Measurements of Plutonium Isotopes in Urine at Microbecquerel Levels: AMS Results of a NIST Interlaboratory Exercise

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Introduction

The Center for Accelerator Mass Spectrometry (CAMS) at the Lawrence Livermore National Laboratory (LLNL) has recently added the capability of measuring ^{239}Pu and other actinides with a sensitivity of ~10^6 atoms per sample, i.e., ~1 µBq of ^{239}Pu. This new capability is possible because of the implementation of a heavy-ion beam line in 2000. Accelerator mass spectrometry (AMS) has a large dynamic range, typically 5 orders of magnitude, and is less demanding on sample preparation than similarly sensitive techniques because of its high rejection of molecular isobaric interferences and low susceptibility to matrix effects. These advantages combined with the high throughput design of the CAMS spectrometer offers a sensitive and efficient instrument to measure actinides at very low levels in a large number of samples.[1] Hundreds of environmental and bioassay samples have already been measured for ^{239}Pu and ^{240}Pu at CAMS, many in support of the Department of Energy (DOE) Marshall Islands Program, and work on other heavy nuclides is under way. Among the applications of this technology, one of the most important is the determination of ^{239}Pu in urine to assess dose or exposure in humans. Therefore, we have participated in a blind interlaboratory exercise designed to evaluate the capability of various techniques to measure ^{239}Pu and ^{240}Pu in this matrix.

In 1997, the Department of Energy requested the National Institute of Standards and Technology (NIST) to make a quantitative assessment of sensitive analytical methods to determine ^{239}Pu in urine, and chose two national laboratories to participate in the study. NIST provided the two laboratories with synthetic samples of urine containing

3-56 µBq ^{239}Pu per 200 g. Los Alamos National Laboratory analyzed the samples using thermal ionization mass spectrometry (TIMS), while Brookhaven National Laboratory employed fission track analysis (FTA) and inductively coupled mass spectrometry (ICP-MS). The authors concluded that the three techniques were capable of making measurements at those concentrations but with different biases and uncertainties. The authors also estimated that each measurement technique was capable of detecting ^{239}Pu activities as low as ~1 µBq.[2] However, they cautioned that the results should be considered valid only under optimum conditions because of the absence of isobaric and chemical interferences in the synthetic urine matrix. The absence of any uranium in this sample matrix was a special concern because uranium can produce isobaric interferences during ionization in mass spectrometric measurements (e.g., ^{238}UH$^+$ at mass ^{239}Pu$^+$, ^{238}U^{17}O$^+$ or ^{238}U^{16}OH$^+$ at mass ^{239}Pu^{16}O$^+$; similar cases occur in the case of negative-ion selection). In addition, any residual ^{235}U remaining in the purified sample will produce fission tracks that are indistinguishable to those produced by ^{239}Pu.

A second interlaboratory study was planned in 1999 and executed during 2001.[3] The DOE Office of International Health sponsored the study with the participation of LANL, the University of Utah, and LLNL, measuring Pu by TIMS, FTA, and AMS, respectively. NIST prepared synthetic urine samples almost identical to those of the first study with the addition of natural uranium and ^{240}Pu. The amount of uranium added was 0.05 Bq per sample, which is approximately the background level observed in human urine samples from the vicinity of Los Alamos, NM. Plutonium-240 was added at the global fallout ratio ^{240}Pu/^{239}Pu ~0.15. Cesium-134 and 137 were added as tracers to

verify dilutions. Five testing levels of ^{239}Pu were prepared: 0 (blank), 20, 50, 150, and 280 µBq/L; five samples per nonzero level and eight blanks were submitted randomly and blindly to each of the participating laboratories. In this report we present the results of our measurements using AMS. In addition, we present data from the preliminary evaluation performed by NIST and Duke Engineering Services, disclosed after completion of the exercise.[4]

Experimental method

Samples were prepared following the standard protocol used for Pu alpha spectrometry by the LLNL Marshall Islands Program[5] with a few modifications to obtain a suitable target for AMS measurement. Plutonium-242 was added as a recovery tracer, which is common practice in alpha spectrometry, and is also required for the AMS determination of Pu isotopes. After acid digestion and ion exchange separation, Pu(IV) is coprecipitated with ~0.3 mg of Fe(III) and Nb(V) by adding ammonia. The precipitate is centrifuged, washed, calcined at 800°C in a quartz crucible, and loaded in an aluminum target holder. The AMS ion source accommodates up to 64 targets on its sample wheel.

The AMS system for measurement of Pu isotopes is depicted in Figure 1. The cesium sputtering ion source[6] produces 40 keV PuO$^-$ ions that are transported first to a 90º energy-analyzing electrostatic deflector, then to a 90º mass-analyzing double-focusing magnet, and are injected into a tandem accelerator† operated at 6.5 MV for actinide measurements. In the tandem central terminal, a gas stripper converts the

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† High Voltage Engineering Corporation, Model FN Tandem Accelerator

negatively charged molecular ions into atomic positive ions in a variety of charge states. The positive ions are accelerated out of the tandem and transported through a 30º mass-analyzing magnet into the heavy-ion beam line equipped with an energy-analyzing 45º cylindrical electrostatic deflector. The spectrometer is set to select Pu^{5+} ($E_{kinetic}$ = 39 MeV) for measurement in a two-anode ionization detector. A charge gate is established to count the 5^+ events using an interactive two-dimensional plot of the energy signal of one anode versus the other. The AMS system alternates the mass measurement between analyte (e.g., ^{239}Pu or ^{240}Pu) and reference (^{242}Pu) in a time scale of a few hundreds of milliseconds. This fast switching system improves the accuracy and precision of the measurement because the ion source output remains essentially constant during each measurement cycle. Isotopic ratios and other parameters are monitored on-line while a continuous measurement file is generated for subsequent off-line analysis. Data is analyzed and reported as the ratio of the analyte (^{239}Pu or ^{240}Pu) to the reference isotope (^{242}Pu).

Results and discussion

We present the AMS measurement of the ratios $^{239}Pu/^{242}Pu$ and $^{240}Pu/^{242}Pu$ in the synthetic urine samples in Table 1. We added 3.0×10^9 atoms of ^{242}Pu to each sample and used this known addition to calculate the total number of atoms of ^{239}Pu and ^{240}Pu (also shown in Table 1). We utilized traceable Pu isotopic standards (CRM 128 and CRM 138) to test the overall instrument performance and determine—if needed—a mass-dependent normalization factor for the isotopic ratio measurement. We concluded the measured ratios were accurate within their uncertainty and did not require normalization.

Rejection of the interference of ^{238}U in mass 239 was ~10^7 as determined by measuring samples containing ~1×10^{14} atoms of depleted ^{238}U. After converting the results to activities, total and per unit mass in the sample, we submitted the results with the corresponding standard deviations (SD) to the exercise evaluators. Note that reagent blanks have been subtracted (^{239}Pu 0.3 ± 0.2 µBq, and ^{240}Pu 0.5 ± 0.3 µBq, n = 5, ±1 SD).

The exercise evaluators have recently provided us with a first draft of the exercise report[4] where the reference activities of the coded samples were disclosed. We present the measured and NIST reference values in Table 2. Figure 2 is a plot of measured ^{239}Pu versus NIST reference values. The relative uncertainties of the NIST ^{239}Pu activities are estimated at ~0.736-0.763% at the 2 SD level, and the values of ^{240}Pu correspond to an atomic ratio ^{240}Pu/^{239}Pu of 0.154 for all the samples with a 1.08% uncertainty at the 2 SD level. The evaluators performed a detailed statistical analysis of the AMS data as well as the TIMS and FTA data provided by the other laboratories. Following is a summary of some of their results pertaining to the AMS data.

1. A normal probability plot of the normalized ^{239}Pu data (AMS/NIST) shows two outliers, one above 95% and the other below 5%. The same occurs with the normalized ^{240}Pu data (AMS/NIST). With the exception of the two outliers out of 28 data points, the data has a normal distribution indicating a well-controlled measurement.

2. The correlation between AMS and NIST data is given in the following equations:

$$^{239}\text{Pu}_{\text{AMS}} \, [\mu\text{Bq}] = 0.99 \, ^{239}\text{Pu}_{\text{NIST}} - 0.24 \qquad (r^2 = 0.99),$$

$$^{240}\text{Pu}_{\text{AMS}} \, [\mu\text{Bq}] = 1.00 \, ^{240}\text{Pu}_{\text{NIST}} - 0.28 \qquad (r^2 = 0.90).$$

3. The precision of the analysis was evaluated for each test level using two methods. The fist method uses the coefficient of variation for each test level while the second method, taken from ANSI N13.30,$^€$ relies on the standard deviation of the bias and can not be used for blanks. For the AMS results, the precisions obtained by both methods are similar with average values of 6.3, 6.5, 11, and 30% for ^{239}Pu activities of 55, 28, 8.9, and 3.6 µBq, respectively. In the determination of ^{240}Pu the precision averages are 26, 26, 80, and 81%, for activities of 31, 16, 5.1, and 2.0 µBq, respectively.

4. The AMS measurements met the ANSI N13.30 precision and bias criteria for both ^{239}Pu and ^{240}Pu at all test levels.

5. The minimum detectable amount (MDA) was determined by two methods. One based on the work of Currie[7] and the other on a regression method reported by Hubaux and Vox,[8] that result in MDA values of 0.82 and 6.1 µBq for ^{239}Pu, and 2.1 and 14 µBq for ^{240}Pu, respectively.

The results of this exercise demonstrate that AMS is capable of measuring ^{239}Pu and ^{240}Pu at µBq levels in urine far exceeding the ANSI performance criteria for routine radiobioassay. The AMS sensitivity and precision were unsurpassed by the other techniques used in the study.

References

$^€$ ANSI N13.30 is a standard published by the Health Physics Society as a guideline to assess the performance of radiobioassays.

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Table 1. AMS analysis of NIST synthetic urine samples[a]

NIST sample code	^{239}Pu/^{242}Pu		^{240}Pu/^{242}Pu		^{239}Pu (10^6 atoms)		^{240}Pu (10^6 atoms)	
MS8	0.00025	± 0.00012	0.00000	± 0.00012	0.8	± 0.4	0.0	± 0.4
MS47	0.00070	± 0.00022	0.00043	± 0.00025	2.1	± 0.7	1.3	± 0.7
MS81	0.00029	± 0.00010	0.00000	± 0.00006	0.9	± 0.3	0.0	± 0.2
MS96	0.02079	± 0.00103	0.00277	± 0.00051	62.7	± 3.1	8.4	± 1.5
MS109	0.00164	± 0.00030	0.00022	± 0.00016	5.0	± 0.9	0.7	± 0.5
MS92	0.00285	± 0.00042	0.00116	± 0.00039	8.6	± 1.3	3.5	± 1.2
MS101	0.01161	± 0.00097	0.00138	± 0.00046	35.0	± 2.9	4.2	± 1.4
MS115	0.01049	± 0.00071	0.00169	± 0.00039	31.6	± 2.1	5.1	± 1.2
MS119	0.00024	± 0.00009	0.00000	± 0.00007	0.7	± 0.3	0.0	± 0.2
MS151	0.00306	± 0.00044	0.00040	± 0.00023	9.2	± 1.3	1.2	± 0.7
MS51	0.00299	± 0.00043	0.00026	± 0.00018	9.0	± 1.3	0.8	± 0.5
MS72	0.00009	± 0.00006	0.00000	± 0.00010	0.3	± 0.2	0.0	± 0.3
MS108	0.02204	± 0.00129	0.00425	± 0.00080	66.8	± 3.9	12.9	± 2.4
MS118	0.00016	± 0.00009	0.00000	± 0.00011	0.5	± 0.3	0.0	± 0.3
MS178	0.00015	± 0.00011	0.00015	± 0.00015	0.5	± 0.3	0.5	± 0.5
MS2	0.02020	± 0.00219	0.00380	± 0.00135	61.3	± 6.6	11.5	± 4.1
MS20	0.01989	± 0.00126	0.00239	± 0.00062	60.1	± 3.8	7.2	± 1.9
MS31	0.00279	± 0.00041	0.00036	± 0.00021	8.4	± 1.2	1.1	± 0.6
MS37	0.01014	± 0.00062	0.00203	± 0.00038	30.6	± 1.9	6.1	± 1.1
MS40	0.00988	± 0.00082	0.00101	± 0.00036	29.8	± 2.5	3.0	± 1.1
MS79	0.01861	± 0.00104	0.00252	± 0.00051	55.5	± 3.1	7.5	± 1.5
MS126	0.00358	± 0.00041	0.00018	± 0.00013	10.9	± 1.2	0.5	± 0.4
MS136	0.00132	± 0.00019	0.00000	± 0.00006	4.0	± 0.6	0.0	± 0.2
MS145	0.00140	± 0.00025	0.00034	± 0.00017	4.2	± 0.8	1.0	± 0.5
MS150	0.00009	± 0.00009	0.00000	± 0.00018	0.3	± 0.3	0.0	± 0.5
MS28	0.00010	± 0.00006	0.00000	± 0.00007	0.3	± 0.2	0.0	± 0.2
MS61	0.01027	± 0.00056	0.00196	± 0.00034	31.0	± 1.7	5.9	± 1.0
MS121	0.00162	± 0.00022	0.00017	± 0.00010	4.9	± 0.6	0.5	± 0.3

[a]Pu-242 added as tracer in the amount of 3×10^9 to all samples; total atoms calculated from tracer added and ratio; uncertainties correspond to ±1SD.

Table 2. **Comparison between AMS and NIST values**[a]

NIST sample code	Level	NIST value (mBq)	^{239}Pu Total Activity (mBq)	Uncertainty (% 1 SD)	^{240}Pu Total Activity (mBq)	Uncertainty (% 1 SD)
MS2	L4	56.3	56.0	11%	40.0	36%
MS20	L4	56.1	54.0	7%	20.0	27%
MS79	L4	56.5	50.0	7%	20.0	21%
MS96	L4	56.2	57.0	6%	30.0	19%
MS108	L4	56.4	61.0	7%	40.0	19%
MS37	L3	29.2	28.0	7%	20.0	19%
MS40	L3	28.7	27.0	9%	10.0	37%
MS61	L3	28.9	28.0	7%	20.0	18%
MS101	L3	29.1	32.0	9%	10.0	35%
MS115	L3	28.9	28.0	8%	20.0	24%
MS31	L2	9.3	7.4	16%	3.0	65%
MS51	L2	9.2	7.9	16%	2.0	84%
MS92	L2	9.2	7.5	16%	10.0	35%
MS126	L2	9.2	9.6	12%	1.0	93%
MS151	L2	9.3	8.1	15%	4.0	64%
MS47	L1	3.7	1.6	40%	4.0	64%
MS109	L1	3.7	4.2	21%	2.0	87%
MS121	L1	3.7	4.1	16%	1.0	81%
MS136	L1	3.7	3.3	18%	-0.3	247%
MS145	L1	3.7	3.6	21%	3.0	58%
MS8	Blk	0	0.4	110%	-0.3	426%
MS28	Blk	0	0.0	644%	-0.3	272%
MS72	Blk	0	-0.1	434%	-0.3	355%
MS81	Blk	0	0.5	72%	-0.3	258%
MS118	Blk	0	0.1	259%	-0.3	397%
MS119	Blk	0	0.4	91%	-0.3	268%
MS150	Blk	0	-0.1	592%	-0.3	597%
MS178	Blk	0	0.1	380%	1.0	133%

[a]Relative uncertainties of NIST reference activities for ^{239}Pu are ~0.736-0.763% at the 2 SD level; values of NIST ^{240}Pu correspond to an atomic ratio ^{240}Pu/^{239}Pu of 0.154 for all the samples with a 1.08% uncertainty at the 2 SD level.
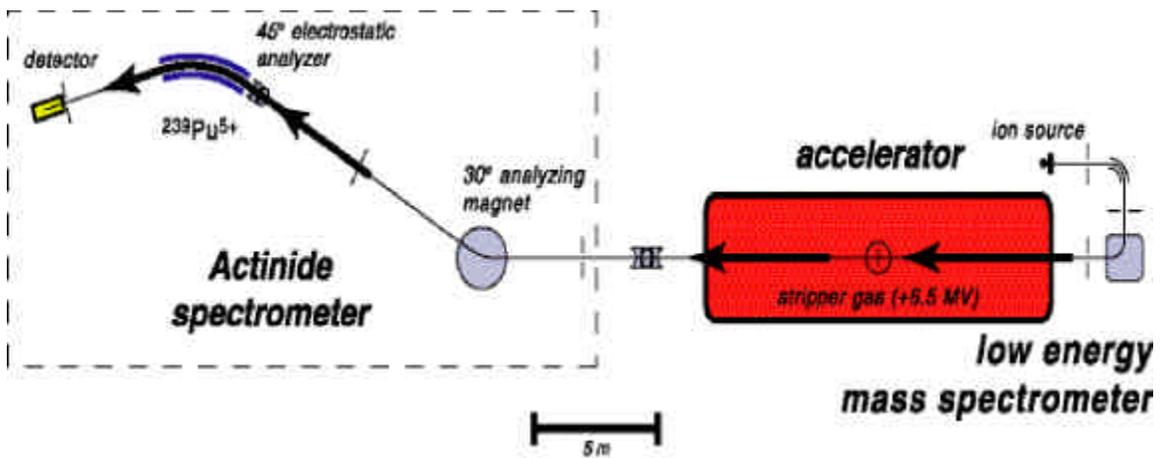
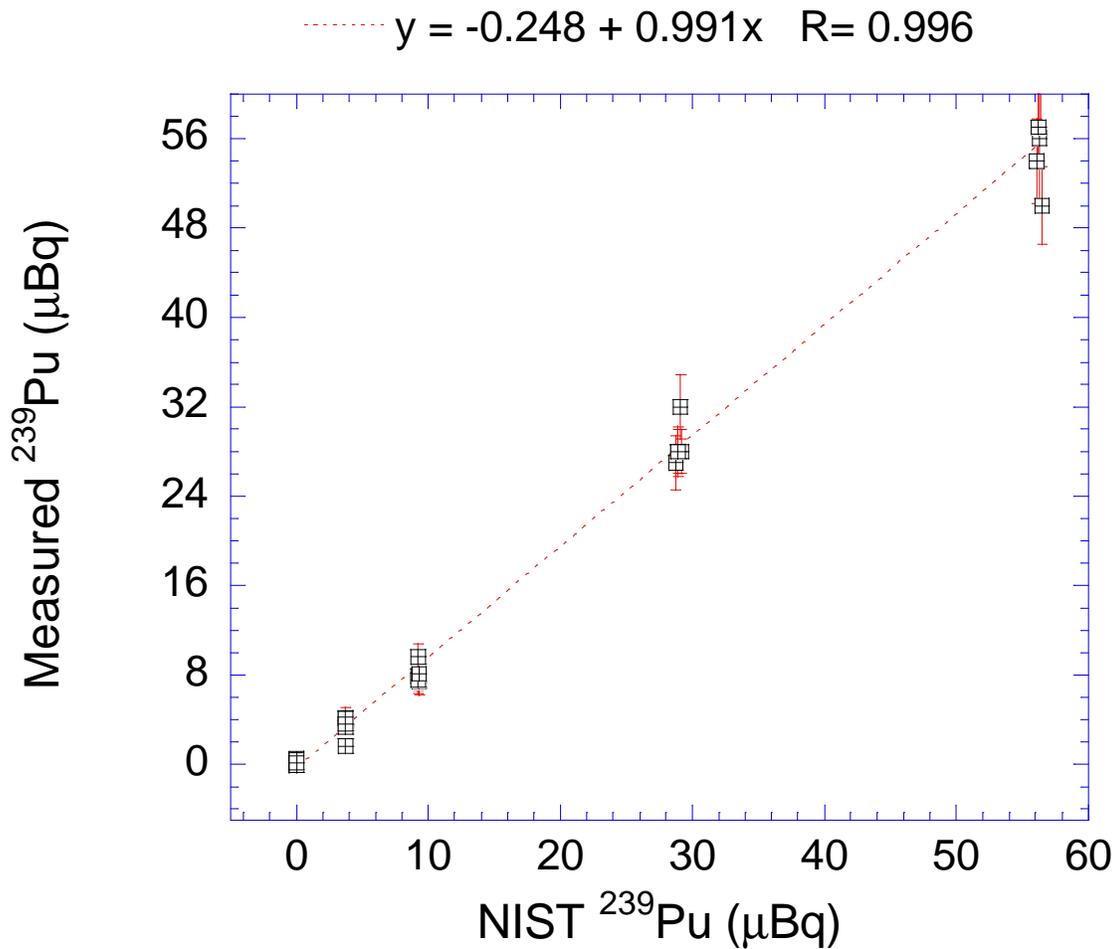Figure 1. Schematic view of the heavy-ion spectrometer.

Figure 2. Plutonium-239 measured in samples versus NIST reference values. The dotted line corresponds to a linear least square fit to the data. Each concentration consists of 4 replicates and the blank (0 μBq) consists of 8 replicates. The reagent blank (0.3 ± 0.2 μBq, n = 5, ±1SD) has been subtracted from the measured values; the uncertainty bars represent ±1SD for each replicate.

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