). This sample had very high particulate content, and the analytical result apparently depended on the shaking time and vigor before removal of an aliquot, as further indicated from the high RSD. The result for this sample confirmed that the concentration that was previously reported using a different method (23 ± 6 fg mL^{-1})[10] was lower than originally characterized. Thus, accurate results may not be obtained with this method on unfrozen or unpreserved samples after long but indefinite periods.

The relative precisions were better, based on RSD, for samples with ^{239}Pu concentrations above the method LOD (total within and between run RSDs were 2.1–3.7%) than for the Pu001 sample, which was at a concentration below the method LOD, and the 5 year old ORNL sample which had never been frozen, as would be expected.

Verification of ^{239}Pu concentration in base urine

To affirm the assertion that sensitivity was sufficient and the method equivalent to analysis of ^{239}Pu from normal absorption on a scaled basis, one 1.0-L base urine sample to which no exogenous U or Pu had been added was analyzed as described. Addition of the quantities measured in the two ^{239}Pu-containing fractions gave a ^{239}Pu concentration of 8.7 ± 0.4 fg L^{-1} or $2.2 \pm 0.1 \times 10^7$ atoms L^{-1}. No widespread creatinine-normalized population data are available for reference range comparison, nor is this value creatinine-normalized. The ^{239}Pu concentration for this particular base urine, however, was roughly 10 times a typical excretion level reported elsewhere.[9] Because the urine did not originate from an exposed person, lifetime exposure and daily quantity of liquid consumption may have been factors in the higher than reportedly average urine ^{239}Pu concentration. Assuming this unexposed concentration is a non-elevated exposure, the LOD of the 1-mL method described here is capable of measuring an exposure of only 50 times this unexposed urine concentration.

While the Nuclear Regulatory Commission has established radiation dose limits for nuclear industry workers and for members of the public as a result of licensed activities, no federal public dose limits exist for emergencies resulting from hostile actions. Thus, any action level would be hypothetical. The International Commission on Radiological Protection recommends treatment of an inhalation exposure to Pu in an unknown form as Class M (unspecified Pu compounds) for dose assessment purposes.[21] A more conservative hypothetical action level for a one-day post-intake urine sample could be based on assumption of a Class S (insoluble oxides) inhalation exposure. A hypothetical urine action level was calculated and obtained for use as a resource by personal communication acknowledged below, with the assumption of a class S (insoluble oxides) 239Pu inhalation exposure and ICRP reference man urine volume excretion.[22] The maximum dose conversion factor was conservatively based on exposure to the public, whereas the bioassay intake retention fraction was based on exposure to an adult worker[17] because none are available from public exposure studies. The calculation was derived as follows:

Urine ^{239}Pu Action Level = (Dose Action Level/Maximum Dose Conversion Factor)(Intake Retention Fraction)(1 pCi/0.037 Bq)/1.4 L urine;

Urine ^{239}Pu Action Level = [(0.5 Sv)/(1.80 $\times$ 10^{-4} Sv/Bq)] [2.50 $\times$ 10^{-6} Bq in urine/Bq inhaled] [1 pCi/0.037 Bq]/1.4 L.

The hypothetical urine ^{239}Pu action level calculation described above yields a value of 0.13 pCi L^{-1} (2.1 fg mL^{-1}). This concentration is just above the method LOD reported here. On this hypothetical basis, the method described here is appropriate for measuring and assessing exposures based on urine ^{239}Pu excretion that would be conservatively considered significant for health risk.

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