Title: First AID (Atom counting for Isotopic Determination)

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FIRST AID (Atom counting for Isotopic Determination)

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ABSTRACT

Los Alamos National Laboratory (LANL) has established an in vitro bioassay monitoring program in compliance with the requirements in the Code of Federal Regulations, 10 CFR 835, Occupational Radiation Protection. One aspect of this program involves monitoring plutonium levels in at-risk workers. High-risk workers are monitored using the ultra-sensitive Thermal Ionization Mass Spectrometry (TIMS) technique to ensure compliance with DOE standards.

TIMS is used to measure atom ratios of $^{239}\text{Pu}$ and $^{240}\text{Pu}$ with respect to a tracer isotope ($^{242}\text{Pu}$). These ratios are then used to calculate the amount of $^{239}\text{Pu}$ and $^{240}\text{Pu}$ present. This low-level atom counting technique allows the calculation of the concentration levels of $^{239}\text{Pu}$ and $^{240}\text{Pu}$ in urine for at risk workers. From these concentration levels, dose assessments can be made and worker exposure levels can be monitored. Detection limits for TIMS analysis are on the order of millions of atoms, which translates to activity levels of 150 aCi ($10^{-6}$ pCi) for $^{239}\text{Pu}$ and 500 aCi for $^{240}\text{Pu}$.

Our poster presentation will discuss the ultra-sensitive, low-level analytical technique used to measure plutonium isotopes and the data verification methods used for validating isotopic measurements.
TIMS Low-Level, Ultra-Clean Chemistry

All TIMS operations are performed in Class 10,000 laboratories while chemistry is performed in Class 100 work areas.

Bioassay urine samples are chemically processed, electroplated onto a stainless steel planchette, and alpha counted for $^{238}\text{Pu}$, $^{239}\text{Pu} + ^{240}\text{Pu}$, and $^{242}\text{Pu}$ (Tracer isotope). Next, they are submitted for TIMS chemistry and stripped from the stainless steel planchettes. The Plutonium is then isolated and purified using anion exchange chemistry. Samples are then evaporated on hot plates and delivered for TIMS analysis in solid form. This insures that sample integrity is maintained until analysis.
Low-Level TIMS Chemistry Lab
(Class 100 air)
Sample Planchettes
(from Alpha Counting)

Stripping
Sample Planchettes
Anión Exchange Columns
Loading Filaments for TIMS analysis

TIMS samples are dissolved in a solution of 1.5M HCl and loaded onto a rhenium filament for electrodeposition. The plutonium is co-plated onto the filament surface using a platinum solution and then over-plated with a more concentrated platinum solution. This allows the samples to be run at high temperatures which:

✓ Increases sublimation (solid atoms to gas atoms), helping to remove impurities from the sample that can cause isobaric interferences.

✓ Controls the diffusion rate of the sample to extend the amount of time available for analysis

✓ Efficiently ionizes sample atoms through electron bombardment
Sample Loading Station
(Class 10 air)
Thermal Ionization Turret
NBS 12-90 TIMS
Source
Sample Measurement

Filaments are loaded into a $10^{-8}$ Torr vacuum chamber (source can). A current is applied to the filament, heating the sample to approximately 1580°C and creating gas-phase atoms. Through electron bombardment, the gas atoms from the sample are ionized (electrically charged). This allows the ions to be electro-statically accelerated and focused through a series of slit openings from the source can and into the flight tube. Here, the isotopes enter a magnetic field within the flight tube and are electro-magnetically separated by mass. By changing the Gauss field on the magnet, charged ions of the same mass unit are focused on the multiplier. The charged ions enter the multiplier and impinge on the collector dynode, creating secondary electrons. These electrons cascade down the multiplier dynode string, increasing the intensity of the signal created by each ion. This electron pulse is then amplified and counted.
Balzers Electron Multiplier
Isotopic measurements to determine:

The use of TIMS to measure Plutonium isotopes provides low-level quality data.

<table>
<thead>
<tr>
<th></th>
<th>Alpha Detection Limit</th>
<th>DOE mandated Detection Limit</th>
<th>TIMS Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>239Pu in Urine</td>
<td>0.01 pCi</td>
<td>0.00035 pCi</td>
<td>0.00015 pCi</td>
</tr>
</tbody>
</table>

TIMS capabilities include the independent analysis of 239Pu and 240Pu, allowing us to calculate their concentration levels (Alpha counting can not differentiate between 239Pu and 240Pu). These two isotopes are used in conjunction with 238Pu values acquired from Alpha counting to monitor plutonium worker exposure levels and to determine the source of the exposure. The measured 240Pu / 239Pu isotopic ratio of the sample can be compared to the established isotopic ratios and their source.

**Known 240Pu / 239Pu Isotopic Ratios and Their Source**

- ~0.06 (6%) = Weapons Grade Plutonium
- ~0.18 (18%) = Natural Fallout from Atmospheric Testing
- ~0.30 (30%) = Reactor Grade Plutonium
- ~0.01% (1%) = WWII era Plutonium
Data Verification:

Use of Loading Blanks to validate cleanliness of TIMS sample loading

- Analyzed on each instrument bimonthly
- (99.99%) $^{242}\text{Pu}$ tracers used to monitor sample loading for $^{239}\text{Pu}$ and $^{240}\text{Pu}$ contamination.

Use of CBNM U standards to validate instrument performance, detection limits, dead time corrections, and background/baseline corrections.

- Analyzed a minimum of every 3 months
- Validate instrument performance and qualify data
- Measured isotopic ratios within 5% of the certified ratios are acceptable; however, our measured values are well within 1% of the certified ratios.
CBNM Uranium Standard Data
Fractionation/Mass Unit = 0.0016 ± 0.00083
Average $^{239}$Pu Atoms = $1.3 \times 10^5 \pm 4 \times 10^4$
Derived from Loading Blank Measurements
Instrument Detection Limit = $150 \mu$Ci = $0.00015$ pCi = $6 \times 10^6$ Atoms
Average $^{240}\text{Pu}$ Atoms = $4.5\times10^4 \pm 5.0\times10^4$
Derived from Loading Blank Measurements
Instrument Detection Limit = 500 aCi = 0.00050 pCi = $5.5\times10^6$ Atoms
This one time, at Band Camp......
Welcome to the Bioassay Project Team Homepage

DOE regulations require routine bioassay monitoring for all workers who have a reasonable potential for intakes of radioactive materials. Prompt and accurate information about potential or actual employee exposure is necessary to accurately assess does equivalent quantities associated with those intakes.

Individuals are monitored for work related intakes through a series of routine and special bioassay measurements. The bioassay program includes both direct (in vivo) and indirect (in vitro) measurements. The C Division Bioassay Project provides radio-analytical services in support of the in vitro (materials removed from the body) portion of the LANL internal dosimetry program, managed by ESH Division.

C Division has committed to providing analytical data of the highest quality within rigid time-frames specified by the customer. Three groups within the division provide integrated/cooperative radio-analytical support for the analysis of plutonium, americium and uranium by alpha-spectroscopy; plutonium by thermal ionization mass spectrometry; and tritium by liquid scintillation. The C Division Bioassay Project team responds to crisis sample requests to provide quick and reliable information to potentially exposed workers -- both a legal and moral obligation. State-of-the-art equipment, procedures, and dedicated personnel allow the C Division Bioassay Project team to set the standard for radio-bioassay in the DOE complex.
The Sample Management Office (SMO) accepts LANL Bioassay Project samples for login and distribution to the analysis laboratories. Customer and Quality Control (QC) sample information are entered into the Laboratory Information Management System. After login a service agreement customer report and a chain of custody are generated. Paperwork and samples are then delivered to the appropriate analysts. Approximately 5,000 samples along with appropriate QC are processed yearly.
Sample Receiving and Preparation
Sample Management Office
Sample Receiving Quality Control

Analytical Processes
Thermal Ionization Mass Spectroscopy
TIMS Sample Preparation
Alpha-Spec Pu Sample Preparation - Separation
Alpha-Spec Pu Sample Preparation - Electroplating
Plutonium Analysis by Alpha-Spectrometry

Other Links
Project Documentation

The C-ACS group provides QA/QC support to the Bioassay Project. They are responsible for the preparation and assignment of spikes and blanks for all of the analyses conducted for the Bioassay Project. Additionally, they evaluate the QC sample performance and have final approval authority for data packages generated from all Bioassay analysis. The QC program prepares approximately 1,000 QC samples per year.

The C-ACS group provides QA/QC support to the Bioassay Project. They are responsible for the preparation and assignment of spikes and blanks for all of the analyses conducted for the Bioassay Project. Additionally, they evaluate the QC sample performance and have final approval authority for data packages generated from all Bioassay analysis. The QC program prepares approximately 1,000 QC samples per year.
The solution is electroplated onto a rhenium filament, which is inserted into the ion source of the mass spectrometer. A current is passed through the filament, which causes the plutonium isotopes in the sample to ionize. The ions are accelerated through a magnetic field, resulting in separation of the ions by mass, with heavier ions having more momentum. An electron multiplier allows the number of ions of each isotope to be counted. The amount of Pu-239 in the original sample is calculated by comparing the number of those ions to those resulting from a known amount of Pu-242 spike. The Pu-242 tracer was added to the sample prior to electroplating. These operations are conducted in a Clean Room environment, and there are two mass spectrometers available for sample analysis. The nominal detection limit for this analytical method is 0.5 fCi/l. Approximately 1,000 samples, plus QCs, are analyzed per year for the LANL Bioassay Project.
Sample Receiving and Preparation
Sample Management Office
Sample Receiving Quality Control

Analytical Processes
Thermal Ionization Mass Spectroscopy
TIMS Sample Preparation
Alpha-Spec Pu Sample Preparation - Separation
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Plutonium Analysis by Alpha-Spectrometry

Other Links
Project Documentation
Bioassay Homepage

All chemistry done to support the preparation of the TIMS samples is conducted in a clean room environment. The stainless steel planchette from alpha-spectroscopy analysis is washed with a hydrofluoric/nitric acid solution to remove the plutonium. The plutonium solution is passed through an anion exchange column and the plutonium is eluted from the column by addition of a hydrochloric/hydroiodic acid solution. The sample is evaporated to dryness and re-dissolved in a hydrochloric acid/peroxide solution. The sample is loaded on a second anion exchange column and plutonium is eluted from the anion exchange column with hydrobromic acid, into a pre-cleaned quartz test tube. Approximately 1,500 samples per year are processed for TIMS analysis.
The preparation of samples for analysis of plutonium by alpha-spectroscopy is performed in a clean room environment to minimize background levels. The sample is treated with calcium phosphate to precipitate the plutonium from solution. The sample is centrifuged, and the supernatant liquid decanted and discarded, leaving the precipitated plutonium solids. The solids are then dissolved in 8M nitric acid and heated to convert all of the plutonium to the +4 valence state. Approximately 3,000 samples, including spikes and blanks, per year are prepared for alpha-spectroscopy analysis.
The nitric acid solution is passed through an anion exchange column. The plutonium is eluted from the column with a hydrochloric/hydroiodic acid solution. The solution is evaporated to dryness. The sample is re-dissolved in a sodium sulfate solution and electroplated onto a stainless steel planchette. Approximately 3,000 samples per year are prepared for alpha-spectroscopy analysis.
The electroplated samples are analyzed and quantified by alpha-spectrometry. The samples are counted for 70,000 seconds on passivated ion-implanted junction silicon detectors, which provide an average energy resolution of 16 keV FWHM, allowing the activities of Pu-238 and Pu-239/240 to be determined based on chemical recovery of the Pu-242 tracer. The C-INC counting facility has dedicated 48 individual counting chambers to the LANL Bioassay Project. The nominal detection limit for Pu-238 and Pu-239/240 is less than 10 fCi/sample. This operation analyzes in excess of 3,000 samples per year for the LANL Bioassay Project.
# Certificate

## Standard Reference Material 4334E

### Radioactivity Standard

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Plutonium-242</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source identification</td>
<td>4334E</td>
</tr>
<tr>
<td>Source description</td>
<td>Liquid in flame-sealed NIST borosilicate-glass ampoule</td>
</tr>
<tr>
<td>Solution mass</td>
<td>Approximately 5.8 grams</td>
</tr>
<tr>
<td>Solution composition</td>
<td>Plutonium-242 in 5 mol-L⁻¹ nitric acid</td>
</tr>
<tr>
<td>Reference time (Purification time)</td>
<td>1200 EST, 18 December 1989</td>
</tr>
</tbody>
</table>

### Radioactivity Concentration

26.37 Bq·g⁻¹

### Overall uncertainty

1.12 percent

### Radionuclidic Impurities

See Table 1

### Half-life

(3.733 ± 0.012) x 10⁹ years

### Measuring Instrument

Two 4π liquid-scintillation counters, a calibrated germanium detector system, and a silicon surface-barrier detector

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This standard reference material was prepared in the Physics Laboratory, Ionizing Radiation Division, Radioactivity Group, L.M. Robins Hutchinson, Acting Group Leader.

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Gaithersburg, MD  
January 1993

William P. Reed, Chief  
Standard Reference Materials Program

*Notes on back*
Approximately five milliliters of solution. Ampoule specifications:

- Body diameter: 16.5 ± 0.5 mm
- Wall thickness: 0.60 ± 0.04 mm
- Barium content: less than 0.05 percent
- Lead content: less than 0.02 percent
- Other heavy elements: trace quantities

Solution density is 1.170 ± 0.001 gm/mL at 21.65 °C.

The overall uncertainty was formed by taking three times the quadratic combination of the standard deviations of the mean, or approximations thereof, for the following:

- a) Alpha-particle-emission-rate measurements
- b) Background
- c) Lifetime
- d) Detection efficiency
- e) Count-rate-vs-energy extrapolation to zero energy
- f) Half life
- g) Gravimetric measurements
- h) Radioisotopic impurities

Values for $^{239}$Pu + $^{241}$Am and for $^{239}$Pu + $^{240}$Pu were calculated based upon measurements performed at the Lawrence Livermore National Laboratory (LLNL) shortly after purification of the $^{239}$Pu in December of 1989. Values for $^{238}$Pu + $^{240}$Pu and for $^{240}$Pu were calculated based upon measurements performed at the National Institute of Standards and Technology (NIST) in August of 1990.

Evaluated Nuclear Structure Data File (ENSDF), February 1990.

For further information please contact Dr. Larry Lucas at NIST.
Telephone: (301) 975-3546
FAX: (301) 926-7416
## TABLE 1

**RELATIVE ACTIVITY OF RADIONUCLIDIC IMPURITIES AT REFERENCE TIME**

**1200 EST, 18 DECEMBER 1989**

<table>
<thead>
<tr>
<th>RADIONUCLIDE</th>
<th>HALF LIFE (YEARS)</th>
<th>RELATIVE ACTIVITY AS DETERMINED BY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>LLNL</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>87.74 ± 0.04 <em>(a)</em></td>
<td>$^{238}\text{Pu} + ^{241}\text{Am}$</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>24119 ± 26 <em>(b)</em></td>
<td>$^{239}\text{Pu} + ^{240}\text{Pu}$</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>6570 ± 6 <em>(b)</em></td>
<td>$&lt;0.000,003$ <em>(c)</em></td>
</tr>
<tr>
<td>$^{241}\text{Pu}$</td>
<td>14.35 ± 0.10 <em>(d)</em></td>
<td>———</td>
</tr>
<tr>
<td>$^{242}\text{Pu}$</td>
<td>37300 ± 1200 <em>(d)</em></td>
<td>1.000 000</td>
</tr>
<tr>
<td>$^{244}\text{Am}$</td>
<td>432.2 ± 0.5 <em>(e)</em></td>
<td>$^{238}\text{Pu} + ^{241}\text{Am}$</td>
</tr>
</tbody>
</table>

*(a)* Reference time is the time of purification of the plutonium-242.

*(b)* Evaluated Nuclear Structure Data File (ENSDF), February 1990.

*(c)* Using alpha-particle spectrometry, no alpha-particle emission was detected that could reliably be ascribed to these radionuclides. The value shown is an estimated upper limit based upon background and counting statistics.

*(d)* The plutonium-241 relative activity at reference time was calculated from a gamma-ray measurement of the americium-241 ingrowth as of 18 August 1990.
Isotopic Reference Material CBHM IRM 072/1-15

Uranium Isotopic Reference Material for Testing Isotope Mass Spectrometers

The IRM set is supplied with atomic isotope ratios certified as:

<table>
<thead>
<tr>
<th>Code number CBNM-</th>
<th>Atomic isotope ratios</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{233}\text{U}/^{235}\text{U}$ ($\pm 0.03%$ of value)</td>
<td>$^{233}\text{U}/^{238}\text{U}$ ($\pm 0.03%$ of value)</td>
</tr>
<tr>
<td>072/1</td>
<td>1.000 33</td>
<td>0.991 36</td>
</tr>
<tr>
<td>072/2</td>
<td>0.699 67</td>
<td>0.693 85</td>
</tr>
<tr>
<td>072/3</td>
<td>0.499 85</td>
<td>0.495 91</td>
</tr>
<tr>
<td>072/4</td>
<td>0.299 87</td>
<td>0.297 63</td>
</tr>
<tr>
<td>072/5</td>
<td>0.100 014</td>
<td>0.099 313</td>
</tr>
<tr>
<td>072/6</td>
<td>0.050 091</td>
<td>0.049 746</td>
</tr>
<tr>
<td>072/7</td>
<td>0.019 994</td>
<td>0.019 857</td>
</tr>
<tr>
<td>072/8</td>
<td>0.010 165</td>
<td>0.010 095</td>
</tr>
<tr>
<td>072/9</td>
<td>0.005 000 0</td>
<td>0.004 966 0</td>
</tr>
<tr>
<td>072/10</td>
<td>0.002 001 2</td>
<td>0.001 987 6</td>
</tr>
<tr>
<td>072/11</td>
<td>0.000 968 92</td>
<td>0.000 962 34</td>
</tr>
<tr>
<td>072/12</td>
<td>0.000 500 88</td>
<td>0.000 497 48</td>
</tr>
<tr>
<td>072/13</td>
<td>0.000 101 82</td>
<td>0.000 101 13</td>
</tr>
<tr>
<td>072/14</td>
<td>0.000 019 996</td>
<td>0.000 019 860</td>
</tr>
<tr>
<td>072/15</td>
<td>0.000 001 999 5</td>
<td>0.000 001 985 9</td>
</tr>
</tbody>
</table>

The IRM set is intended to verify and correct non-linearity of the entire mass spectrometer measurement system.
Notes

1. All uncertainties indicated are accuracies, computed on a 2s basis.

2. The atomic masses, used in the calculations, are:
   
   \[
   \begin{align*}
   233\text{U} & : 233.0396280 \pm 0.0000060 \\
   234\text{U} & : 234.0409468 \pm 0.0000048 \\
   235\text{U} & : 235.0439242 \pm 0.0000048 \\
   236\text{U} & : 236.0455627 \pm 0.0000046 \\
   238\text{U} & : 238.0507847 \pm 0.0000046
   \end{align*}
   \]

3. The Reference Material consists of a uranyl nitrate solution. The amount of U per unit is 1.00 ± 0.02 mg contained in a 1.00 ± 0.02 ml solution.

4. The IRM solution has a molality of 6 m HNO₃ (i.e. 6 mol HNO₃ · kg⁻¹ of solvent) or a molarity of 5 M HNO₃ (i.e. 5 mol HNO₃ · l⁻¹ of solution).

Chemical purification of the ²³³U₂O₈, ²³⁵U₂O₈ and ²³⁸U₂O₈ starting materials was performed by Willy Lycke. Preparation of the IRM set was performed by Frans Hendrickx and Willy Lycke. Characterization of the enriched isotopes from which the set was prepared, was performed by René Damen and Kevin Rosman. Verification measurements on the mass spectrometer were done by René Damen.

The overall technical coordination of the establishment of the IRM set was performed by Willy Lycke.

B-2440 Geel
September 1986

Paul De Bièvre
Head
CBNM Mass Spectrometry