Improved Methodology for Assessing Workplace Uranium Intakes Based on Accelerator Mass Spectrometric Measurements of Uranium-236 (^{236}U)

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Lawrence Livermore National Laboratory

Acknowledgments

Title: **Improved Methodology for Assessing Workplace Uranium Intakes Based on Accelerator Mass Spectrometric Measurements of Uranium-236 (^{236}U)**

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Why an interest in uranium isotopes!

- Emerging needs in a number of different fields
  - Human Health
  - Nuclear Forensics
  - Environmental assessments

- Advances in measurement technologies especially in relation to the use of mass spectrometry

Chemistry, Materials and Life Sciences (CMELS)

MC ICP-MS system for low-level actinides measurement

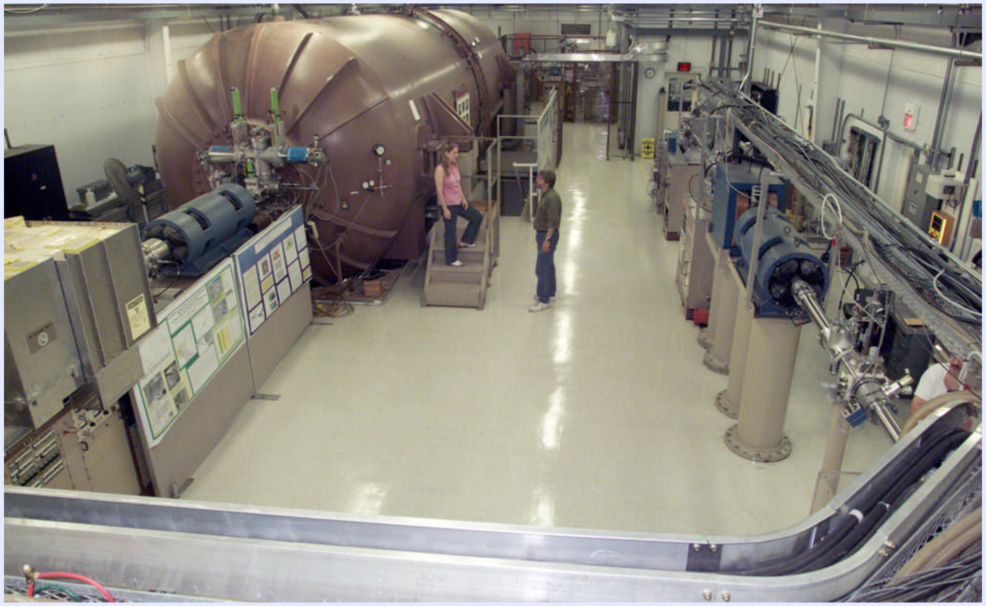
AMS Applications:

- Routine measurements of rare/stable isotope ratios, e.g., very well developed for $^{14}C/^{12}C$
- More recently demonstrated for long-lived radionuclides such as the actinides, ^{129}I, and ^{99}Tc
- AMS heavy-element line at LLNL was designed specifically for low-level detection of actinide elements and ^{129}I

Accelerator Mass Spectrometry at LLNL

Features of the heavy element AMS system at CAMS

- Rapid electrostatic switching between masses of interest
- High abundance sensitivity and a very wide dynamic range
- Simple chemistry and relatively high sample through-put (helps improve operational efficiency)
- AMS is a very robust measurement technique for actinide measurements with a very low susceptibility to interferences



HVEC Model FN Tandem Van de Graff accelerator operated at voltages up to 9 MV with gas or foil stripping

Uranium Isotopes in the Environment or Workplace

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Isotope	Natural Abundance (atom %)	Half-Life (years)	Origin
^{234}U	0.005	4.468×10^{5}	^{238}U decay chain
^{235}U	0.72	2.34×10^{7}	Primordal
^{238}U	99.27	7.038×10^{8}	Primordal
^{236}U	$\sim 10^{-10}$-10^{-12}	2.446×10^{5}	$^{235}U + 1n \rightarrow {}^{236}U$

Initial ^{236}U AMS Application to Bioassay Monitoring

- First sets of analyses performed in 2004
- Initial application of the technique included;
  - **20 Reagent Blank samples**
  - **17 urine samples from the radiation worker population**
    - **9 workers from 4 programs/operations**
    - **Known or potential workplace intake(s) of uranium**
  - **8 "Baseline" urine samples**
    - **8 workers from several LLNL programs**
    - **No current or recent uranium intake potential**
    - **Range of residential locations and ^{238}U-in-urine levels roughly similar to radiation worker population**

^{236}U content of reagent blank samples

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Data Table

Sample ID	^{236}U, ng per sample	1-σ
Reagent Blank_1	6.7×10^{-7}	2.9×10^{-7}
Reagent Blank_2	7.9×10^{-7}	2.8×10^{-7}
Reagent Blank_3	1.0×10^{-7}	1.1×10^{-7}
Reagent Blank_4	7.5×10^{-7}	2.7×10^{-7}
Reagent Blank_5	4.2×10^{-7}	1.9×10^{-7}
Reagent Blank_6	3.5×10^{-7}	1.8×10^{-7}
Reagent Blank_7	2.4×10^{-7}	1.7×10^{-7}
Reagent Blank_8	9.5×10^{-7}	2.9×10^{-7}
Reagent Blank_9	7.9×10^{-7}	3.0×10^{-7}
Reagent Blank_10	6.4×10^{-7}	2.9×10^{-7}
Reagent Blank_11	6.1×10^{-7}	2.9×10^{-7}
Reagent Blank_12	7.1×10^{-7}	2.9×10^{-7}
Reagent Blank_13	3.6×10^{-7}	2.2×10^{-7}
Reagent Blank_14	2.7×10^{-7}	2.4×10^{-7}
Reagent Blank_15	2.8×10^{-7}	2.4×10^{-7}
Reagent Blank_16	4.5×10^{-7}	2.4×10^{-7}
Reagent Blank_17	6.1×10^{-7}	2.5×10^{-7}
Reagent Blank_18	1.7×10^{-7}	2.2×10^{-7}
Reagent Blank_19	2.7×10^{-7}	2.1×10^{-7}
Reagent Blank_20	4.6×10^{-7}	2.4×10^{-7}

Summary Statistics

^{236}U Mean Value

$4.9 \pm 2.4 \times 10^{-7}$ ng per sample

AMS Limit of Detection

~7×10^{-7} ng ^{236}U

c/w

MCICP-MS Limits of Detection
~ 0.2 ng ^{238}U
~ 0.04 ng ^{235}U

^{236}U Results for the Initial LLNL Baseline Cohort

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Sample ID	^{236}U, ng per sample	1-σ	^{236}U, ng per gram	1-σ
Worker_01	1.7×10^{-7}	3.0×10^{-7}	1.8×10^{-9}	5.9×10^{-9}
Worker_02	4.6×10^{-7}	3.4×10^{-7}	8.2×10^{-9}	6.8×10^{-9}
Worker_03	3.6×10^{-7}	3.6×10^{-7}	6.7×10^{-9}	6.8×10^{-9}
Worker_04	3.5×10^{-7}	3.7×10^{-7}	3.8×10^{-9}	4.0×10^{-9}
Worker_05	1.2×10^{-7}	3.0×10^{-7}	1.2×10^{-9}	3.0×10^{-9}
Worker_06	2.6×10^{-7}	3.7×10^{-7}	4.6×10^{-9}	6.6×10^{-9}
Worker_07	1.3×10^{-7}	3.0×10^{-7}	2.4×10^{-9}	5.7×10^{-9}
Worker_08	3.9×10^{-7}	3.7×10^{-7}	5.0×10^{-9}	4.7×10^{-9}
Mean Value	**$2.8 \pm 1.3 \times 10^{-7}$**		**$4.2 \pm 2.4 \times 10^{-9}$**	

Notes:

1. **The associated ^{238}U concentrations ranged from ~0.3 to 20 ng per sample**

Preliminary ^{236}U Data on Bioassay Samples Collected from Radiation Workers at LLNL

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Sample ID	^{236}U, ng per sample	1-σ	^{236}U, ng per gram	1-σ
RadWorker_01	1.7×10^{-4}	6.7×10^{-6}	3.2×10^{-7}	1.3×10^{-7}
RadWorker_02	1.5×10^{-6}	5.5×10^{-7}	2.0×10^{-8}	7.4×10^{-9}
RadWorker_03	4.6×10^{-6}	7.5×10^{-7}	5.9×10^{-8}	9.6×10^{-9}
RadWorker_04	8.4×10^{-5}	3.9×10^{-6}	1.1×10^{-6}	4.9×10^{-8}
RadWorker_05	4.5×10^{-6}	7.5×10^{-7}	5.0×10^{-8}	8.5×10^{-9}
RadWorker_06	8.0×10^{-5}	5.1×10^{-6}	3.9×10^{-7}	2.5×10^{-8}
RadWorker_07	3.4×10^{-5}	2.7×10^{-6}	1.6×10^{-7}	1.3×10^{-8}
RadWorker_08	2.5×10^{-4}	9.1×10^{-6}	1.5×10^{-6}	5.3×10^{-8}
RadWorker_09	9.8×10^{-6}	1.2×10^{-6}	7.5×10^{-8}	9.0×10^{-9}
RadWorker_10	5.4×10^{-5}	3.0×10^{-6}	4.3×10^{-7}	2.3×10^{-8}
RadWorker_11	$<7.0 \times 10^{-7}$		$<4.0 \times 10^{-8}$	
RadWorker_12	6.3×10^{-6}	9.5×10^{-7}	3.1×10^{-8}	4.6×10^{-9}
RadWorker_13	1.6×10^{-5}	1.5×10^{-6}	5.8×10^{-8}	5.6×10^{-9}
RadWorker_14	2.7×10^{-6}	6.7×10^{-7}	3.2×10^{-8}	7.9×10^{-9}
RadWorker_15	1.3×10^{-4}	6.2×10^{-6}	1.6×10^{-6}	8.0×10^{-8}
RadWorker_16	3.8×10^{-5}	2.6×10^{-6}	1.9×10^{-7}	1.3×10^{-8}
RadWorker_17	4.9×10^{-5}	3.0×10^{-6}	6.1×10^{-7}	3.7×10^{-8}
Mean Value	**$5.8 \pm 7.1 \times 10^{-5}$**		**$4.1 \pm 5.3 \times 10^{-7}$**	

^{236}U versus ^{238}U Content of Selected Bioassay Samples Collected from Radiation Workers at LLNL

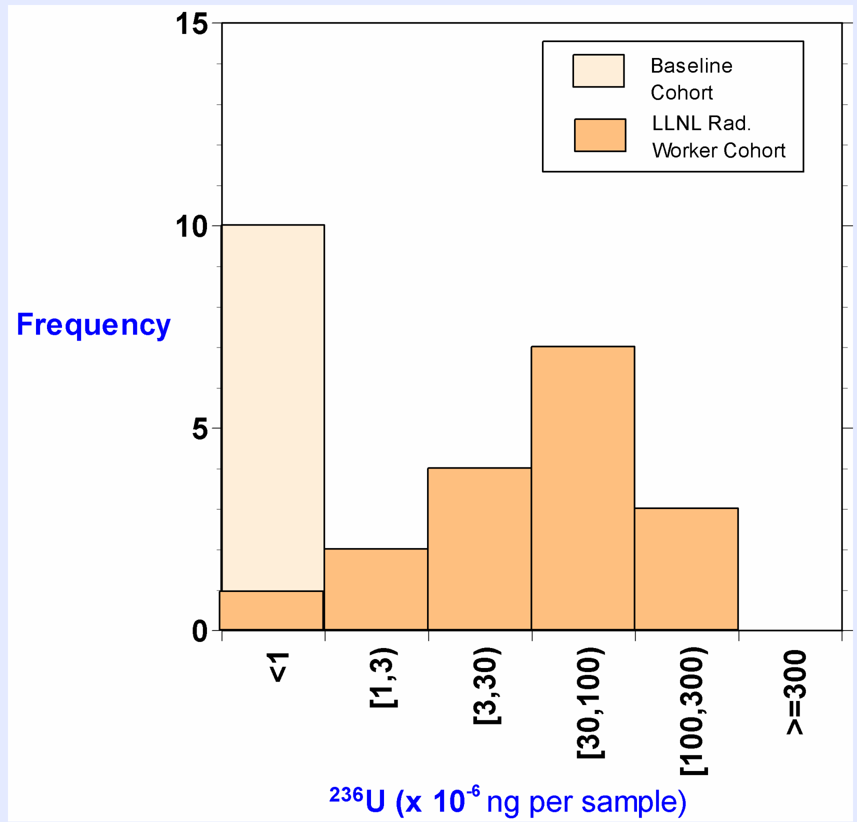
Sample ID	^{238}U, ng per sample (ICP-MS)	1-σ	^{236}U, ng per sample (AMS)	1-σ
RadWorker_01	7.17	0.14	1.7×10^{-4}	6.7×10^{-6}
RadWorker_02	ND		1.5×10^{-6}	5.5×10^{-7}
RadWorker_03	0.23	0.06	4.6×10^{-6}	7.5×10^{-7}
RadWorker_04	3.83	0.09	8.4×10^{-5}	3.9×10^{-6}
RadWorker_05	0.26	0.06	4.5×10^{-6}	7.5×10^{-7}
RadWorker_06	5.79	0.12	8.0×10^{-5}	5.1×10^{-6}
RadWorker_07	3.00	0.08	3.4×10^{-5}	2.7×10^{-6}
RadWorker_08	9.54	0.18	2.5×10^{-4}	9.1×10^{-6}
RadWorker_09	2.40	0.08	9.8×10^{-6}	1.2×10^{-6}
RadWorker_10	3.39	0.09	5.4×10^{-5}	3.0×10^{-6}
RadWorker_11	0.03	0.06	ND	
RadWorker_12	16.0	0.28	6.3×10^{-6}	9.5×10^{-7}

ND, not detected

What Do These Preliminary Measurements Show?

Main Points

- The ^{236}U content of bioassay samples collected from the LLNL radiation workers appears to be clearly elevated over those of the baseline cohort
- Data confirms that some workers have been previously exposed to an anthropogenic source of uranium containing ^{236}U



Subsequent Applications of ^{236}U Bioassay at LLNL

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- **2 additional AMS ^{236}U runs were performed during the period between 2005 and 2006**

2005 Measurements

I. 6 baseline samples (drinking water and urine)

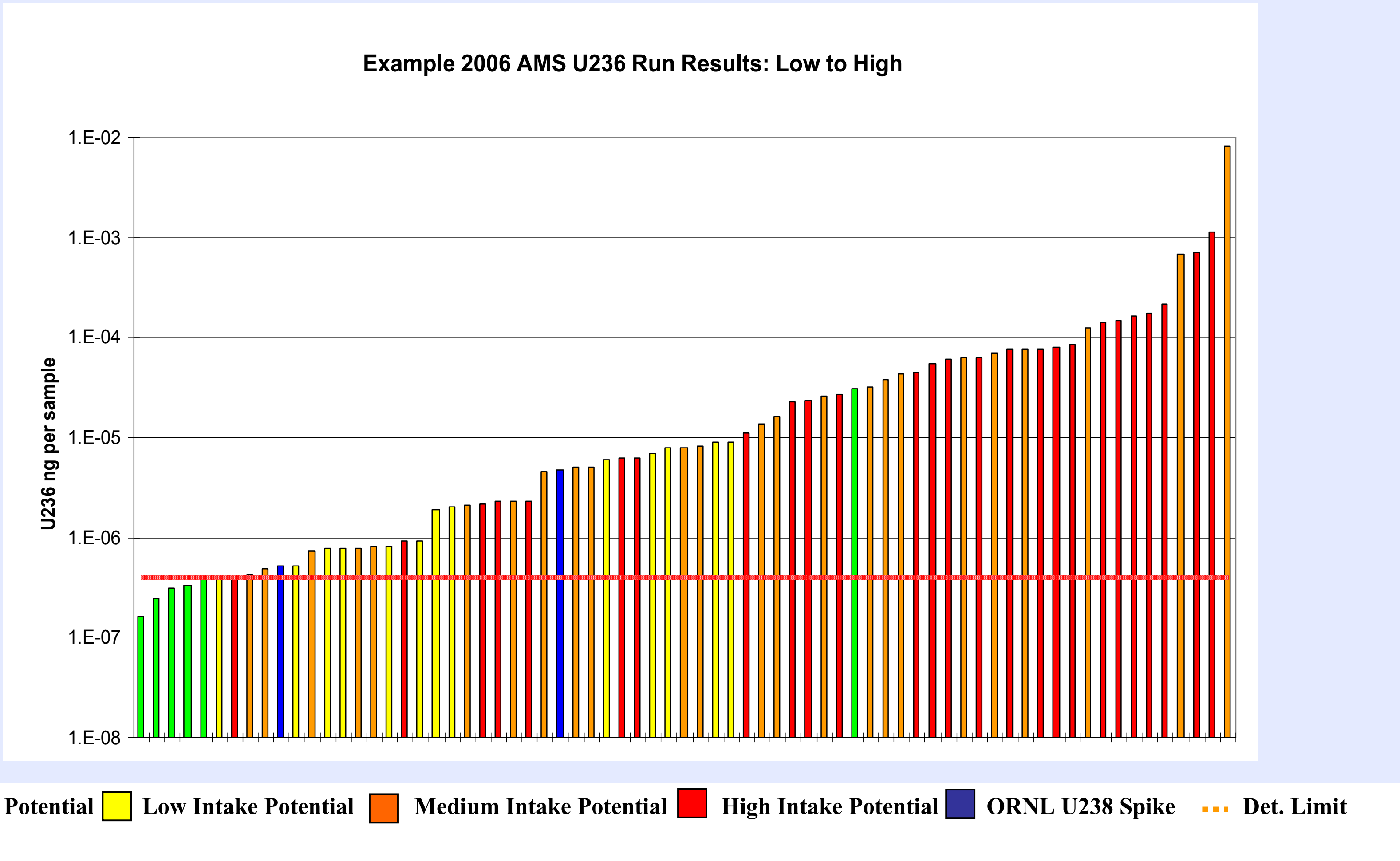
II. 54 radiation worker samples (30 workers, 3 programs)

2006 Measurements

I. 6 baseline samples (drinking water and urine)

II. 74 radiation worker samples (32 workers, 3 programs)

^{236}U Measurement Data from 2005 and 2006



Applications in ^{236}U Bioassay - Findings & Uses

- In general, the level of ^{236}U in bioassay samples increased with the relative exposure potential predicted by a workplace review in advance of the AMS analysis (one exception from 2006)

Applications in ^{236}U Bioassay - Findings & Uses

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- **The ^{236}U content of bioassay samples from the LLNL radiation worker cohort were useful for discerning relatively low-level occupational intakes in the presence of fluctuating environmental uranium excretion rates**

Examples;

- **^{238}U in urine levels from the radiation worker cohort ranged from 0.02 to 1.2 ug/L within same year, while the associated $^{234}U/^{238}U$ ratios were within the expected environmental range**
- **The ^{236}U content of such bioassay samples were often comparable across co-workers performing similar operation(s) with the same relative exposure potential (even in the presence of large variations in the total uranium content of samples)**

Applications in ^{236}U Bioassay - Findings & Uses

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- The ^{236}U excretion rates/patterns and ^{236}U:^{238}U ratios (for operations involving the same and/or very similar uranium source terms), combined with worker ^{238}U excretion history and workplace information, can be used to identify:

  - **The presence of multi-intake scenarios;**
  - **Previously unrecognized intake potential within specific operations and worker handling practices; and**
  - **Material bio-solubility information**

Summary Points

- AMS offers a robust measurement technique for low-level detection of ^{236}U in bioassay samples in the presence of fluctuating amounts of environmental uranium
- The application of ^{236}U in bioassay studies appears to offer new opportunities for improving the standard of occupational safety and risk management at LLNL or elsewhere around the DOE complex
- ^{236}U is a potentially a useful 'fingerprint' for assessing the presence of anthropogenic sources of uranium (to include reprocessed, DU or enriched uranium) either inside the human body or in the environment

Thank you for your attention

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