Plutonium determination in bioassay samples using radiochemical thermal ionization mass spectrometry

S. P. LaMont,1 C. R. Shick,1 P. Cable-Dunlap,1 D. J. Fauth,2 T. R. LaBone3

1 Savannah River Technology Center, Nonproliferation Technology Section, Bldg. 735-A, Aiken, SC 29803, USA
2 Westinghouse Savannah River Co., Site Analytical Services, Bldg. 735-B, Aiken, SC 29808, USA
3 Westinghouse Savannah River Co., Radiation Protection Department, Bldg. 735-4B, Aiken, SC 29808, USA

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A new high-sensitivity plutonium bioassay program employing thermal ionization mass spectrometry (TIMS) has been developed to monitor Savannah River Site employees for intakes of PuO2. The U.S. Department of Energy requires bioassay laboratories which have the ability to detect a 100 mRem, 50-year committed effective dose equivalent (CEDE) intake of radioactive material. For PuO2, traditional alpha-spectrometry methods are not sensitive enough to meet this specification. To comply with this requirement, a radiochemical TIMS method was developed to determine Pu in urine bioassay samples. Four radiochemical separation steps were used to purify Pu from urine to ensure samples were free from matrix effects that interfere with TIMS analysis. These included precipitation, ion-extraction chromatography, electrodeposition, and ion-exchange chromatography. A batch of reagent blanks determined the detection limit for this method was 0.59 fg 239Pu/1 (1.3 μBq 239Pu/l). The 239Pu concentration was also measured in 20 urine blank samples to determine the minimum 239Pu concentration that would indicate an occupational intake. A Probit plot was constructed for the results and the 99th percentile of the urine blanks showed that the minimum 239Pu concentration that would indicate an uptake was 2.4 fg/l (5.5 μBq/l).

Introduction

Current U.S. Department of Energy regulations require the ability to detect all occupational exposures that result in a worker receiving a 50 year, 100 mrem or greater committed effective dose equivalent (CEDE).1 While it is simple for external dosimetry programs to meet this requirement, it presents a formidable technical challenge for internal dosimetry monitoring of workers. For exposures to highly insoluble, or Type S forms of plutonium, traditional bioassay methods are not capable of detecting plutonium in urine at the concentration expected for a 50 year, 100 mrem CEDE inhalation uptake. A theoretical plutonium excretion curve for a worker exposed to Type S material (Fig. 1) shows that alpha-spectrometry, the typical method used in bioassay programs, would not detect a small uptake. However, high-sensitivity methods such as thermal ionization mass spectrometry (TIMS) are able to detect the minimum required dose up to a year after the intake.

Thermal ionization mass spectrometry (TIMS) is the benchmark method for measuring ultra-trace plutonium in environmental samples.2-4 In recent years, TIMS has been used to determine plutonium in urine bioassay samples to meet regulatory requirements for monitoring workers for occupational uptakes.5 Because extensive radiochemistry is required to process samples for analysis by TIMS, it is typically only used to monitor workers who are at the highest risk for exposure to Type S plutonium.

* E-mail: stephen.lamont@srs.gov

Fig. 1. Excretion curve for an 100 mrem, 50 year CEDE inhalation uptake of Type S plutonium. Note that traditional bioassay methods that use alpha-spectrometry would not be able to detect this uptake. High-sensitivity methods, such as TIMS, are needed to detect an uptake and monitor the excretion rate of the Pu

The Savannah River Site (SRS), a U.S. Dept. of Energy facility, recognized the need to institute a high-sensitivity bioassay program after a 1999 occupational exposure incident. A flaw in the welding in a bagless transfer can containing plutonium allowed some PuO2 to escape, and become airborne. Several workers had inhalation intakes of this material, immediately confirmed by whole body counting. From the whole body counting data, urine excretion rates were calculated, and urine bioassay samples were collected
and analyzed. However, the observed plutonium concentrations in the urine were 1–2 orders of magnitude lower than estimates, in some cases barely detectable. Concentrations quickly fell below the levels detectable by alpha-spectrometry, indicating the PuO₂ was far more insoluble than any form of PuO₂ previously encountered at SRS.

Samples of the PuO₂ collected on filters at the time of the incident were sent to the Lovelace Inhalation Toxicology Research Institute (ITRI), who determined that the dissolution half-time of the material was 10⁵ days. This dissolution half-time is extremely long, even for Type S Pu, and emphasized the need to have a high-sensitivity bioassay method readily available at SRS to monitor workers with the potential for exposure to this material.

While several other methods, such as accelerator mass spectrometry (AMS), inductively coupled plasma mass spectrometry (ICP-MS), and fission track analysis (FTA) have been used to make high-sensitivity bioassay measurements,⁶ TIMS was the only high-sensitive method readily available at SRS. The Nonproliferation Technology Section (NTS) at the Savannah River Technology Center maintains a TIMS capability and the associated clean room and radiochemistry facilities necessary to make ultra-low level plutonium measurements. The Radiation Protection Department (RPD), who is responsible for maintaining internal dosimetry programs at SRS, and Site Analytical Services (SAS), who analyzes bioassay samples at SRS, requested the assistance of NTS in developing a high-sensitivity bioassay program. Through a collaborative effort between RPD, SAS, and NTS a TIMS bioassay measurement program is now operational at SRS.

**Experimental**

**Radiochemistry**

Samples requiring Pu analysis by TIMS would also initially be analyzed by alpha-spectrometry for ²³⁹Pu determination. Therefore, radiochemistry developed to purify Pu sufficiently for analysis by TIMS had to be compatible with existing chemistry used to prepare samples for analysis by alpha-spectrometry. Sample preparation for alpha-spectrometry is described in detail elsewhere,⁷ but a summary is as follows. An aliquot of urine, usually 500 ml, was acidified with 8M HNO₃ and spiked with ²³⁶Pu or ²⁴²Pu as a chemical yield tracer. The sample was heated to allow the tracer to equilibrate with the Pu in the sample, then Pu was co-precipitated with Ca₃(PO₄)₂ by raising the pH of the solution with NH₃(aq). After the Ca₃(PO₄)₂ precipitate settled to the bottom of the beaker, the supernate was decanted and the precipitate was transferred to a centrifuge tube, where it was resuspended, rinsed, and centrifuged twice. The Ca₃(PO₄)₂ was redissolved in 4M HNO₃, and the Pu is purified by selectively trapping the Pu on a TEVA-Spect ion-extraction chromatography column. The Pu was eluted from the TEVA-Spect column with 0.1M HCl, and electrodeposited onto a stainless steel planchet for alpha-spectrometry. The stainless steel planchet served as the source of the sample for analysis by TIMS.

The stainless steel planchets were transferred to the Class 10,000 clean room facilities and handled in Class 100 clean hoods for all additional sample preparation required for analysis. The Class 100 conditions are imperative to ensure that no airborne particles can contaminate the sample with impurities that may hinder the ionization of the Pu during mass spectrometry. All reagents used were Fisher Optima® grade ultra-high purity reagents to prevent the introduction of unnecessary contaminants into the samples.

Samples analyzed by TIMS were all initially spiked with approximately 8 mBq of ²³⁹Pu as a tracer for alpha-spectrometry, and 1–5 pg (0.1–0.7 mBq) of ²⁴²Pu as a tracer for TIMS. Each sample was placed in the bottom of 50 ml pre-cleaned, sterile, polyethylene centrifuge tubes. Approximately 3 ml of 8M HNO₃, just enough to cover the planchet, was added to each tube and the planchet was allowed to leach overnight. The solution was transferred from the tube to a 5-ml Teflon conical vial, rinsing the tube and planchet twice with 0.5 ml of 8M HNO₃ and adding the rinse solutions to the vial. The solution was then dried under a heat lamp, and the residue in the bottom of the conical vial was redissolved in 0.5 ml of 8M HNO₃.

A 0.20 ml pre-packed column of Dowex 1-x4, 100–200 mesh Cl⁻ form (Applied Separations, Inc.) was conditioned with 1 ml of 0.1M HCl followed by 1 ml of 8M HNO₃. The sample was added to the column, and the conical vial was rinsed twice into the column with 0.25 ml of 8M HNO₃. The column was then rinsed with 1 ml of 8M HNO₃ followed by 2 ml of 9M HCl. Plutonium was eluted from the column into a new conical Teflon vial with 1.5 ml of conc. HBr. The sample was dried under a heat lamp, then wetashed 3–4 times with 0.5 ml 8M HNO₃ to remove any residual Br⁻.

The Pu was redissolved in 5 μl of 8M HNO₃ and 3–4 beads of AG-1×2 (20–50 mesh NO₃⁻ form) resin were added. The vials were placed on a slow orbital shaker overnight to allow the Pu to sorb to the resin beads. Resin beads were removed from the solution using a tungsten needle and mounted onto “vee” style rhenium TIMS filaments using collodion as an adhesive.

**Mass spectrometry**

After sample loading, filaments are heated to approximately 1000 °C under vacuum to decompose the resin bead matrix and collodion. Burning this material off prior to analysis helps keep the mass spectrometer