NBL-383
September 2006

MEASUREMENT EVALUATION PROGRAM MEETING MINUTES

NEW BRUNSWICK LABORATORY

RENAISSANCE HOTEL
NASHVILLE, TN

JULY 15, 2006

U.S. DEPARTMENT OF ENERGY • CHICAGO OFFICE • ARGONNE, ILLINOIS

NBL- 383

U.S. DEPARTMENT OF ENERGY

MEASUREMENT EVALUATION PROGRAM MEETING MINUTES

Renaissance Hotel
Nashville, TN.

JULY 15, 2006

NEW BRUNSWICK LABORATORY
9800 South Cass Avenue
Argonne, Illinois 60439

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NBL: HISTORY AND MISSION

The New Brunswick Laboratory (NBL) is owned and operated by the United States Department of Energy through the Office of Security and Safety Performance Assurance (SP-1) and the Office of Technology and Field assistance (SP-30). The laboratory was established in 1949 as an analytical chemistry laboratory in New Brunswick in New Jersey to provide support to the United States Atomic Energy Commission. At that time, it was staffed by scientists from the National Bureau of Standards who had contributed significantly to nuclear material measurement programs in the Manhattan Project. At the New Brunswick Laboratory, they provided the technical expertise and skills to solve problems related to quantitative analyses of uranium-bearing materials. Over the years, these scientists and others following them have expanded the capabilities of the laboratory to include chemical and mass spectrometric analyses of plutonium and other trans-uranium elements, research and development activities in chemical analyses techniques, preparation of certified reference materials, and operation of the nuclear safeguards measurement evaluation program. In 1977, the laboratory moved from New Jersey to its present location at the Argonne National Laboratory site in Illinois.

The major mission of the New Brunswick Laboratory is to provide technical assistance to the Department of Energy in the following areas: measurement evaluation program operation, certified (nuclear) reference materials preparation, measurement techniques development, and actual measurements of special nuclear materials. In addition to fulfilling these tasks, the laboratory helps the Department in three other areas: conducting technical audits, resolving shipper/receiver differences in material transfers, and assisting in nuclear nonproliferation programs within the United States and internationally.

ACKNOWLEDGEMENTS

The organizers of the ME Program Meeting thank the speakers who delivered the technical talks, and the attendees for keeping the proceedings lively. The meeting was successfully organized only because of the efforts expended by several staff at NBL and INMM, and the support received from DOE-HQ.

INTRODUCTION

The New Brunswick Laboratory (NBL) Measurement Evaluation (ME) Program was initiated in 1985 to assess and evaluate the adequacy of measurement technology as applied to materials accounting. In the beginning stages, the Department of Energy facilities alone participated in the measurement evaluation programs. Later on, laboratories outside the DOE complex were permitted to join on a cost-recovery basis. The current program consists of the Safeguards Measurement Evaluation (SME) program for the evaluation of destructive analyses results of uranium and plutonium bearing materials, and the Calorimetric Exchange (CALEX) program for the evaluation of non-destructive analyses results of plutonium materials. The uranium and plutonium test materials used in the SME program are made from certified reference materials or other well characterized materials. The participating laboratories analyze these materials at periodic intervals for elemental content and isotopic abundance. The results of those analyses are evaluated by NBL for accuracy and precision achieved in the analyses. Performance evaluation reports are sent to the participants and their oversight organizations/agencies. In the CALEX program, laboratories analyze repeatedly plutonium oxide standards (Calex I and Calex II) by a combination of two different non-destructive techniques; calorimetry for power measurements and high resolution gamma spectrometry for plutonium isotopes and ^{241}Am abundance. The results for power, isotopes abundance, effective specific power and plutonium mass are evaluated for accuracy and precision.

The evaluation results from the SME and the CALEX programs are discussed once a year at the measurement evaluation program annual meeting. The meeting is usually held a day prior to the start of the International Nuclear Material Management (INMM) annual meeting and at the same venue. This year, the meeting was held on July 15th at the Renaissance Hotel in Nashville, Tennessee. The annual meeting provides an opportunity to the participants in the measurement evaluation program to discuss topics such as those related to measurement techniques, performance evaluation methods, measurement uncertainties, and new test material needs.

The 2006 meeting was held in two half-day sessions, the morning session devoted to destructive analyses and the afternoon to non-destructive analyses. The agenda for the 2006 meeting is shown in page 5.

SYNOPSIS

Jon Neuhoff welcomed the attendees. Chino Srinivasan delivered the first talk that dealt with performance evaluation of destructive analyses results submitted during October 2004 – June 2006. Amy Wong spoke next on LANL facilities upgrade; her talk included an evaluation of the "100 minus impurities" method for plutonium assay. Elmer Lujan spoke on precision achieved in D&G titrations of uranium using Ce(IV) sulfate instead of potassium dichromate as the titrant. Steve Balsley provided an account of the operations of the Safeguards Analytical Laboratory at IAEA; he also spoke on the qualification of a robotic D&G titration system. It is noteworthy that he was able to use some of the SME test samples supplied by NBL in the qualification work. Stephan Richter summarized the results and conclusions of the REIMEP-18 campaign conducted by IRMM for uranium isotopes measurements. Jose Perrotta described the structure and purpose of the ABACC organization; in his talk, he spoke about the steady improvement made by ABACC laboratories in uranium assay and uranium isotope measurements. Jerome LaRosa spoke next, and gave an account of the NIST plans for a measurement evaluation programs in environmental radioactivity. The last paper in the morning session by Peter Mason was delivered as the first talk in the afternoon session. In the remaining time in the morning session, the participants discussed some of the problems and concerns in Calex I and Calex II standards measurement; the discussion was initiated by Mark Mount of LLNL with active participation by many attendees. The importance of defining ^{241}Am abundance in calorimetric standards with high accuracy and precision, and the use of appropriate half-lives of plutonium and americium isotopes (e.g., ASTM values) for making decay corrections were emphasized.

The afternoon session started with introductory remarks by Usha Narayanan of NBL. Peter Mason gave a talk on high accuracy measurements of minor isotope ratios of uranium and plutonium by a modified total evaporation method using TIMS. Chino Srinivasan gave a talk on the evaluation of cal/gamma measurement results of Calex I standards gathered during January 2005- December 2005; his talk also included NBL efforts in preparing a working reference material certificate for the Calex II standard to be issued in September 2006. The next three talks were given by Bud Summers of LLNL. Since LLNL placed some restrictions in incorporating the slides from these talks into the minutes, only short abstracts of the talks, as provided by the authors, are included. Peter Santi of LANL provided a review of new developments in three different non-destructive assay techniques; gamma spectrometry, calorimetry and neutron measurements. The concluding talk in the afternoon session was given by Roger Wellum; he spoke on the IRMM NUSIMEP campaign.

AGENDA

9:00 AM	Introductory Remarks	Jon Neuhoff, NBL
9:10 AM	SME Program: Uranium and Plutonium	B. Chino Srinivasan, NBL
9:30 AM	Present and Future Analytical Chemistry Measurements at Los Alamos	Amy Wong* and Laurie Walker, LANL
	Uranium Assay - Control and Precision Measurements	Elmer Lujan, LANL
10:00 AM	2005 SAL Summary; Qualification of Robotic Titration System for D&G Analysis of Uranium	Steven D. Balsley*, Josef Berger, Alfred Zoigner, IAEA
10:30 AM	The REIMEP 18 Inter-Laboratory Comparison for Measurements of Uranium Isotopic Ratios in Nitric Acid Solution	Stephan Richter, IRMM
11:00 AM	ABACC-NBL Collaboration	Jose Augusto Perrotta, ABACC
11:30 AM	Measurement Evaluation Programs in Environmental Radioactivity at NIST	Kenneth G.W. Inn, Lisa Outola, Svetlana Nour, Hiromu Kurosaki and Jerome J. La Rosa*, NIST
12:00 PM	High accuracy determination of minor isotopes in uranium and plutonium materials by thermal ionization mass spectrometry	Peter Mason*, Richard Essex, Steven Goldberg, Rebecca Thomas, and Stephan Richter[+], NBL
12:30 PM	Lunch Break	
2:00 PM	Introductory Remarks	Usha Narayanan, NBL
2:15 PM	CALEX Program & Calex 2 certification	B. Chino Srinivasan* and Usha Narayanan, NBL
2:45 PM	a Uranium Isotopic masses in 3013 containers filled with MOx	Bud Summers, LLNL
	b) Accuracy/precision of CRM uranium standards in two isotopic counters	
	c) Accuracy/precision of CALEX I and CALEX II) Urani plutonium standards in three isotopic counters	
4:00 PM	Some Recent Developments in Non-Destructive Assay Technologies	Peter Santi, LANL
4:15 PM	IRMM NUSIMEP 5 Campaign	Roger Wellum, IRMM
5:00 PM	Close of ME Program Meeting	

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GRAPHICS USED IN TALKS

The graphics (slides, pictures etc.) used in the presentation of the 2006 ME Program Meeting talks are included in the following pages. The graphics for the talks are shown in the same order as shown in the agenda. Note that no graphics were used in the two introductory remarks (by Jon Neuhoff and Usha Narayanan). Also no graphics were made available for the talks given by Bud Summers of LLNL.

NEW BRUNSWICK LABORATORY

Measurement Evaluation Program Annual Meeting

Safeguards Measurement Evaluation: Uranium and Plutonium

July 15, 2006
Nashville, TN.

B. Srinivasan

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Safeguards Measurement Evaluation Program: October 2004 – June 2006

Evaluations

- Uranium assay
- Uranium isotope abundance
- Plutonium isotope abundance

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Participants

- ABACC (6 labs in Argentina and 2 in Brazil)
- IAEA (new participant)
- INL
- IRMM (new participant)
- LANL
- NBL
- NFS
- SRS
- Tokai
- Y-12

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Test Samples

- Uranium Assay and Isotope Abundance
  - UNH solution
  - UO_2 pellet
  - UO_3 powder
  - UF_6
- Plutonium Assay and Isotope Abundance
  - Dried plutonium sulfate

Methods

- Uranium Assay
  - Davies-Gray titration
  - IDMS
  - XRF
- Uranium Isotope Abundance
  - TIMS
  - ICP-MS
  - GSMS
- Plutonium Isotope Abundance
  - TIMS

Analysis schedule

- Quarterly or semi-annual or annual
- Each sample in each cycle analyzed
  - At least on two different days
  - At least in duplicate on each day

Statistical Evaluation

- % RD of measurement result
- Outliers
- Day-to-day variation
- Mean % RD
- Standard deviation of mean % RD
- 95% C.L.
- Bias and precision ITVs

Quarterly Evaluation Report: Example

Day to Day ANOVA analysis
Report for Laboratory A
UNH Solution - U Concentration
IDMS
Date of Report: January 17, 2006

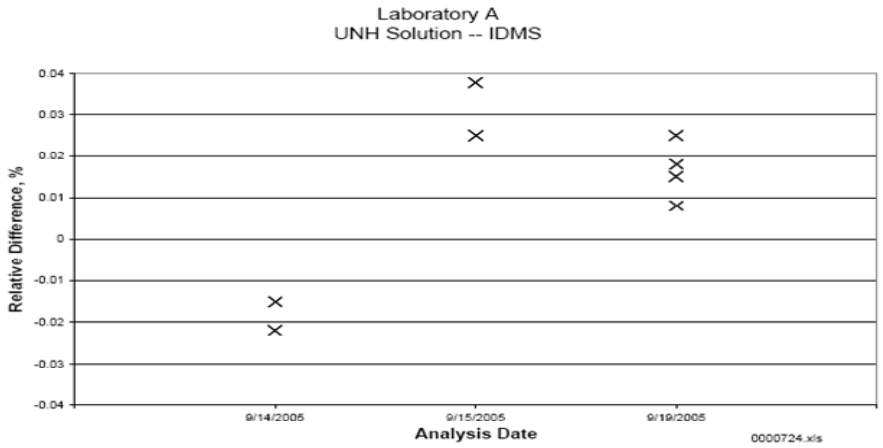
Sample Number	Aliquant Number	Analysis Date	Reported %U	% Relative Difference	Analyst Code
98NU0076-01-036	1	09/14/05	1.00040	-0.0150	BLM/GPW
98NU0074-01-042	1	09/14/05	1.00300	-0.1016 **	BLM/GPW
98NU0076-01-036	2	09/14/05	1.00040	-0.0150	BLM/GPW
98NU0074-01-042	2	09/14/05	1.00380	-0.0219	BLM/GPW
98NU0076-01-036	3	09/15/05	1.00080	0.0250	DLB/GPW
98NU0074-01-042	3	09/15/05	1.00500	0.0976 **	DLB/GPW
98NU0076-01-036	4	09/15/05	1.00080	0.0250	DLB/GPW
98NU0074-01-042	4	09/15/05	1.00440	0.0378	DLB/GPW
98NU0076-01-036	5	09/19/05	1.00080	0.0250	WS/GPW
98NU0074-01-042	5	09/19/05	1.00420	0.0179	WS/GPW
98NU0076-01-036	6	09/19/05	1.00070	0.0150	WS/GPW
98NU0074-01-042	6	09/19/05	1.00410	0.0060	WS/GPW

**This measurement value was rejected by the NBL statistical outlier evaluation program. The value is not included in the summary below.

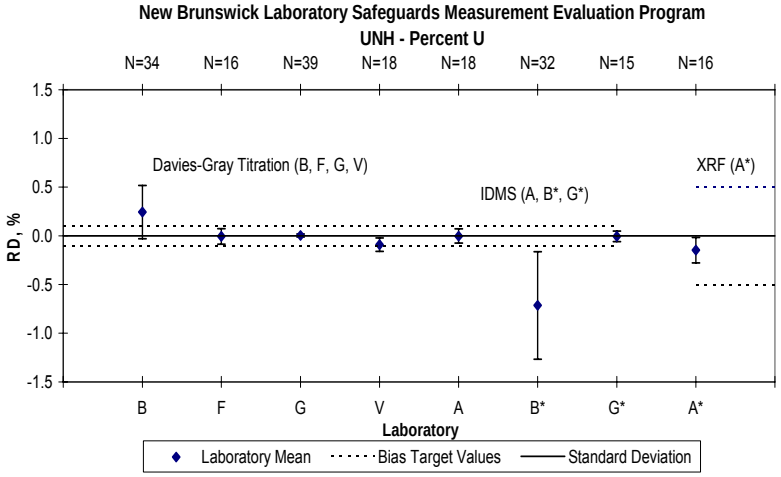
Quarterly Evaluation Report: Example (continued)

Number of Results Analyzed	10
Mean % Difference	0.010
Mean Absolute % Difference	0.021
95% C.L. of Mean (df = 2)	0.058
Standard Deviation	0.021
Between-Day Standard Deviation (df = 2)	0.042
Within-Day Standard Deviation (df = 7)	0.006
Statistical Significance of Between-Day Standard Deviation	100%

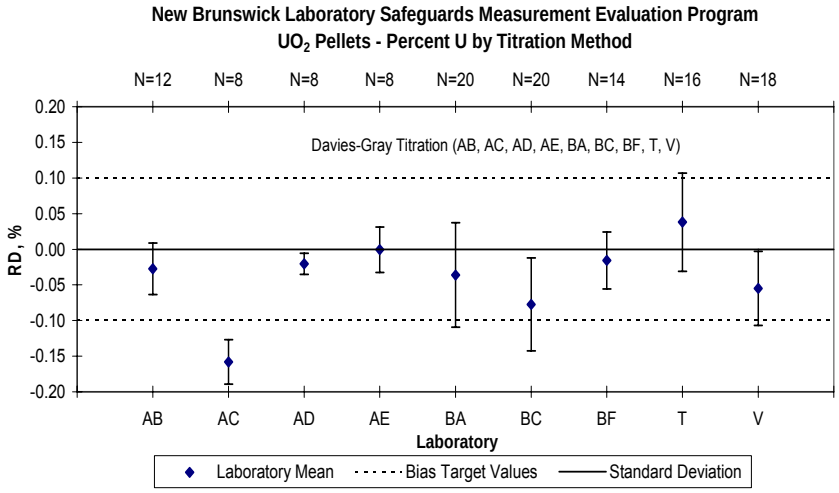
Quarterly Evaluation Report: Example (continued)



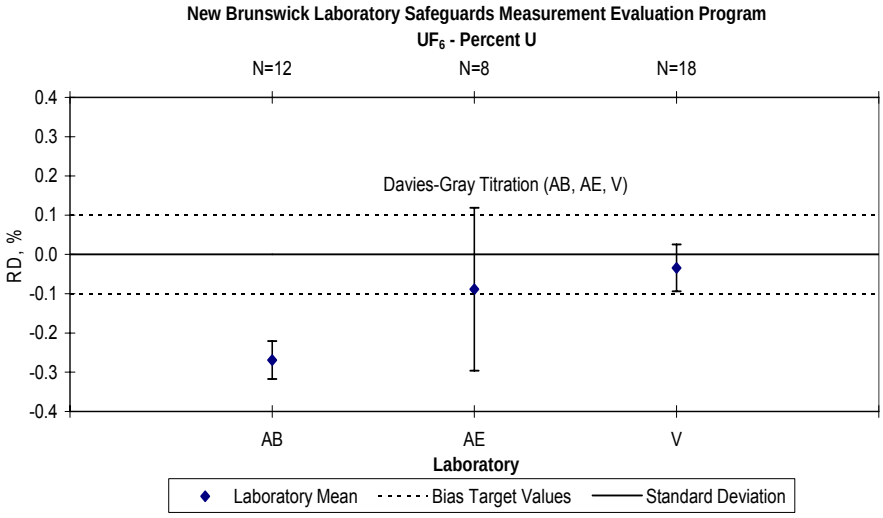
Results Evaluation: UNH Solution



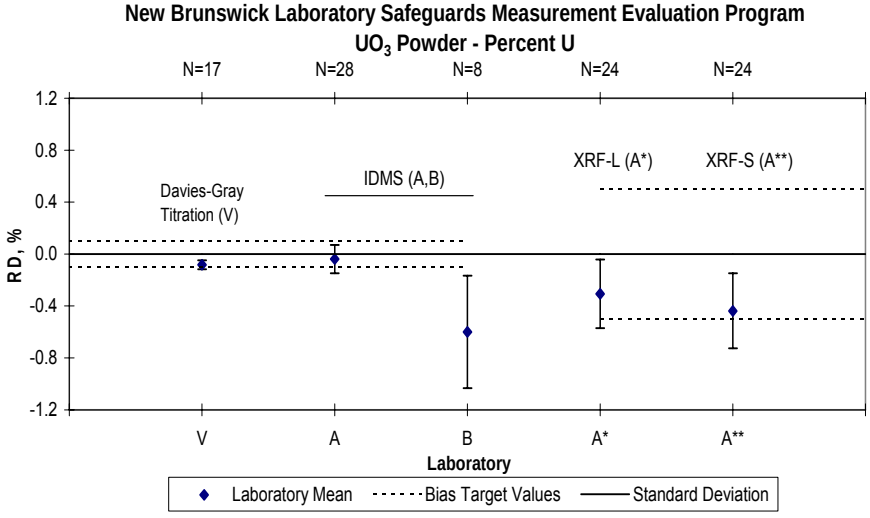
Results Evaluation: UO_2 Pellet



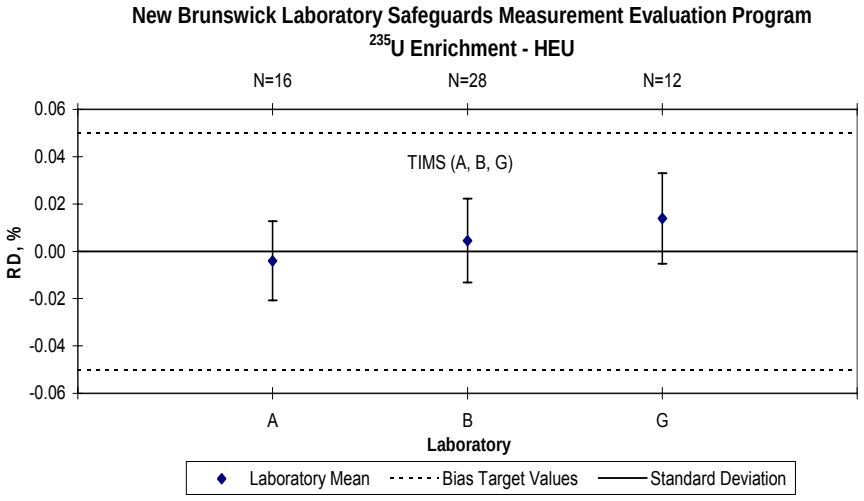
Results Evaluation: UF_6



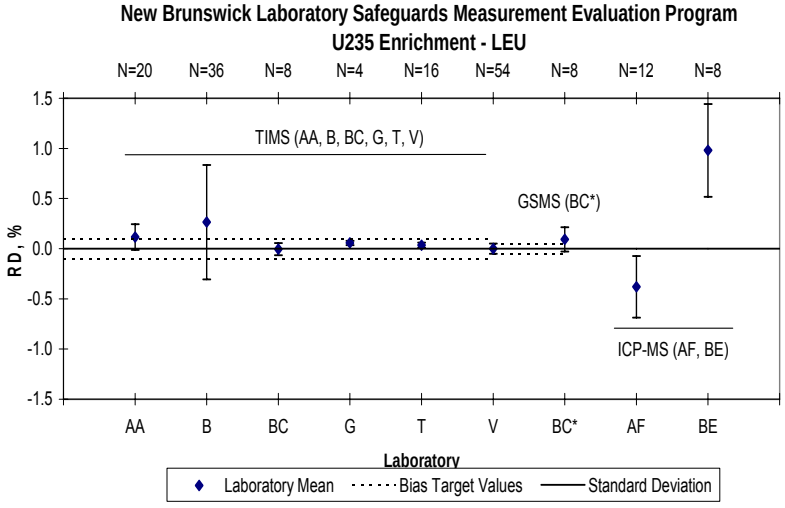
Results Evaluation: UO_3 Powder



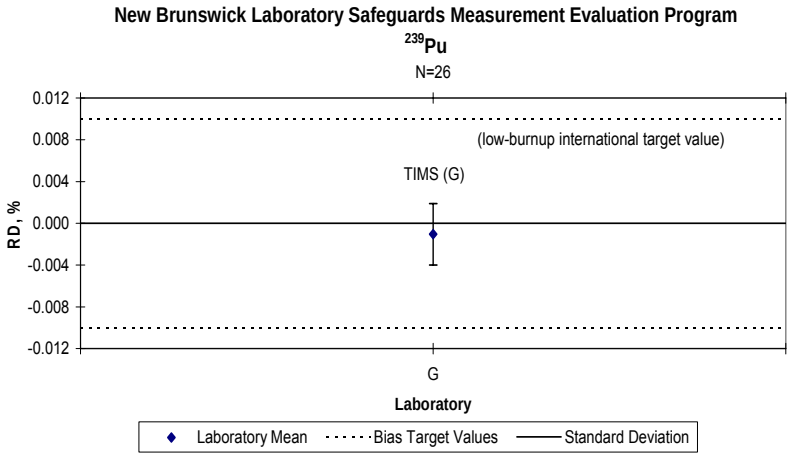
Results Evaluation: ^{235}U Abundance in HEU



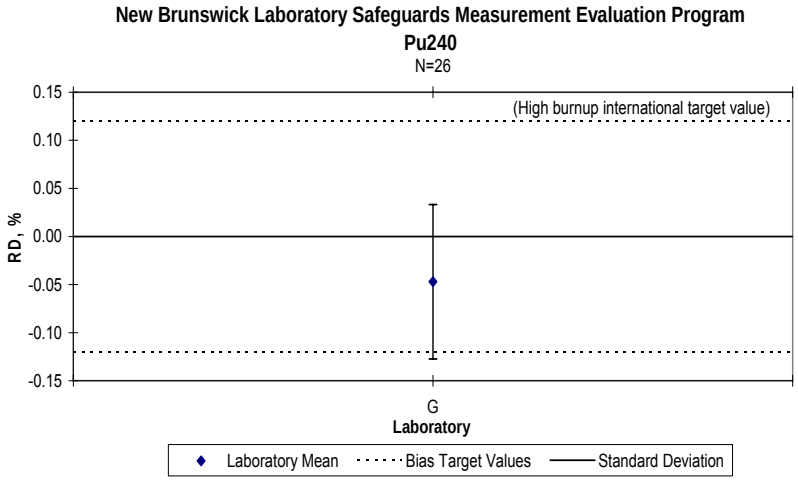
Results Evaluation: ^{235}U Abundance in LEU



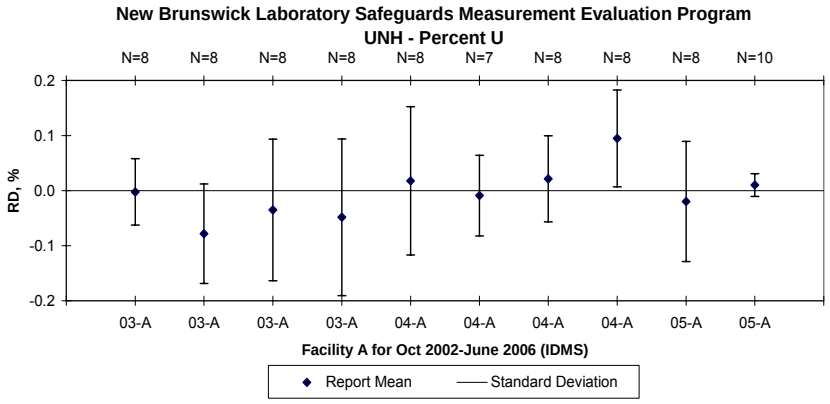
Results Evaluation: ^{239}Pu Abundance



Results Evaluation: ^{240}Pu Abundance



Long-term Evaluation: UNH Solution



Summary

Evaluation reports to:

- ABACC
- IAEA
- LANL
- NBL
- SRS
- Tokai
- Y-12

NEW BRUNSWICK LABORATORY

Summary (continued)

Measurement results yet to be submitted

- Laboratory J (instrument problem). Successfully solved. Results awaited

Test sample problem

- Laboratory A observed problems with UO_3 sample possibly due to moisture uptake. Needs re-characterization experiments at NBL

IDMS spike recovery

- Laboratory G noticed incomplete recovery of spike; successfully solved by addition of HF

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Concluding Remarks

New organization at NBL

- A-76
- PWS and MEO proposal: October 2004 – January 2006
- MEO declared winner: April 2006
- Organizational change: April – September 2006
- MEO new organization: October 2006
- Emphasis on two programs
  - Measurement Evaluation
  - Certified Reference Materials

Concluding Remarks (continued)

Safety inspection and audit

- Stand down of laboratory operations December 2004

Remedial measures

- Rewrite documents including DSA
- Decrease plutonium inventory (Safety Cat 2 to Cat3)
- Restart laboratory operation following thorough review of procedures

Expected date for full scale operation

- Uranium laboratories by December 2006
- Plutonium laboratories (yet to be determined)

ME Program Plans: July 2006- June 2007

- Minutes of 2006 Annual Meeting: issue August 2006
- Ship test samples to participants by October 2006
- Characterize one new test sample for uranium assay and uranium isotopics: August 2006
- Characterize UF_6 test samples for uranium assay: December 2006
- Characterize Brazil UO_2 test samples for uranium assay and uranium isotopics: December 2006
- Verify UO_3 powder test sample results: December 2006
- Develop new database application software: December 2006
- Evaluation reports to participants: within 3 weeks of receipt of results
- Annual report preparation: June 2007
- Re-start Plutonium laboratory operations: Work towards to re-start within 1 year!!!

Present and Future of Analytical Chemistry Measurements at Los Alamos

Amy S Wong and Laurie F Walker

NBL Measurements Evaluation Program Meeting
July 16, 2006
Nashville, TN

Outline

- Current Status
- Challenges
- Can we use "100 – impurities" for Pu Assay?
- Future direction for development

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Actinide Analytical Chemistry Group at Los Alamos National Laboratory

- The group was established in 1943 (Manhattan Project)
- Our focus is on analysis of samples in actinide matrices, including Pu and U assay, isotopic and trace impurities determinations in metals and oxides
- We provide full analytical service in Chemistry Metallurgy Research (CMR) Wings 3, 5 and 7 (~28,000 ft^2) and limited onsite analysis support in Plutonium Facility (~2,300 ft^2)
- Samples are shipped from the Plutonium Facility (TA-55) to the analytical laboratories in CMR building

Chemistry Metallurgy Research (CMR) Building

Completed in 1952. Houses analytical chemistry and material characterization capabilities in 550,000 ft^2 space

Provide full analytical capabilities for analyses of feed, product and waste

Process	Materials to be Analyzed
Disassembly	Metals, impure oxide from direct metal oxidation
Aqueous Purification	Purified oxide, process and waste solutions
Pyrochemical Processes	Metals from direct oxide reduction (DOR), molten salt extraction (MSE), electro-refinery process (ER), salt residues
Foundry	Cast metal
^{238}Pu Heat Source	Oxide, ceramic pellet, process and waste solutions
Advanced Actinide Fuel	Oxide, nitride, ceramic pellet
Facility Operations	Liquid waste analysis
Safeguards	Materials control and accountability
Standard Fabrication	Oxide, metal, and solution

Infrastructure Challenges

- Analytical Chemistry has 28,000 ft^2 laboratory space in 54 years old CMR building – contaminated and leaky infrastructure
- Facility availability is ~85% for normal business hours, i.e., frequent ventilation and power failure → interrupt sample preparation and instrument operations
- Authorization for operating CMR facility is scheduled to end in 2010
- The replacement buildings (CMR-R) will not be ready for occupying until 2009 and 2014

Technical and Production Challenges

- Establish interim analytical capabilities to provide surety of materials used in manufacturing and certification, and basic analytical chemistry support for the entire cycle of nuclear materials programs at Los Alamos
- Meet the production schedule and budget constraints

We must transform analytical chemistry, determine the analysis requirements for nuclear materials programs, and enable a responsive infrastructure

Can we use "100 – Impurities" instead of Pu Assay?

- In Pu Metal Exchange Program using well characterized metals and consensus values, we observed good agreement between Pu assay value and "100-impurities"

$$\text{Ratio} = \frac{\text{Pu (by chemical assay)}}{\text{Pu (100\% - } \sum \text{impurities)}}$$

- "Dirty Dozen Impurities"
  - Decay products – ^{241}Am, total U, ^{237}Np
  - Fe, Ga, Al, Ni, C, O, Si, W, Cr
- Other impurities
  - Ca, Mo, Mg, Cu, Ta, B, Mn, Zn, Zr, Th, Pb, Be, Sn, Ti, Cd

Pu Metal Exchange Data

(100-impurities) data independently verified the chemical Pu assay data

Metal 465, 4130.7 ppm total impurities (100% - impurities) = 99.587				
Ratio	4/01	8/01	3/03	3/04
Lab 1	0.999	0.999	1.001	1.000
Lab 2	0.992	0.988	1.002	0.999
Lab 3	1.003	1.003	0.999	0.984
Lab 4	0.999	1.001	1.001	
Lab 5	0.999	0.999	0.999	
Lab 6			0.999	0.999
Lab 7	1.000			

Metal D, 497.5 ppm total (100% - impurities) = 99.950		
Ratio	5/04	stdv of ratio
Lab 1	1.000	0.0001
Lab 2	1.002	0.0007
Lab 3	1.000	0.0017
Lab 6-1	0.999	0.0006
Lab 6-2	0.985	0.0014

Metal C, 6579.9 ppm total (100% - impurities) = 99.342		
Ratio	5/04	stdv of ratio
Lab 1	0.999	0.0005
Lab 2	1.004	0.0009
Lab 3	0.992	0.0017
Lab 6-1	1.006	0.0016
Lab 6-2	0.980	0.0056

Metal 442, 3172.0 ppm total impurities (100% - impurities) = 99.683				
Ratio	4/01	8/01	3/03	3/04
Lab 1	0.999	1.000	0.999	1.000
Lab 2	0.998	0.990	1.002	1.000
Lab 3	1.002	1.003	1.001	0.996
Lab 4	0.999	1.001	1.000	
Lab 5	1.000	0.999	1.000	
Lab 6			1.000	0.999
Lab 7	0.999			

Good Analytical Measurements

- If you are interested in the Pu value, analyze for Pu
- If you want to know the impurity levels of certain elements, analyze for the impurities

BONUS

The Pu assay value should be close to the (100% – impurities) if all impurities are accurately accounted for.

Goals for Future Analytical Chemistry Development and Improvements

- Provide analysis tools for production control at line and within the production facility
- Choose the right analysis tools and methods for manufacturing – analytical tolerance for current and future specifications
- Maintain high precision and accuracy reference methods for certain programs, standardization, and problem solving

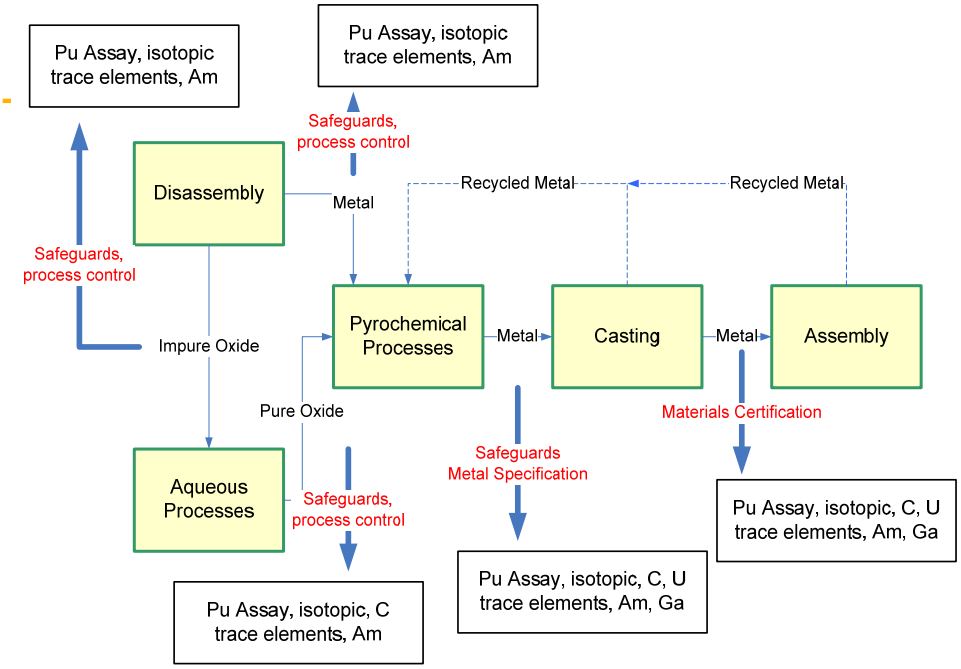
Key Considerations

- Customers' requirements – what are the required analyses? accuracy and precision?
- Must meet production schedule and budget constraints

- Improve safety
- Reduce residue and waste generation
- Reduce space requirements
- Reduce labor intensive steps
- Improve operations efficiency

Typical Precision and Accuracy for Selected Analytical Methods

Method	Matrix	Typical Conc.	Precision	Detection Limit
Pu Assay by Coulometry	Pu metal	>99%	0.07%	n/a
Pu Isotopic	Pu metal/Oxide	^{238}Pu	<10%	n/a
		^{239}Pu	0.002%	n/a
		^{240}Pu	0.010%	n/a
		^{241}Pu	0.8%	n/a
		^{242}Pu	1.2%	n/a
Trace Ga by IDMS	Pu metal	< 50ppm	0.5 to 1%	1.5 ppm @50mg
Trace Ga by ICP-AES	Pu oxide	< 50 ppm	20%	0.01ppm @250mg
Iron by Visible Spectrometry	Pu metal	300 to 400 ppm	7%	20 ppm
Iron by ICP-AES	Pu metal	300 to 400 ppm	10%	< 10 ppm



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Summary

- We must integrate the current and future analytical needs with the customers to
  - determine chemical analysis requirements based on technical evaluations
  - maintain analytical capabilities for production, certification and problem solving
- We are the only analytical laboratory in the US, who have full analysis capabilities to support the entire cycle of nuclear materials programs
- We must transform analytical chemistry in the next few years to improve our ability to support program goals and enable a responsive infrastructure

Mission Space Constraints
(NA-10 Sept 1, 2004. $850 M CMRR Project)

CHEMISTRY & METALLURGY RESEARCH REPLACEMENT

- Security Cat. 1, Hazard Cat. 2 Nuclear Facility (NF):
  - For analytical chemistry and materials characterization:
    - New CMRR NF – 22,500 ft^2
    - Existing Plutonium Facility – 5,400 ft^2
- Hazard Cat. 3, Radiological Laboratory (< 8.4 g ^{239}Pu):
  - CMRR RLUOB (Radiological Laboratory Utility Office Building)
    - Total space: 19,500 ft^2 (secured and open areas)
    - To support nuclear facility: 10,000 ft^2
    - Office space: 350 employees
    - Training center with classrooms and simulated laboratory space

Typical Laboratory Setup


Silicon analysis by spectrophotometry


Iron analysis by spectrophotometry


Thermal ionization mass spectrometry


Inductively-coupled atomic emission spectrometry (ICP-AES) at CMR and TA-55 Wavelength-dispersive x-ray fluorescence

Analytical Chemistry Development – FY07 and beyond (proposed)

- Assessment of analytical needs for Pit Manufacturing
- Feasibility study of centralization in sample preparation
- Micro column concept and chromatography separation
- Pu isotopic analysis by gamma spectroscopy
- Np trace analysis method
- Hand-held XRF – a quick diagnostic tool
- Work flow development for future operations
- Instrument interface with analytical data tracking - laboratory information management system (LIMS)
- Improve radiochemistry analysis for high Am residues

PRECISION AND CONTROL OF DAVIES AND GRAY PROCEDURE

2006 MEASUREMENT EVALUATION ANNUAL MEETING

Elmer Lujan

Kathy Garduno

Laurie Walker

Precision and Control of Davies and Gray Procedure (Modified)

- This Method is modified to use less sample material, 25 mg verses 100 mg and $Ce(SO_4)_2$ is substituted for $K_2Cr_2O_7$.
- This method is applicable to the determination of uranium compounds and solutions containing uranium with/without plutonium.
- Uranium is reduced to U(IV) by excess Fe(II) in strong phosphoric-sulfamic acid.

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Precision and Control of Davies and Gray Procedure (Modified) *(continued)*

- Excess Fe(II) is selectively oxidized by nitric acid in the presence of a Mo(VI) catalyst.
- V(IV) is added to sharpen the end point.
- U(IV) is titrated potentiometrically with cerium (IV) titrant to an end point of 600 mV.

Analysis of Sample and Standards

- Dissolve a 25 mg U sample aliquot that has been dried with 0.5 M H_2SO_4. in a 100 ml beaker.
- Place a stir bar into the beaker containing the sample aliquot or standard.
- Add 2 ml of 1.7 M sulfamic acid and turn on magnetic stirrer.
- Add 25 ml of reducing solution,(11.8 M H_3PO_4, 0.09 M $FeSO_4$, and 0.17 M H_2SO_4) stir solution for 60 s (solution is cloudy.)
- Add 5 ml of oxidizing solution,(8 M HNO_3, 0.24 M sulfamic acid, and 0.4% ammonium molybdate) wait an additional 3 m after solution clears.

Analysis of Sample and Standards (*continued*)

- Turn off stirrer and rinse the walls of beaker with 10-15 ml of vanadyl sulfate (0.008M in 0.5M H_2SO_4).
- Insert electrode into solution and add more $VOSO_4$ solution until volume of ~80 ml is reached.(~430 mV).
- Turn on stirrer, titrate carefully to end point of 600 mV.

Calibration and Standardization

- During the course of a day's operation, sample assays are interspersed with a total of three calibration assays on NBL CRM 112-A (NBS 960) normal uranium metal or equivalent.
- Stated daily precision of method is 0.10% rsd as demonstrated by analysis of standards.

Calculations

$$\text{Titer} = \frac{\text{U Standard, mg}}{\text{wt. Ce (IV) solution used, g}}$$

$$\text{U}(\%) = \frac{(\text{Ce}(\text{SO}_4)_2 \text{ titer, } \overline{\text{T}})\,(\text{wt. of } \text{Ce}(\text{SO}_4)_2 \text{ used, g})\,(100\%)}{\text{wt. of sample, mg}}$$

NBS 960(CRM 112 A) Standard Verification

- Several times annually (usually each quarter), adjust the concentration of the NBS-960 parent working standard solution concentration using two small portions of independently and freshly prepared portions of NBS-960 metal.
- Run two analyses from each "verification" standard.

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NBS 960(CRM 112 A) Standard Verification *(continued)*

- Analysis of these "verification" standards are used to adjust the concentration of the large NBS-960 working standard solution if needed.
- Typical adjustment of the NBS-960 working standard solution is <0.10 % annually.

  i.e. Conc. on 3/22/04 = 29.358_2 mg U/g sol.

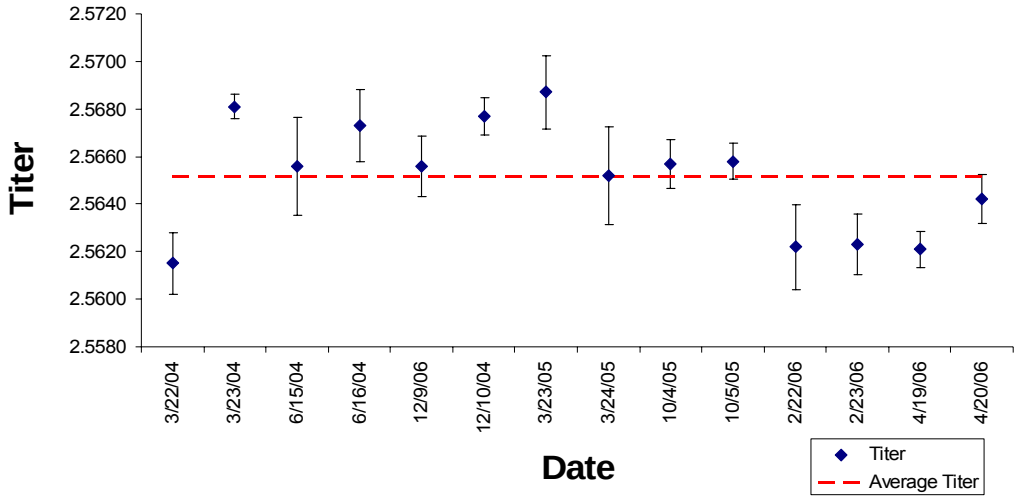
  Conc. on 4/20/06 = 29.399_4 mg U/g sol.

  Δ = 0.14% over two years

Average Titer and Precision

Date	Titer	Percent RSD
3/22/2004	2.5615	0.053
3/23/2004	2.5681	0.022
6/15/2004	2.5656	0.084
6/16/2004	2.5673	0.065
12/9/2004	2.5656	0.046
12/10/2004	2.5677	0.034
3/23/2005	2.5687	0.058
3/24/2005	2.5652	0.077
10/4/2005	2.5657	0.036
10/5/2005	2.5658	0.032
2/22/2006	2.5622	0.074
2/23/2006	2.5623	0.049
4/19/2006	2.5621	0.028
4/20/2006	2.5642	0.042

Average Titer mg U/g CeTritrant
n=3 for each day

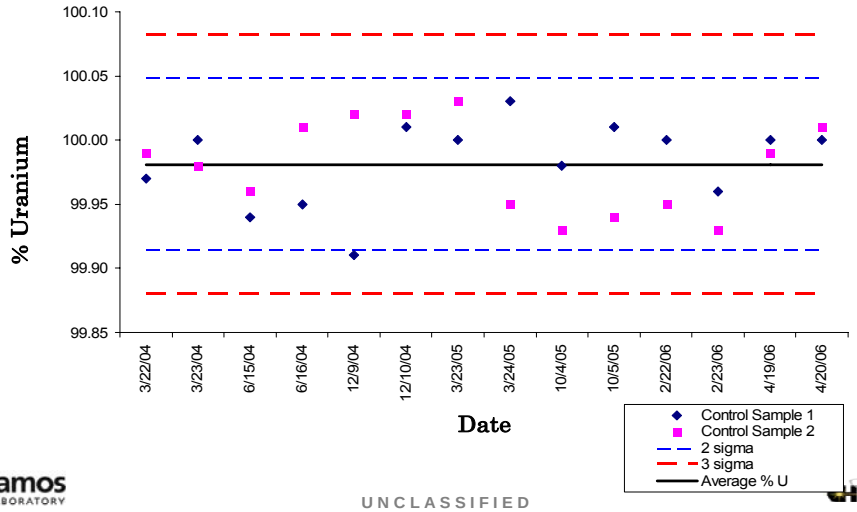


Control Sample (CF 83-18-52)

- A high purity depleted U metal from AWE-UK (under JOWOG 22).
- Prepare aliquots from dissolved metal (~2 gm. U metal/dissolution) and distributed in 25 mg portions for analysis as a control sample.
- Analyze two portions on each day that Davies Gray is run.

Control Samples

n=2 per date, Average = 99.981%, σ = 0.034%

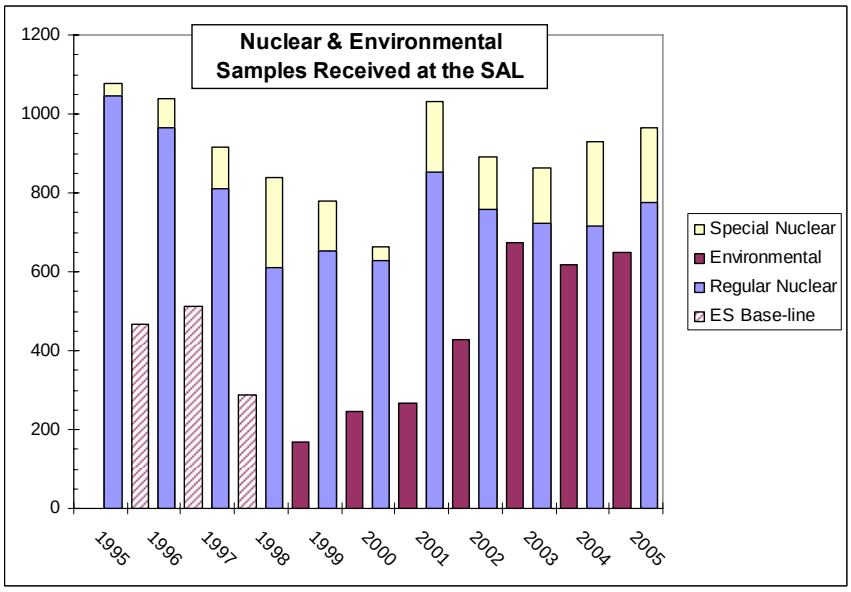


2005 Summary Nuclear Sample Destructive Analysis

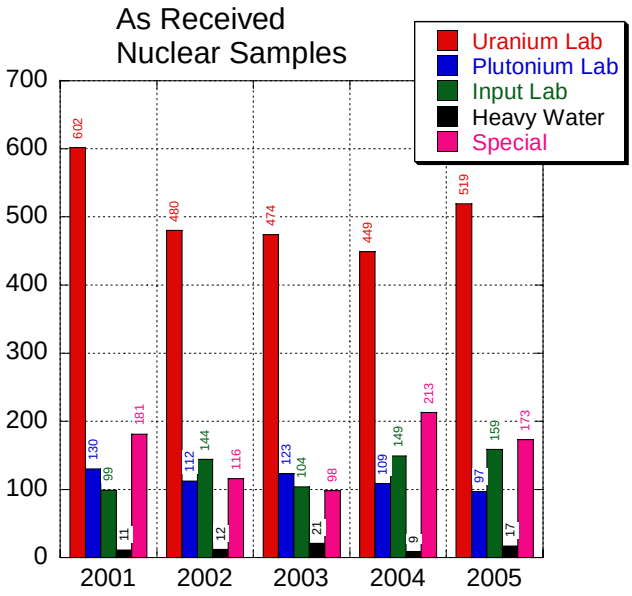
Steve Balsley

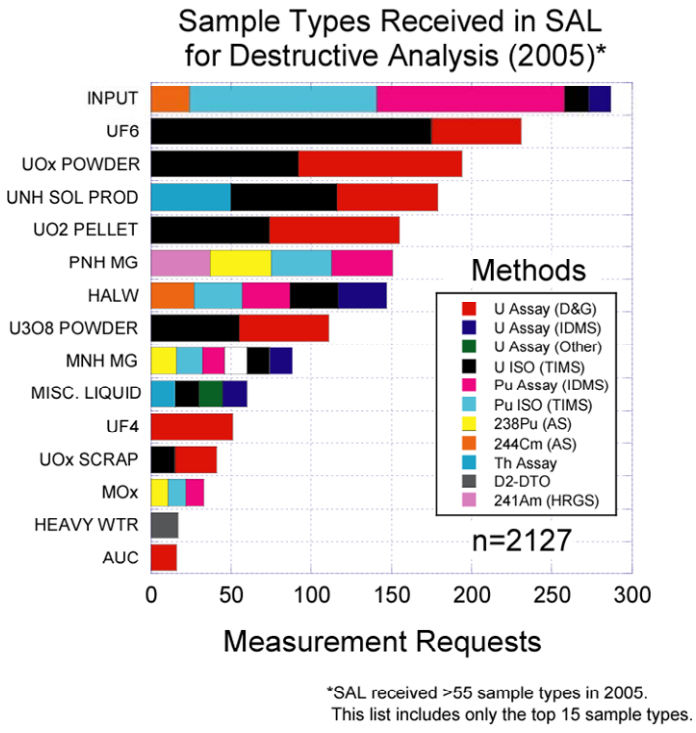
IAEA Safeguards Analytical Laboratory (SAL)

10-Year Trend

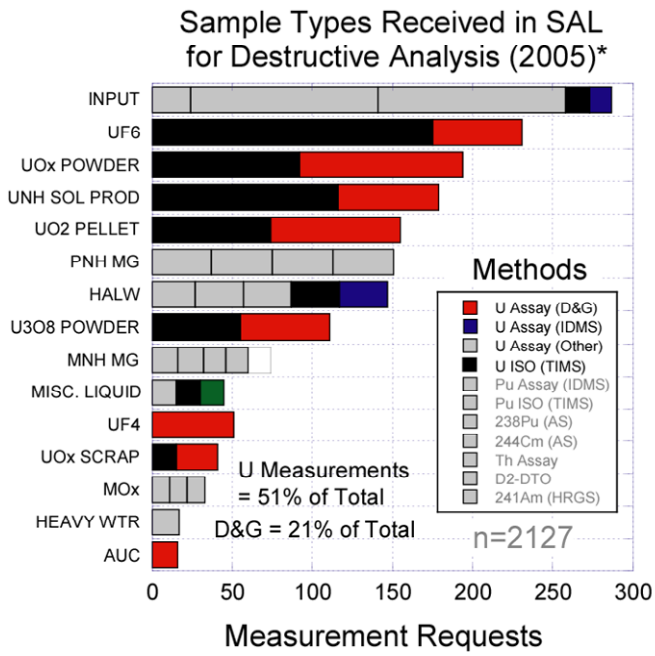


5-Year Nuclear Sample Trend





*SAL received >55 sample types in 2005.
This list includes only the top 15 sample types.



*SAL received >55 sample types in 2005.
This list includes only the top 15 sample types.

Conclusions

- The Davies & Gray method represents approximately 20% of all measurement requests for nuclear samples collected during IAEA inspections in 2005.
- The D&G method is the second most frequently applied method in SAL (IDMS is the #1 used method).
- Participation in NBL SME Program is most welcomed in SAL.

Qualification of a Robotic System for Potentiometric Titrations (Davies & Gray Method)

Steve Balsley, Josef Berger, Alfred Zoigner

IAEA Safeguards Analytical Laboratory (SAL)

Robot D&G Titration System

- TIMS 900 titrator
- Mitsubishi robot arm
- Computer control
- Custom software for robot arm control
- Custom titration stand and sample holders

- Established in 2005
- Validation in 2006

Justification

- The Uranium Laboratory receives ~600 samples per year for assay.
- 1200 Samples + 350 Stds + 230 Controls = 1780 titrations made in 2005.
- A good chemist can make 80 titrations per day.
- Robot system can make 30-40 titrations per day.

Qualification Approach

- A validated method (modified D&G) is to be qualified on new equipment.
- Criteria for qualification:
  - Precision (repeatability, reproducibility)
  - Accuracy
  - Measurement reliability
- Archived NBL SME (2006) UO_3 powder and UO_2 pellet samples were chosen to facilitate the testing.

Qualification Approach

- A combination of archived original solutions and freshly dissolved powders and pellets from SME 2006 was used.
- Samples were measured in duplicate over 10 different dates.
- Results are compared against these NBL values:
  - UO_3 powder: 82.671% uranium
  - UO_2 pellet: 88.129% uranium

3 October 2006 11

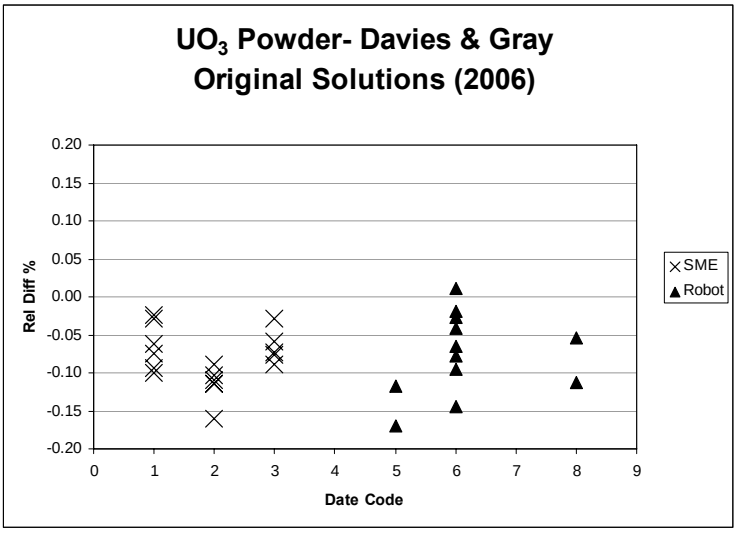
Date Codes

SME Measurements

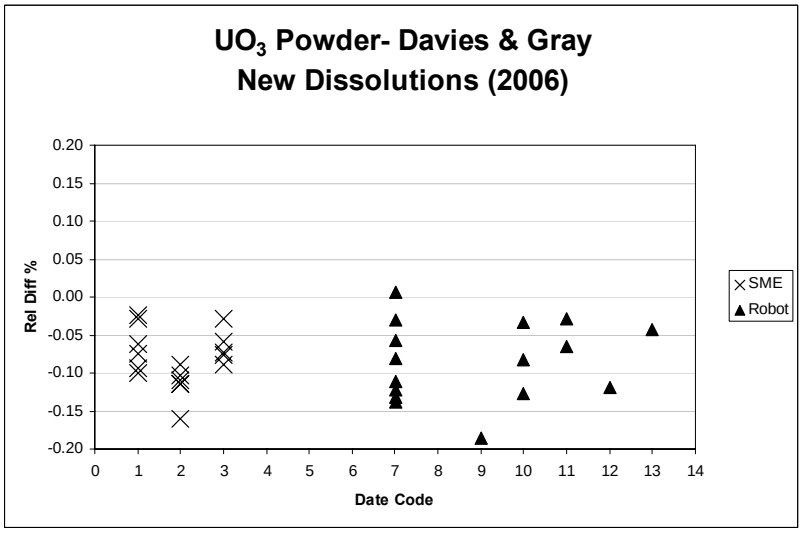
Date Code	Analysis Date
1	March 21, 2006
2	April 4, 2006
3	April 25, 2006
4	June 14, 2006
5	June 15, 2006
6	June 18, 2006
7	June 22, 2006
8	June 29, 2006
9	June 30, 2006
10	July 3, 2006
11	July 4, 2006
12	July 5, 2006
13	July 11, 2006

8 August 2006 12

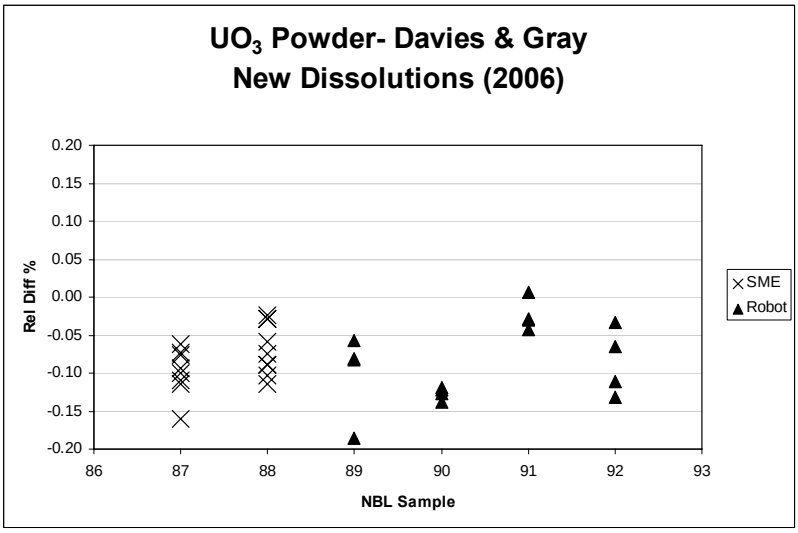
Sample Results- UO_3 Powders



Sample Results- UO_3 Powders



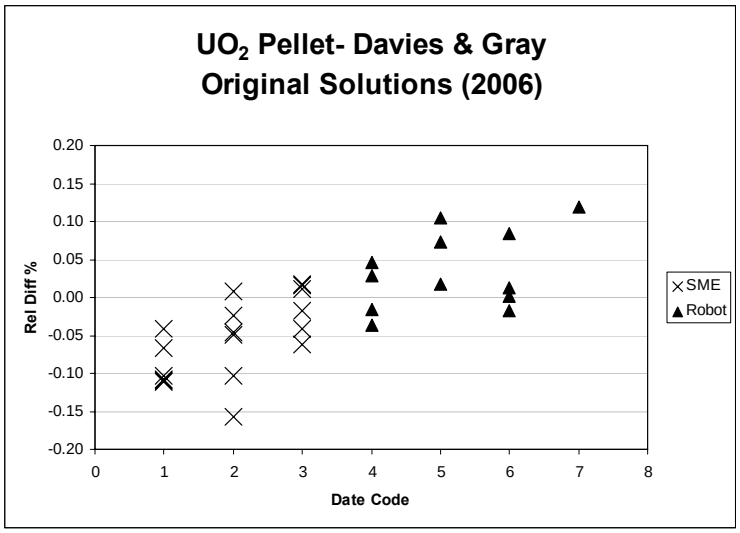
Sample Results- UO_3 Powders



UO_3 Powder Summary- Robot System

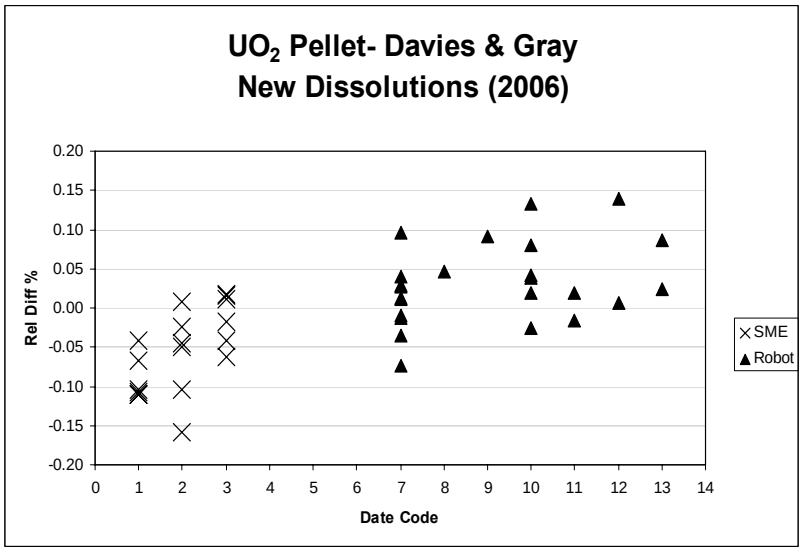
- Assay of archived SME powder solutions are in good agreement with the NBL stated value.
- Assays of freshly dissolved SME powders are in good agreement with the NBL stated value.
- There is ~0.08% negative bias against the NBL stated value.

Sample Results- UO_2 Pellets

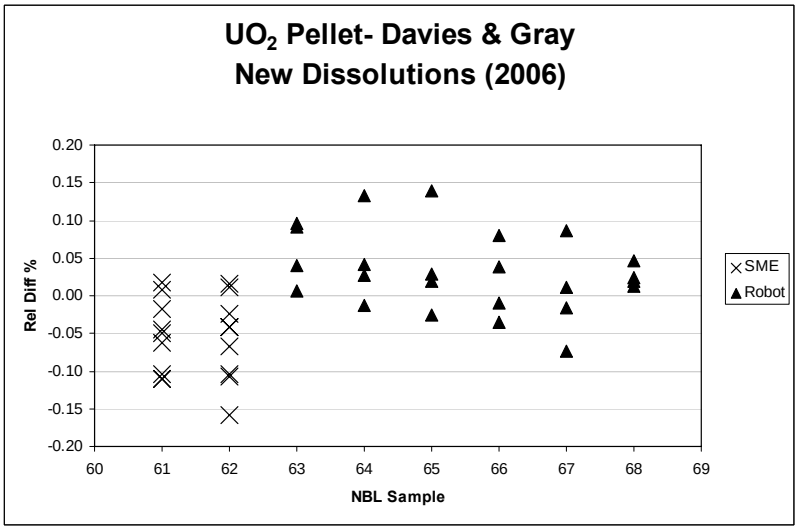


Sample Results- UO_2 Pellets

Sample Results- UO_2 Pellets



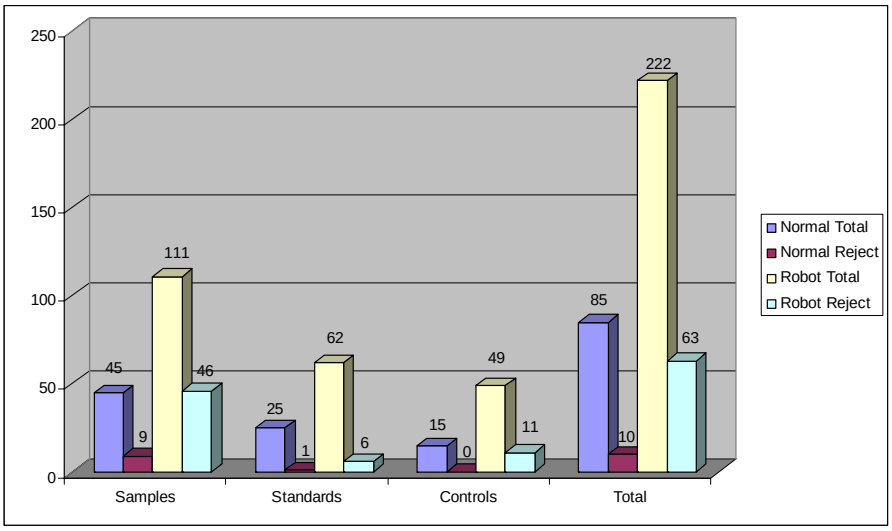
Sample Results- UO_2 Pellets



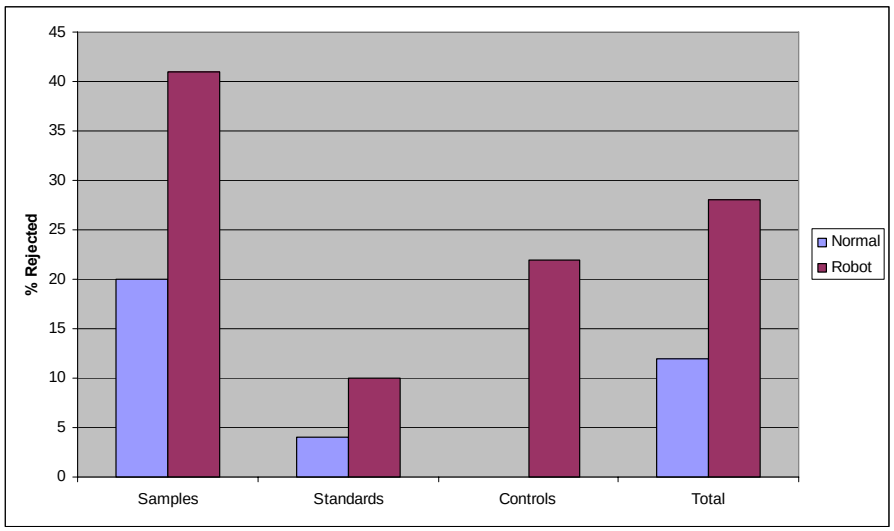
UO_2 Pellet Summary- Robot System

- Assay of archived SME pellet solutions are in good agreement with NBL stated value.
- Assay of new SME pellet dissolutions are in good agreement with NBL stated value.
- Robot assay data (archived and new solutions) are bias slightly above original SME assay data.

Rejected Results Normal vs. Robot



Robot Titrator: Not as Reliable



Summary

- SAL robotic titration system produces repeatable and reproducible data that matches the operator-assisted system performance.
- Robotic system accuracy is good.
- The robotic system has a failure rate ~2x higher than the operator-assisted titration system.
- The robot system may be qualified for routine use, however the challenge is to reduce the number of rejected measurements.

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REIMEP 18 Inter-Laboratory Comparison for Uranium Isotope Ratio Measurements in Nitric Acid Solution

Stephan Richter, Adolfo Alonso-Muñoz, Jan Truyens, André Verbruggen, Roger Wellum

Institute for Reference Materials and Measurements (IRMM)
Geel, Belgium

http://www.irmm.jrc.be
http://www.jrc.cec.eu.int

irmm

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The REIMEP 18 Campaign:

- **REIMEP=Regular European Inter-laboratory Measurement Evaluation Programme**
- **Samples: U, Pu, in various forms, to be analyzed for isotopics and assay**
- **REIMEP 18: Campaign for the measurement of uranium isotope ratios in nitric acid solution**
- **Designed to show the present state of uranium isotope measurements**
- **Gives the opportunity for participating laboratories**
  - **to evaluate their own performance,**
  - **to identify possible problems and**
  - **to improve their own measurement procedures**

irmm

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The REIMEP 18 Samples:

- **4 Samples: REIMEP 18 A-D:**
  - **0.2%< Relative Abundance of ^{235}U <4.5%**
- **Uranium Amount:**
  - **2.5mg of U for each of REIMEP 18-A-D**
- **Solution:**
  - **0.5mL of 0.5M Nitric Acid**
- **Uranium Concentration:**
  - **5mg/mL**
- **Total activity for all REIMEP 18-A-D:**
  - **< 1000Bq, therefore the shipment is**
- **NOT CONSIDERED A RADIOACTIVE TRANSPORT !**

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The REIMEP 18 Tasks:

- **<u>Task for Participants:</u> Measure Isotopic Composition**
  - Measure ratios $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$
  - Calculate abundances and mass fractions for ^{234}U, ^{235}U, ^{236}U, ^{238}U
- **<u>Task for IRMM:</u> Measure & Certify Isotopic Composition**
  - $^{235}U/^{238}U$ measured using a UF_6-gas source mass spectrometer MAT511, calibrated using synthetic isotope mixtures. Relative Uncertainty about 0.05% (k=2).
  - $^{234}U/^{238}U$ and $^{236}U/^{238}U > 2x10^{-5}$: measured on a TRITON TIMS Faraday-Multi-collector, no need for ion counting on ^{234}U.
  - New 10^{12}-Ohm amplifiers used to detect ^{234}U to improve signal to noise ratio.
  - $^{236}U/^{238}U < 2x10^{-5}$: measured on a TRITON TIMS, ^{236}U detected using ion counter, ^{238}U on Faraday cup.
  - Method for $^{236}U/^{238}U$ measurements validated using new synthetic mixtures with certified $^{236}U/^{238}U=10^{-6}$, 10^{-7}, 10^{-8}.

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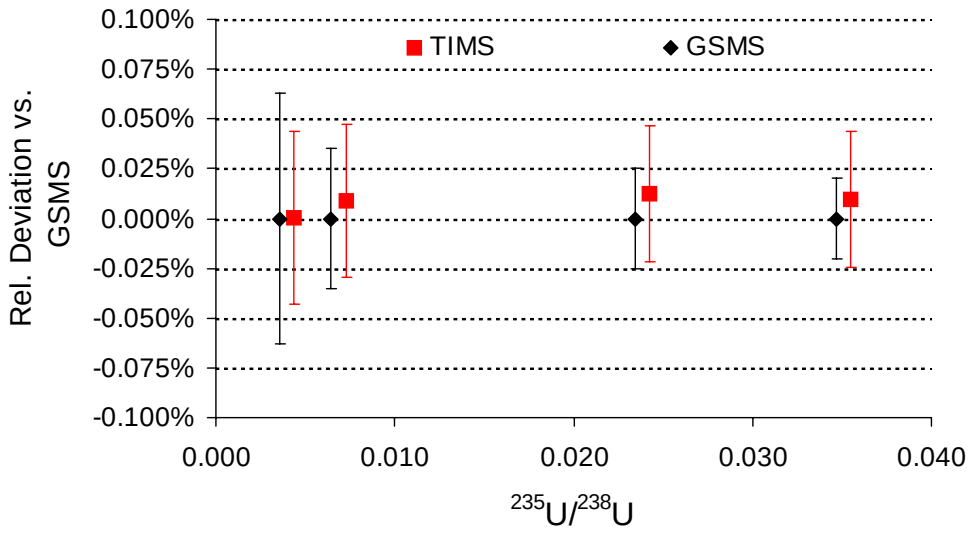
Verification Measurements for $^{235}U/^{238}U$ Ratios by TIMS:

Comparison TIMS vs. GSMS (MAT511 using UF6 Gas)



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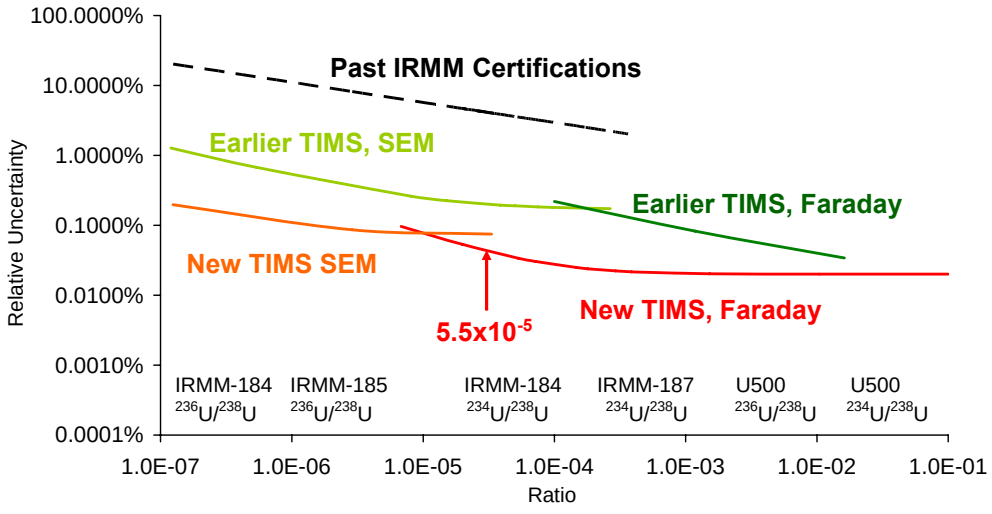
Uncertainties for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratio measurements



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Milestones:

- **Registration: 81 Laboratories registered, largest REIMEP**
  - Countries: Australia(4), Austria(3), Belg.(2), Bosnia-Herz.(1), Canada(4), Czech(1), France(4), Germ.(8), Hung.(1), Israel(2), Japan(5), S-Korea(1), Lith.(1), Netherl.(2), Poland(1), Port.(1), Russia(2), Serbia-M.(2), Spain(2), Sweden(2), Swiss(2), Turkey(2), UK(13), USA*(15)
    **within the USA co-organized by New Brunswick Laboratory (NBL)*
  - Included Fields: Nuclear Safeguards & Fissile Material Control, Research & Development (mainly Geochemistry, Physics).
  - Instrumentation: TIMS, ICP-MS, AMS, RIMS, α-Spectrometry
- **Shipment: by DHL / FedEx (USA), non-radioaktive transport**
- **Data submission until end of June 2006: 63 participants**
- **Reporting by IRMM:**
  - Certification Report issued, sent to participants after data submission
  - Report to Participants, after all data reporting finished (Oct/Nov 2006)

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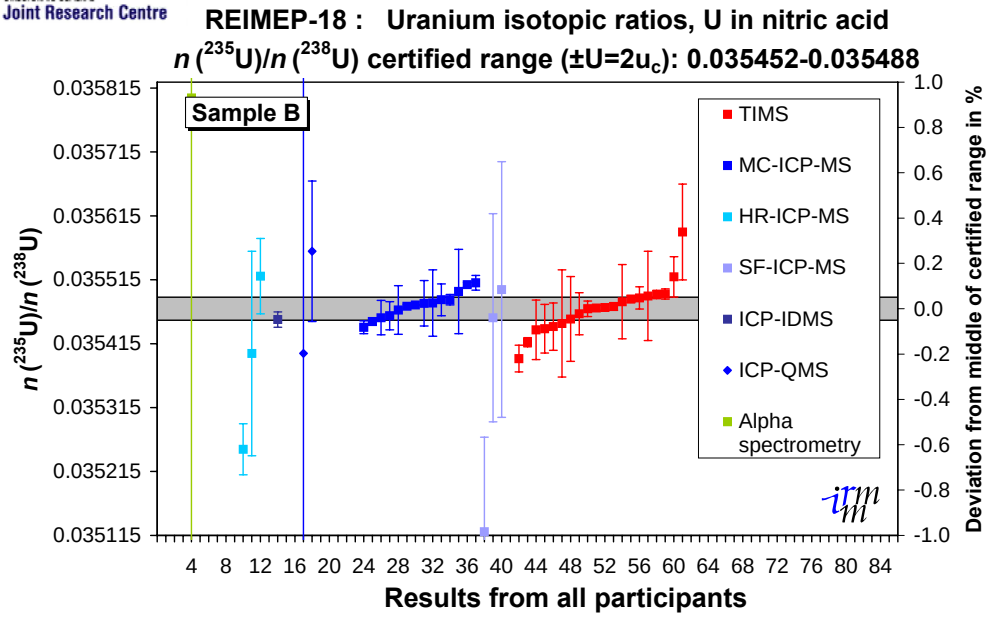

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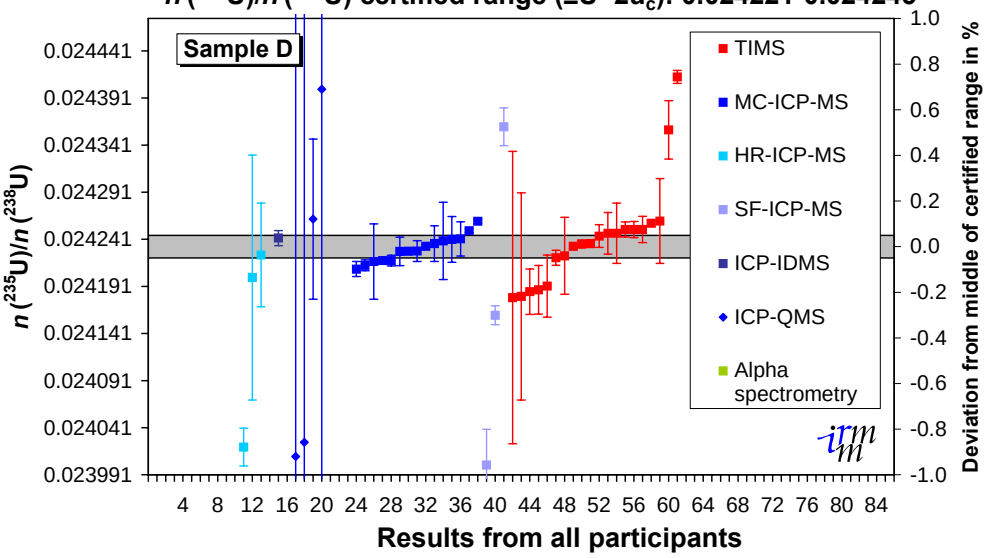
REIMEP-18 : Uranium isotopic ratios, U in nitric acid

$n(^{235}U)/n(^{238}U)$ certified range (±U=2u_c): 0.024221-0.024245



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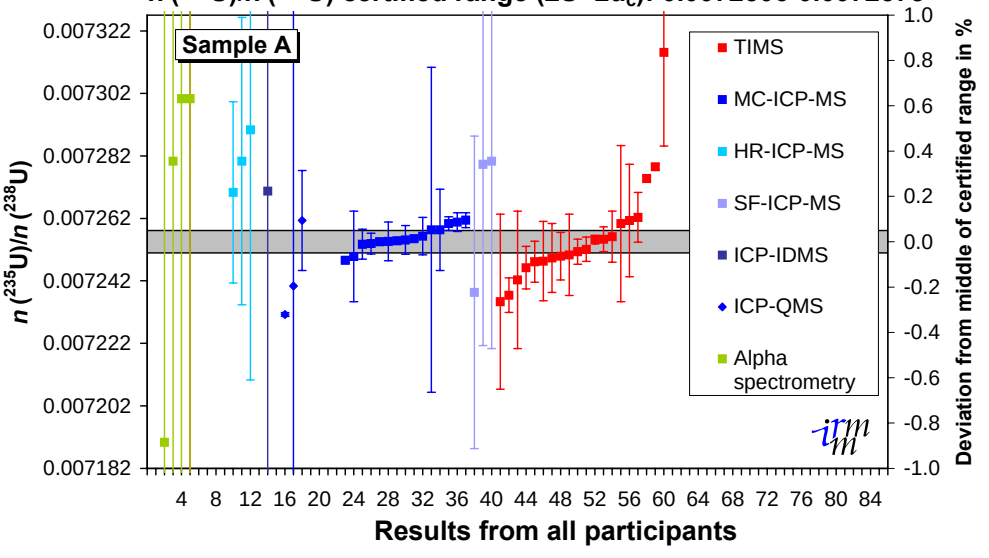
REIMEP-18 : Uranium isotopic ratios, U in nitric acid

$n(^{235}U)/n(^{238}U)$ certified range (±U=2u_c): 0.0072506-0.0072578



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REIMEP-18 : Uranium isotopic ratios, U in nitric acid

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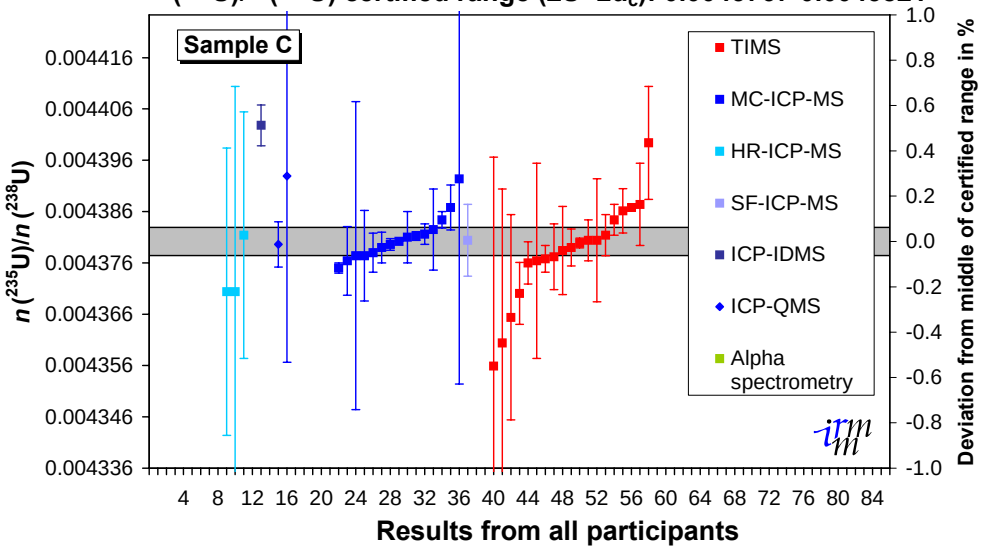

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REIMEP-18 : Uranium isotopic ratios, U in nitric acid

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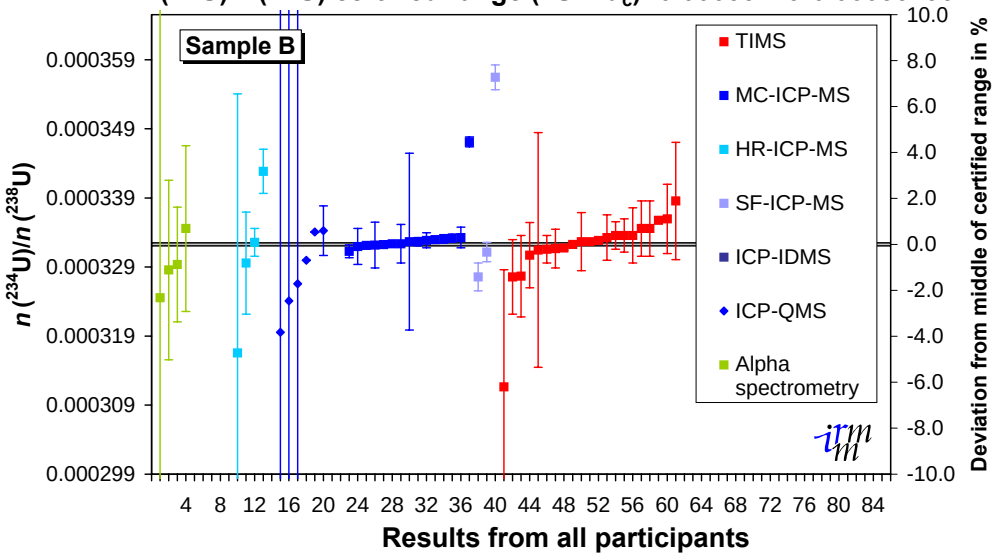

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REIMEP-18 : Uranium isotopic ratios, U in nitric acid

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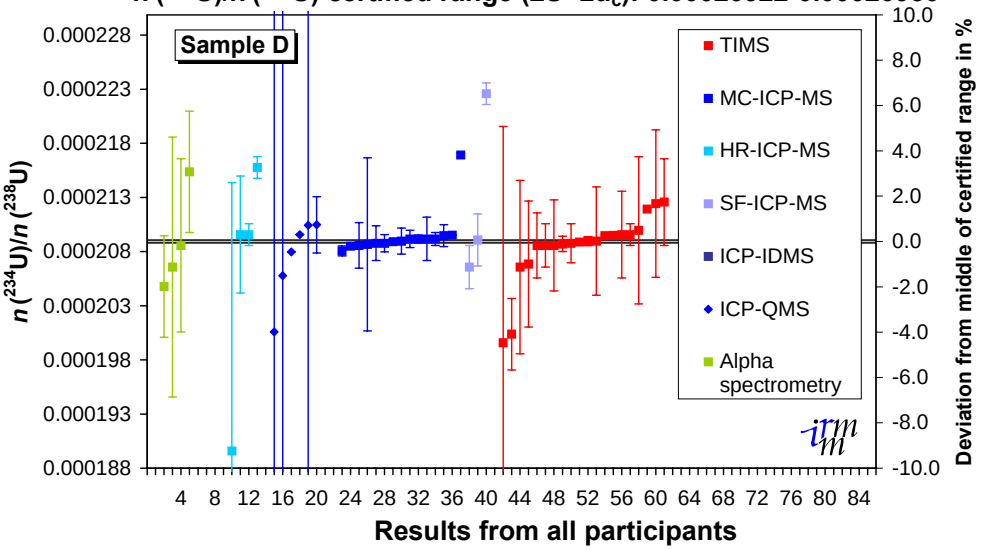

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REIMEP-18 : Uranium isotopic ratios, U in nitric acid

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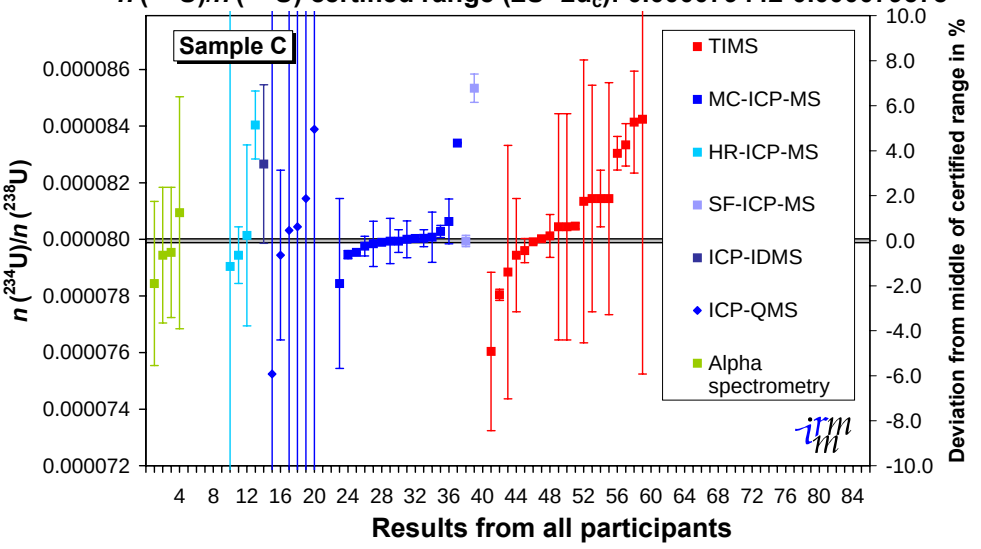

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REIMEP-18 : Uranium isotopic ratios, U in nitric acid

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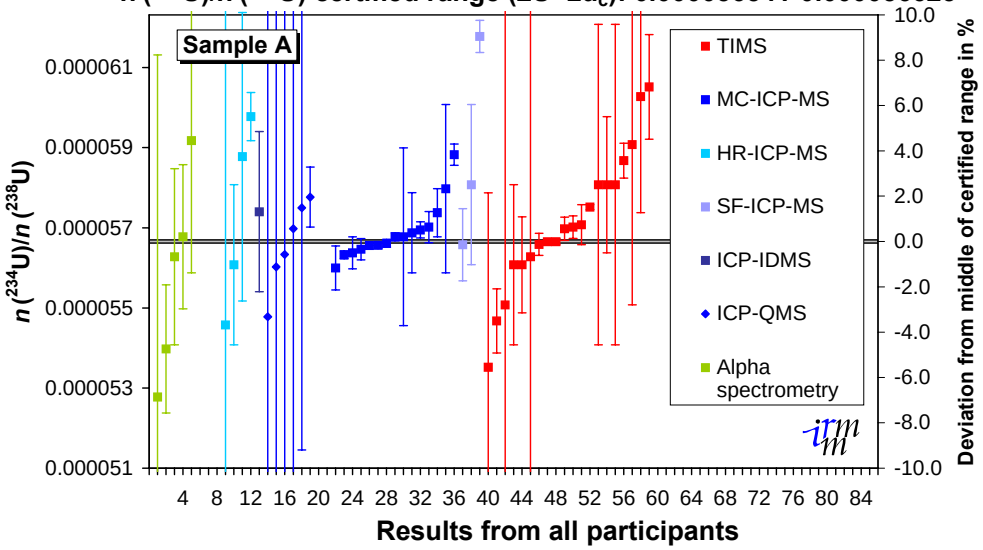

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REIMEP-18 : Uranium isotopic ratios, U in nitric acid

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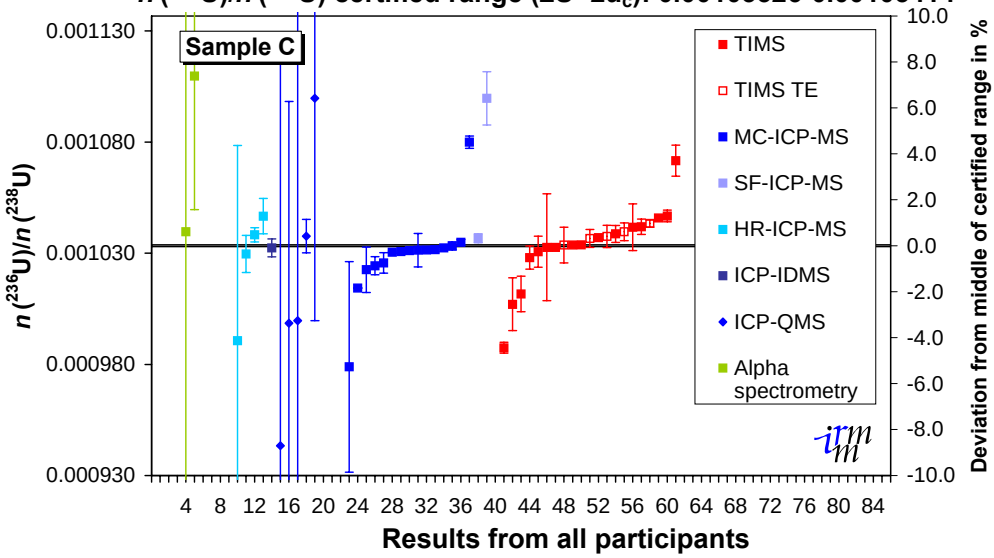

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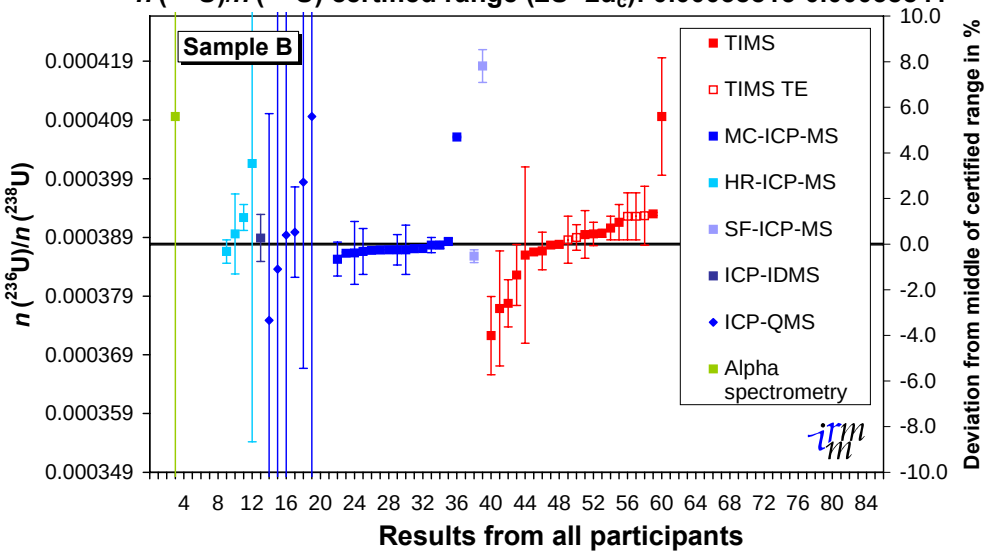
REIMEP-18 : Uranium isotopic ratios, U in nitric acid

$n(^{236}U)/n(^{238}U)$ certified range (±U=2u_c): 0.00038815-0.00038841



EUROPEAN COMMISSION
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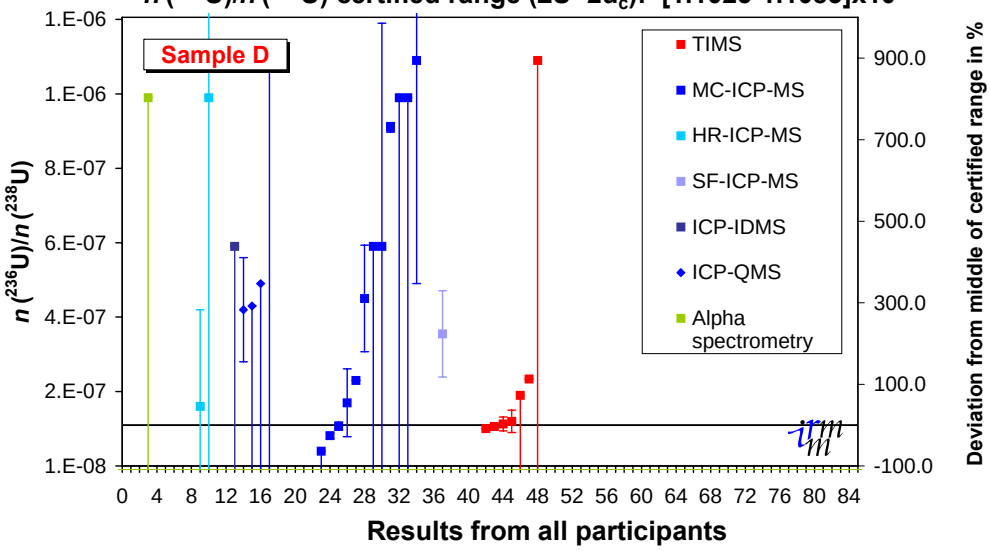
REIMEP-18 : Uranium isotopic ratios, U in nitric acid

$n(^{236}U)/n(^{238}U)$ certified range (±U=2u_c): [1.1025-1.1083]x10^{-7}



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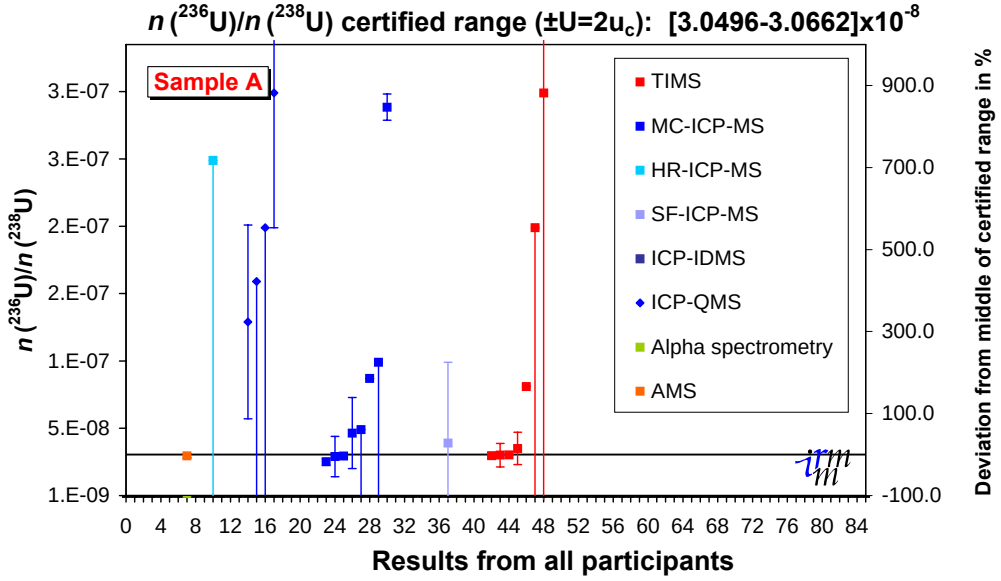
REIMEP-18 : Uranium isotopic ratios, U in nitric acid

$n(^{236}U)/n(^{238}U)$ certified range (±U=2u_c): [3.0496-3.0662]x10^{-8}



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REIMEP-18 : Uranium isotopic ratios, U in nitric acid

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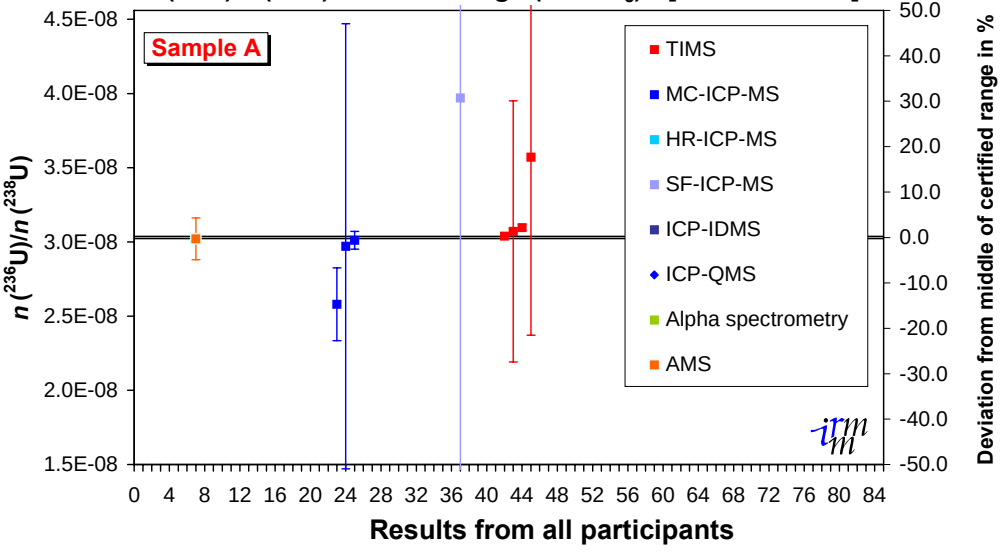

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Conclusions I:

- All Ratios $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$:
  - Spread among participants is in-creasing if ratio is de-creasing
- Minor Ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$:
  - Problems due to tailing correction, non-linearity of SEM, inter-calibration of SEM versus Faraday cup.
- In Particular Minor Ratios $^{236}U/^{238}U$:
  - All $^{236}U/^{238}U$: Problems with tailing correction for routine TIMS, e.g. in total evaporation (TIMS TE)
  - $^{236}U/^{238}U < 10^{-6}$: Significant deviations for ICP-MS, even with energy filter
  - $10^{-8} < ^{236}U/^{238}U < 10^{-7}$: Waiting for more TIMS (using energy filter) and AMS results.

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Conclusions II:

- Use of isotope reference materials (IRMs) for mass fractionation correction: 78%
  - Use of JRC-IRMM isotope reference materials: only 10%...
  - TIMS-Total Evaporation: 0% !
- Use of IRMs for method validation: 57%
- Use of IRMs for linearity correction of SEM: 13 (out of 30)
- Reporting of Uncertainties:
  - According to GUM: 52% (32 out of 61)
  - Standard uncertainty: 56% (18 out of 32)
  - Coverage factor k≥2: 44% (14 out of 32)
  - Occasionally also k=0 or Uncertainty=0 reported…
- Need for fine-tuning of individual measurement procedures
- More details in Participant's Report


ABACC
BRAZILIAN-ARGENTINE
AGENCY FOR ACCOUNTING
AND CONTROL OF NUCLEAR MATERIALS
INTERCOMPARISON PROGRAM
ABACC-NBL Cooperation
José Augusto Perrotta
NBL Measurement Evaluation Program – Nashville July 15, 2006


ABACC Foundation and Purpose
Binational organization created in July 1991 by the Federative Republic of Brazil and the Republic of Argentina
ABACC manages and applies the Common System of Accounting and Control of Nuclear Materials (SCCC), in order to verify if Argentina and Brazil utilize their nuclear materials exclusively for pacific purposes
Its headquarters are located in Rio de Janeiro, Brazil. ABACC also has an office in Buenos Aires, Argentina
ABACC

Declarations and Other Documents in the Field of Nuclear Safeguards between Brazil and Argentina

1985 – Declaration of Foz do Iguaçu

1987 – Declaration of Viedma

1988 – Declaration of Iperó

1990 – Declaration of Foz do Iguaçu

1991 –Bilateral Agreement for for the Exclusively Pacific Use of Nuclear Energy (18/07/91) (foundation of ABACC)

1991 – Quadripartite Agreement for the Application of Comprehensive Safeguards (13/12/91) (AR-BR-ABACC-IAEA)

1994 – Enforcement of the Quadripartite Agreement (INFICIRC/435)

1994 – Full adhesion of Argentina (in January) and of Brazil (in May) to the Treaty of Tlatelolco

1995 – Adhesion of Argentina to the Treaty of Non-proliferation of Nuclear Weapons (TNP)

1997 – Adhesion of Brazil to the Treaty of Non-proliferation of Nuclear Weapons (TNP)

2005 – Puerto Iguazú Commitment ("importance of ABACC and the SCCC")

ABACC

Safeguards Under INFCIRC/435

- Full scope safeguards agreement in force since March 1994
  - ABACC and IAEA shall coordinate activities to avoid unnecessary duplication of ABACC's safeguards
  - When performing their activities, ABACC and IAEA shall work jointly in accordance with compatible safeguards criteria of the two organizations
  - ABACC and IAEA shall reach independent conclusions
- Guidelines for Coordination of Routine and Ad-hoc Inspections approved in 1997

ABACC

ABACC Information

- 78 Nuclear facilities under safeguard
  - Argentina (43); Brazil (35)
  - Nuclear Power Reactors, Enrichment Plants; Fuel Fabrication Plants; Research Reactors; Laboratories; Nuclear Material Storage Facilities
- ~ 120 inspections per year
- ~ US$ 3 million budget per year
- ~ 30 DA samples analysis per year
- ~ 8 swipe samples analysis (particle analysis) per year

ABACC

ABACC Organization

- Commission
  - 2 Argentine Members
  - 2 Brazilian Members
- Secretariat
  - Secretary
  - Deputy Secretary
  - Officers (10)
  - Auxiliary staff (5)
  - Inspectors (83) (under convening)

ABACC

Secretariat Organization

- The Secretariat is headed by a Secretary and a Deputy Secretary, an Argentine and a Brazilian, who exchange their position each year
- Planning and Evaluation (2 officers)
- Operations (2 officers)
- Accounting of Nuclear Materials (2 officers)
- Technical Support (2 officers)
- Institutional Relations (1 officer)
- Management and Finances (1 officer)

ABACC

Technical Support (1)

- Coordinate the technical analyses (DA; NDA; C&S) necessary to safeguards application
- Identify, purchase, assemble, calibrate, install and provide for the maintenance of equipment and materials
- Prepare the safeguard equipment for utilization during inspections
- Organize the training of ABACC inspectors
- Coordinate the development of new equipment and methodologies to be used by ABACC or in collaboration with the IAEA

ABACC

Technical Support (2)

- Technical Support has the responsibility of analyzing by *DA* the samples taken by ABACC during safeguards inspections
- Having no analytical laboratory, ABACC relies on an Analytical Network of existing laboratories on both countries (Brazil and Argentina)
- Technical Support evaluates the performance of these laboratories

ABACC

Technical Support (3)

- Established an Intercomparison Program as a permanent activity, counting with the highest possible number of participating laboratories from both countries; and taking into account the existing infrastructure in both countries

ABACC

Intercomparison Program
Main Objectives

- To provide the participants with the opportunity to verify and improve their performance through the *identification* of statistically significant *sources of error* and the estimation of their magnitude
- To detect any possible abnormal results and apply corrective actions
- To maintain an Analytical Network of reliable laboratories analyzing ABACC's samples from safeguards inspections

ABACC

US-DOE / ABACC Safeguards Agreement

- Agreement signed on April 18, 1994
- Cooperation on research, development, testing and evaluation of technologies, equipment and procedures for the application of international safeguards
- *16 Action Sheets* have been established and developed up to now

ABACC

US-DOE / ABACC Safeguards Agreement

- The NBL is cooperating with ABACC in the implementation of Intercomparison Programs, Sample Exchange Programs and Laboratory Quality Assurance through Standards and Samples Exchange Programs
- 2 Action Sheets: 1 finished, 1 active

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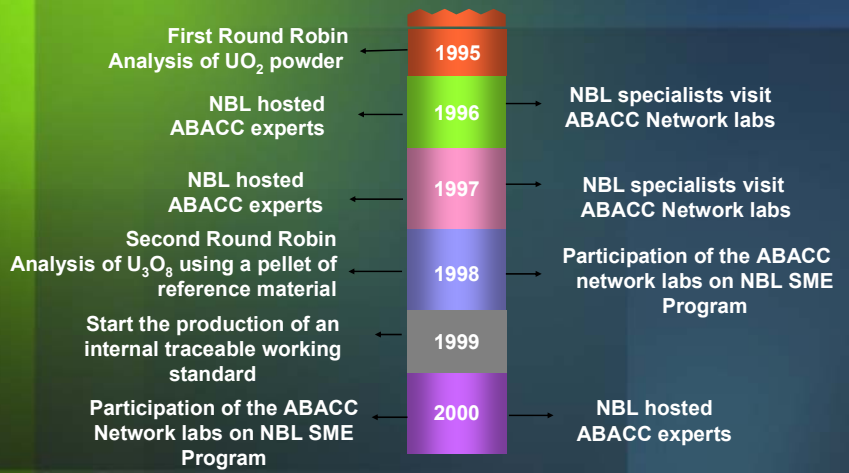
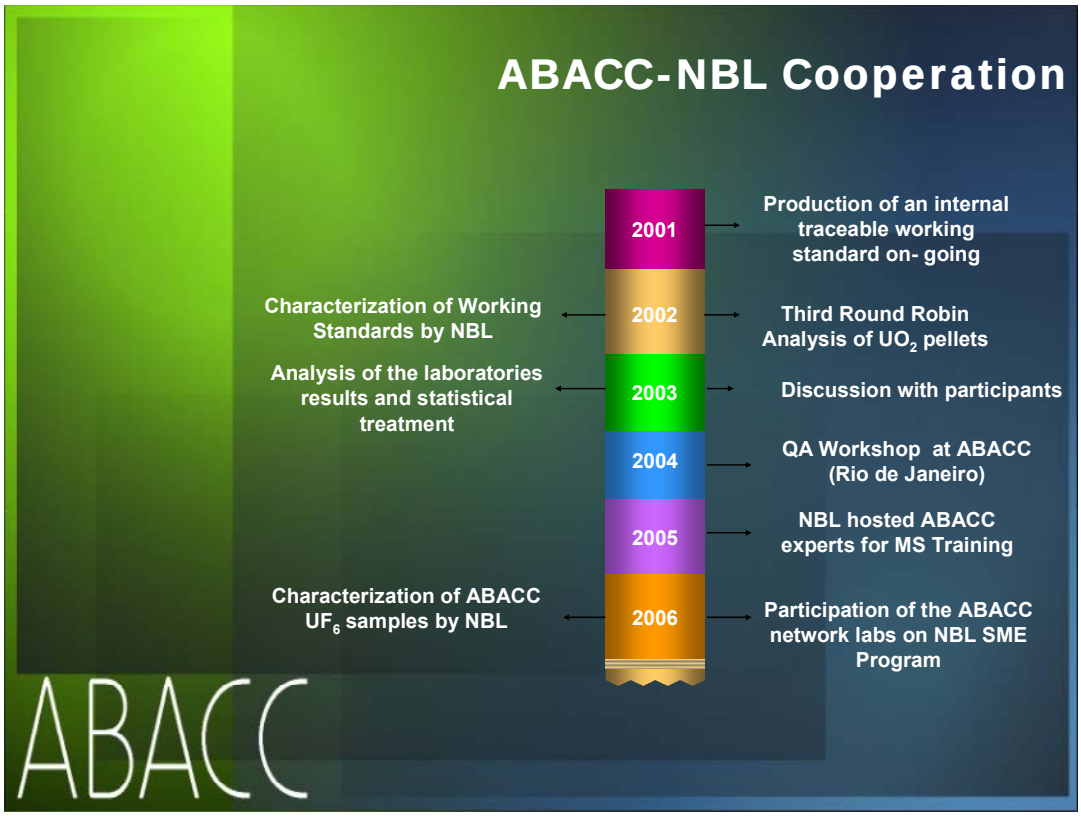
ABACC-NBL Cooperation



ABACC


ABACC-NBL Cooperation
2001
Production of an internal traceable working standard on- going
2002
Characterization of Working Standards by NBL
Third Round Robin Analysis of UO_2 pellets
2003
Analysis of the laboratories results and statistical treatment
Discussion with participants
2004
QA Workshop at ABACC (Rio de Janeiro)
2005
NBL hosted ABACC experts for MS Training
2006
Characterization of ABACC UF_6 samples by NBL
Participation of the ABACC network labs on NBL SME Program
ABACC


NBL-SME 2006
ABACC Network Laboratories Participation
4 laboratories from Brazil
6 Laboratories from Argentina
Measurements
UO_2 Pellets
Uranium Concentration
Uranium Enrichment
UF_6
Uranium Concentration
Uranium Enrichment
ABACC

Participating Laboratories in Argentina
RAW DATA

Laboratory	Material	Analysis Method	Uranium Concentration Wt%		^{235}U Enrichment Wt%	
			Mean	STD	Mean	STD
AB	UO_2	D&G Tritation	88.123	0.022		
			88.087	0.031		
	UF_6	D&G Tritation	67.418	0.025		
			67.455	0.029		
AC	UO_2	D&G Tritation	88.005	0.033		
			87. 975	0.006		
AA	UO_2	TIMS			4.0051	0.0000
					4.0051	0.0000
	UF_6	TIMS			0.7114	0.0011
					0.7108	0.0014

ABACC

Participating Laboratories in Argentina
RAW DATA

Laboratory	Material	Analysis Method	Uranium Concentration Wt%		^{235}U Enrichment Wt%	
			Mean	STD	Mean	STD
AD	UO_2	D&G Tritation	88.114	0.013		
			88.108	0.015		
AE	UO_2	D&G Tritation	88.113	0.023		
			88.144	0.026		
	UF_6	D&G Tritation	67.428	0.010		
			67.689	0.017		
AF	UO_2	ICP-MS			3.9975	0.0068
					3.9885	0.0160

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Participating Laboratories in Brazil
RAW DATA

Laboratory	Material	Analysis Method	Uranium Concentration Wt%		^{235}U Enrichment Wt%	
			Mean	STD	Mean	STD
BF	UO_2	D&G Tritation	88.089 88.135	0.026 0.028		
BA	UO_2	D&G Tritation	88.054 88.031	0.063 0.066		
BE	UO_2	HRICP-MS			4.0490 4.0460	0.0230 0.0150
BC	UO_2 UF_6	D&G Tritation TIMS GSMS	88.108 88.014	0.042 0.017	4.0069 4.0091 3.1893 3.1994	0.0018 0.0026 0.0024 0.0034

ABACC

Measurement Evaluation
Uranium Concentration

Laboratory	Analysis Method	Target Values Satisfied?		Measurement Bias	Day-to-Day Variation
		Bias	Precision		
UO_2					
AB	D&G Tritation	Yes	Yes	Negligibly Small	Absent
AC	D&G Tritation	No	Yes	Negative Bias	Marginal
AD	D&G Tritation	Yes	Yes	Negligibly Small	Absent
AE	D&G Tritation	Yes	Yes	No Bias	Marginally Significant
BA	D&G Tritation	Yes	Yes	No Bias	Significant
BC	D&G Tritation	Yes	Yes	Negative Bias	Absent
BF	D&G Tritation	Yes	Yes	No Bias	Absent
UF_6					
AB	D&G Tritation	No	Yes	Negative Bias	Significant
AE	D&G Tritation	Yes	No	No Bias	Not Evaluated

NBL Report – B.Srinivasan

ABACC

Measurement Evaluation
Uranium Enrichment

Laboratory	Analysis Method	Target Values Satisfied?		Measurement Bias	Day-to-Day Variation
		Bias	Precision		
UO_2					
AA	TIMS	Yes	Yes	Negative Bias	Absent
AF	ICP-MS	No	No	Negative Bias	Marginally Significant
BC	TIMS	Yes	Yes	No Bias	Absent
BE	HRICP-MS	No	No	Positive Bias	Significant
UF_6					
AA	TIMS	Yes	Yes	No Bias	Absent
BC	GSMS	Yes	No	No Bias	Absent

NBL Report – B.Srinivasan

ABACC

FUTURE ACTIONS
ABACC / NBL Cooperation

- UF_6 samples characterization by NBL and analysis by ABACC Network Laboratories
- Second Round of 2006 SME
- Critical analysis on measurement evaluation results and laboratories performance
- Advisory meetings with ABACC Network Laboratories for improvements identification
- Plan new intercomparison exercise (2007-2008)

ABACC

Summary

- ABACC is completing 15 years of existence
- ABACC applies the SCCC between Brazil and Argentina and performs safeguards activities jointly with the IAEA
- US-DOE through NBL is cooperating with ABACC in the implementation of Intercomparison Programs, Sample Exchange Programs and Laboratory Quality Assurance through Standards and Samples Exchange Programs
- ABACC support network laboratories are participating in the SME-2006
- New activities and intercomparison exercises are foreseen to the ABACC/NBL cooperation

ABACC

ABACC

Thank you!

www.abacc.org perrotta@abacc.org.br

Measurement Evaluation Programs in Environmental Radioactivity at NIST

Kenneth G. W. **INN**
Iisa **OUTOLA**
Svetlana **NOUR**
Hiromu **KUROSAKI**
Jerome J. **LA ROSA**

NBL Measurement Evaluation Program Meeting
15 July 2006
Nashville, TN

Goals of Environmental Radioactivity Unit:

- Promote the **accurate measurement** of environmental-level radionuclide concentrations in naturally occurring materials
- Provide a **traceability** link between organizations engaged in this type of measurement and the primary national metrology laboratory, NIST

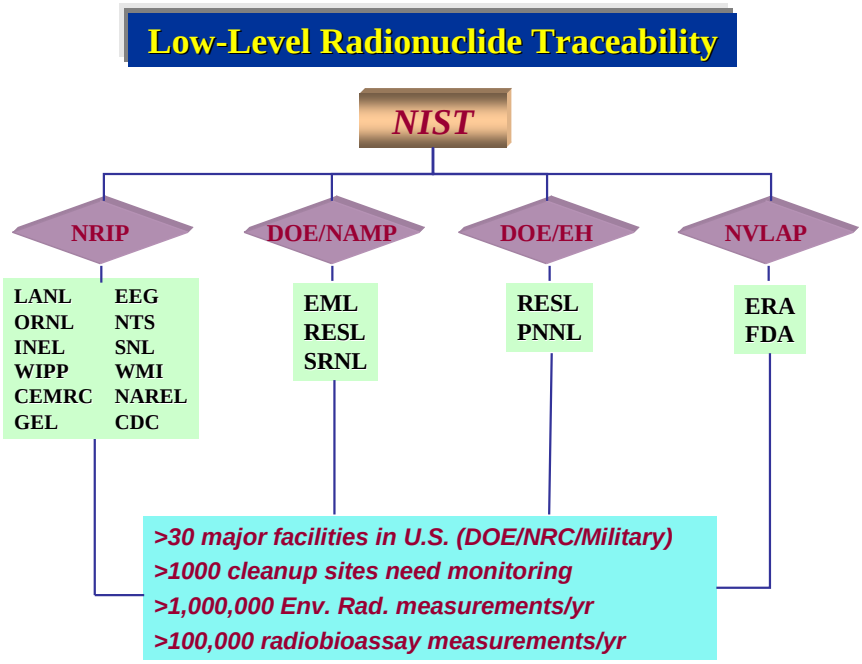
Examples of naturally occurring materials (matrices):

Soil **Sediment** **Vegetation** **Water**

Biological materials (shellfish, seaweed)

Bioassay substances (bone ash, urine, feces, lung, liver)

Radionuclides: natural (cosmogenic, primordial) and anthropogenic



How does NIST strive towards attaining these goals?

- **NRIP** (**N**IST **R**adiochemistry **I**ntercomparison **P**rogram)
- **RTP** (**R**adiological **T**raceability **P**rogram)
- **SRM** (**S**tandard **R**eference **M**aterial) Natural Matrix Program
- Intercomparison Program for Radionuclide Isotopic Studies **Workshop** (February 28 – March 2, 2006)

NRIP and RTP are performance evaluation (PE) programs

All of these programs/efforts require active involvement with participating laboratories and organizations which seek to maintain or achieve a high level of radioactivity measurement accuracy (most commonly, measurement of radionuclide concentration)

NRIP = **N**IST **R**adiochemistry **I**ntercomparison **P**rogram*

- Established in **1997** [special emergency NRIP started in 2003]
- Supports low-level radioanalytical labs performing environmental radioactivity and radiobioassay measurements
- Implements traceability according to ANSI N42.23 (ANSI, 1996), ANSI N42.22 (ANSI, 1995) and HPS N13.30 (HPS, 1996)
- **Specific objectives**
  1. Assess measurement **traceability**
  2. Evaluate **capability** for matrix and radionuclide interference(s)
  3. Validate existing and new **radiochemical methods**
- **Overall objective:**
  Improve quality of low-level radioactivity measurements of participating laboratories

*Reference: Z. Wu et al., Appl. Rad. Isotopes **56** (2002) 379 - 385

NRIP – continued

Radionuclides:
- gamma ^{54}Mn, ^{60}Co, ^{65}Zn, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{152}Eu
- beta ^{90}Sr
- alpha ^{230}Th, ^{234,235,238}U, $^{238,239+240}$Pu, ^{241}Am

Activity levels: 0.03 – 0.3 Bq/sample

Sample types: air filter, water (acidified), soil, synthetic urine, synthetic feces

NIST responsibility: high quality, traceable PE materials

- use available NIST SRM solutions as starting materials
- calibrate others (short-lived ^{54}Mn, ^{65}Zn, ^{134}Cs)
- traceability chain through gravimetry, verified by radioactivity measurement
- consistency evaluation: individual samples of each set of PE materials are measured (comparative gamma) to ensure relative conformity

NRIP – continued

2 types of exercises (choice of participants):

Routine - participants (typically 5 – 10) select ≤ 4 matrices

- time for analyses ~ 3 months
- pass/fail traceability assessment based on reported results and uncertainties

Emergency – ≤ 4 matrices selected by participants (typically ~ 6)

- notified by NIST just before shipment on "surprise" date
- participant selects radionuclides and/or gross alpha/beta
- report results/uncertainties ≤ ***8 hours*** of actual sample receipt!!!!
- pass/fail traceability assessment based on reported results and uncertainties

NRIP – continued

Acceptance criteria

ANSI N42.22 (environmental and radiobioassay)

$$|X_{LAB} - X_{NIST}| \leq 3 \times [\, U_C(LAB)^2 + U_C(NIST)^2 \,]^{1/2}$$

where X refers to measured value
and U_C refers to total combined standard uncertainty of mean

HPS N13.30 (radiobioassay)

$$-25\% \leq [(X_{LAB} - X_{NIST})/X_{NIST}] \leq +50\%$$

and $U_C(LAB) \leq \pm 40\%$ (1s)

NRIP – continued

Report of Traceability issued by NIST for <u>each radionuclide</u> includes:

- reported mean value, X_{LAB}
- NIST gravimetric value, X_{NIST}
- corresponding reported and NIST value uncertainties (k = 2)
- $[(X_{LAB} – X_{NIST})/X_{NIST}] \times 100\%$
- traceability limit, based on ANSI N42.22 formula
- pass/fail evaluation based on $|X_{LAB} - X_{NIST}|$ compared to ANSI N42.22 calculated traceability limit
- when appropriate, bias and precision evaluation for HPS N13.30 (pass/fail)

Overall summary of materials, methods and instruments used for NIST PE sample preparation and verification

NRIP Sample Analyses

2004 Emergency Exercise
6 participating laboratories

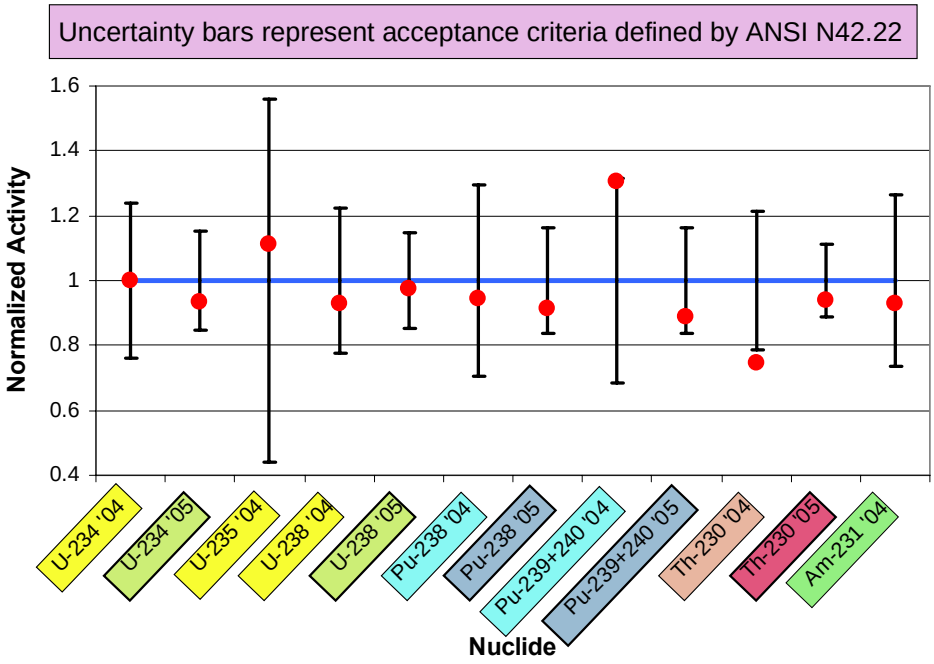
	AF air filter	AW water	SS soil	SU syn urine	SF syn feces
Gamma	5	5	3	1	1
G[Alpha]	1	2	1	0	0
G[Beta]	1	2	1	0	0
Isotopic	0	2	0	0	0

NRIP Sample Analyses

2004 Emergency Exercise
6 participating laboratories

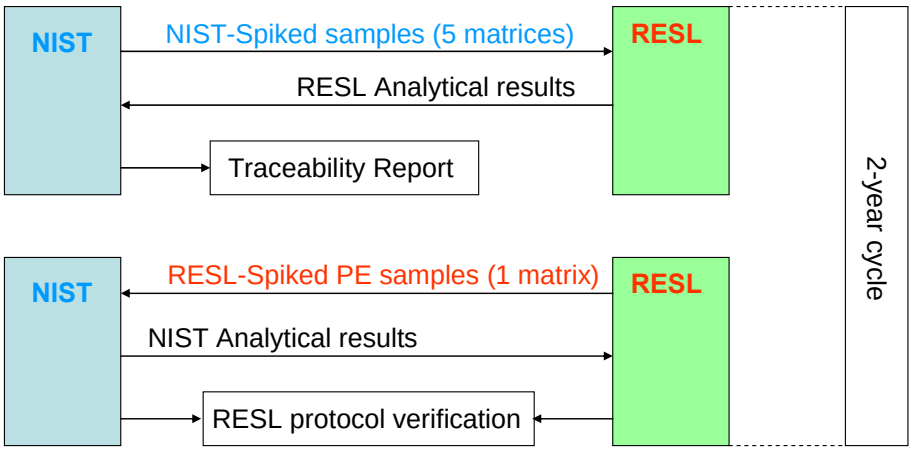
	AF air filter	AW water	SS soil	SU syn urine	SF syn feces
Gamma	5	5	3	1	1
G[Alpha]	1	2	1	0	0
G[Beta]	1	2	1	0	0
Isotopic	0	2	0	0	0

Single Lab Results (Isotopics in **Water**) for '04 and '05 Emergency Exercises



RTP = **R**adiological **T**raceability **P**rogram (RESL and NIST, since 2004)

RESL
- designated reference laboratory for DOELAP and MAPEP
- prepares PE samples for participating labs
- analyzes materials of unknown activities
- must maintain traceability to NIST



RTP – continued

Radionuclides:
- gamma: ^{54}Mn, ^{57}Co, ^{60}Co, ^{65}Zn, ^{125}I, ^{131}I, (^{134}Cs), ^{137}Cs
- beta: ^{3}H, ^{90}Sr
- alpha: ^{230}Th, ^{234}U, ^{238}U, ^{237}Np, ^{238}Pu, $^{239/240}$Pu, ^{241}Am

Matrices:
air filters (glass fiber) water (acidified) soil
vegetation synthetic urine synthetic feces

Activity levels, representative:
- alpha 0.1 – 1 Bq/sample
- ^{3}H 1 – 10 Bq/g
- ^{90}Sr 1 – 10 Bq/sample
- gamma 10 – 100 Bq/sample (except ^{125}I, ^{131}I)
- ^{125}I, ^{131}I 110 – 2000 Bq/g

RTP – continued

Turn-around time of 120 days

Traceability Acceptance Criteria:

For RESL results of NIST-prepared samples:

- synthetic urine and synthetic fecal: $|\textbf{difference}| \leq 9\%$
- soil, water, vegetation, air filter: $|\textbf{difference}| \leq 12\%$

For NIST measurement of RESL-prepared samples:

ANSI N42.22 (ANSI, 1995)

$$|V_{NIST} - V_{RESL}| \leq 3 \times [\, U_C(NIST)^2 + U_C(RESL)^2 \,]^{1/2}$$

where V refers to nuclide concentration value
U_C refers to total combined 1 sigma uncertainty in V

Natural Matrix SRMs

for Environmental Radioactivity Measurement

- Rocky Flats Soil I
- River Sediment
- Peruvian Soil
- Human Lung
- Human Liver
- Lake Sediment
- Ocean Sediment
- Bone Ash
- Shell Fish

New SRMs forthcoming:

Seaweed (ocean) – SRM 4359, featuring bio-accumulated radionuclides (Pu, Am, Cs, K, Pb, Po, U, Th, Ra) in plant tissue

Rocky Flats soil II – SRM 4353A, replacement for Rocky Flats soil I, featuring Pu "hot particles" and elevated Pu levels; certified Pu, U, ^{137}Cs, ^{90}Sr, ^{228}Ra, ^{210}Pb; certified activity ratios ^{238}Pu/$^{239+240}$Pu, ^{228}Th/^{232}Th, ^{230}Th/^{232}Th, ^{234}U/^{238}U

Shellfish (ocean) – SRM 4358, oyster [87.9% Japan Sea, 12% White Sea, 0.1% Irish Sea] with bio-accumulated radionuclides (under development)

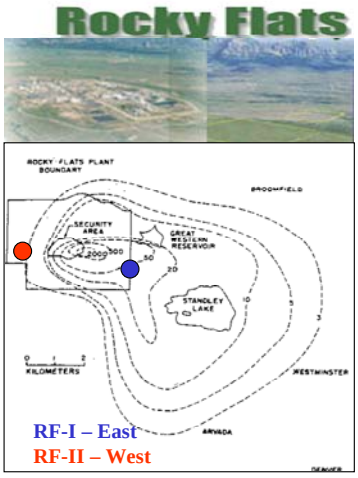
Peruvian soil II – future replacement for Peruvian soil I (SRM 4355), very low Pu content ("blank"), southern hemisphere; possible mass spec Pu application, 240/239 Pu atom ratio different from northern hemisphere

Fish? Building materials?

New Ideas/Needs?

Rocky Flats Soil

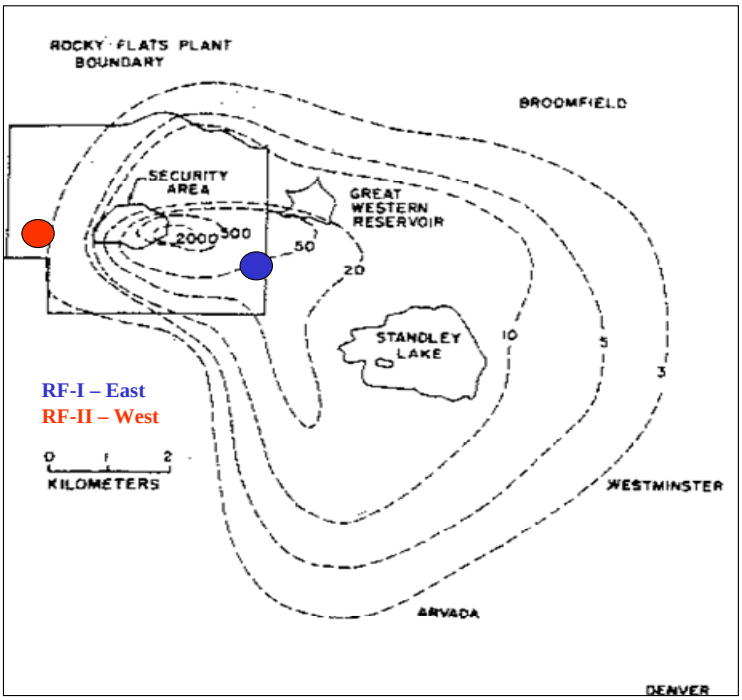
(contact person: Svetlana Nour)



- Low organic – low carbonate content
- The contamination fairly well-known
- The logistics and costs of obtaining the samples and shipping were reasonable
  - Air dried
  - Milled twice
  - Sieved
  - Jet pulverized
  - Blended
  - Bottled and sterilized

NIST National Institute of Standards and Technology

Rocky Flats



Intercomparison Program for Radionuclide Isotopic Studies Workshop

February 28 – March 2, 2006

Goal: **Establish a traceability testing and intercomparison program for isotopic measurement of anthropogenic radionuclides**

Focus:

- **Environment**
  - **Forensics**
    - **Radiobioassay**
      - **Emergency**

About 60 Participants

National Laboratories, NMI, Academia, Defense, Federal Agencies, International Agencies, Commercial PT Laboratories, IAEA

Environment Breakout session

Radiometric

Atom counting

Geochemistry

Waste Acceptance

Radiometric Proficiency Test Needs

Find suitable PT Exercises with Web Base Database

Future PT? Atom Counting, Geochemistry, Transportation
WAC, Treatment, Storage

Radiometric SRM Needs

1. **Matrix : Sludge from Water Treatment, Soil(s)**
2. **Nuclides** : ^{228,230,232,234}Th, ^{210,212,214}Pb, ^{212,214}Bi, ^{40}K, ^{226,228}Ra…… etc
3. **Concentration Range :** 0.3-7 Bq/g
4. **Isotopic Ratio :** Natural

Atom Counting Needs

- **Certify current NIST SRMs for atom counting (to TIMS level)**

- **Isotopic Ratios**

Geochemistry Needs

- Natural and anthropogenic radionuclides in environmental matrices

- All matrices are of potential interest

- **Radionuclides :**
  - Ra-228, Pb-210, Na-22, Sr-90
  - Pu, U, Th, Cs….

Waste Acceptance Criteria Needs

WAC for transportation, treatment, storage, etc

Matrices
- Irradiated graphite/concrete
- Sludge (disposal sites/evaporators)
- Resins/water (primary coolant)

Radionuclides
H-3, C-14, Co-60, Cs-137, Cl-36,
Pu & U isotopes, gamma emitters
long lived radionuclides for disposal sites characterization

Nuclear Forensics, Safeguards, and Nonproliferation Reference Material Needs

- Natural matrix RMs certified for actinide isotopic content (in addition to activity)
- Isotope dilution tracer and isotope ratio standards
- Radiochronometry RMs

Radionuclide Isotopic RMs

- **Round robin for Rocky Flats, Columbia River Sediments (or sub), Peruvian soil (U, Pu) = $600K**
- **Blank matrix & spiked matrix (soil/rock): 2 or 3 Pu, U, Am, Np, Cm, Th, Cs135/137 = $250K per CRM**
- **RDD mix – solutions, Sr90, 137Cs, 60Co, 192Ir, 241Am, 238Pu, 3H = $150K**

Isotope Dilution Tracers and Ratio RMs

Spikes:

- 233U $500K
- **244Pu** **$200K** to improve delivery date
- 229Th $300K
- 243Am $500-1500K
- **236Np** **$3000K**
- 236Pu for alpha $500K with 236Np

Calibration Stds:

- Mixed 241-243Am $500K
- Mixed 230-232Th $500K
- Higher precision alpha stds $200K

Radiochronometry RMs

- 234U-230Th $100K for existing materials
- 235U-231Pa, $100K for existing materials
- 241Pu-241Am $150K for existing materials
- 137Cs-137Ba $175K

Other RM and Test Material Needs Identified

- **Burn-up standard**
  - Cs burn-up standard $300K min for both
  - Nd burn-up standard
- **Trace element** standards for uranium fuel cycle $1000K
- **Oxygen isotope** standard for uranium oxide
- **Trace Pu in U** (1E-06) $300K
- **Particles:**
- U/Pu mixture (1:1, 1000:1) on swipes $1500K
- U with minor isotopes $1500K

Radiobioassay

Need: 1. Pu in synthetic fecal samples
2. Am-241 in natural urine sample;
3. U concentrations and isotopic ratios in synthetic urine for calibration (ICP-MS) and quality control

Matrix: Urine; Fecal; Hair (neutron exposure screen); Fragment (wound materials)

Nuclides: 1. Actinides - U and Pu and their isotopes, Am-241
2. Fission/activation products - Cs-137, Sr-90, Co-60. Ir-192, Se-75
3. Nuclides prioritized against the list from CDC and other agencies.

Conc: mBq – Bq/sample

Isotopics: 1. U-234/235/236/238
2. Pu-238/239/240
3. Ratios for different nuclides (eg. Am-241/Pu-239)

Acceptance Criteria; 1. ANSI N13.30; 2. Draft original standards; 3. ANSI 42.22

Priorities: 1. Consequence management (DHS/DOE/FRMAC) – responder screening
2. Population monitoring (CDC)

Responsibilities/Time lines: 1. The Army looks for funds - U standard preparation
2. Health Canada work on Pu fecal & Am urine

Emergency Response

Need: PT to qualify laboratories to analyze samples for early and intermediate phases of the response to a radiological incident

Matrices: Air particulate filter/air cartridge, swipes, soil, water, bioassay (especially urine), and food/vegetation

Nuclides: H-3, Pu-241. Sr-89/90, Pm-147. I-129, Am-241, Cs-137, Co-60, Y-88, Ir-192, Cf-252. Isotopic Pu, U, Th, Po-210, Ra-226, Cm-244

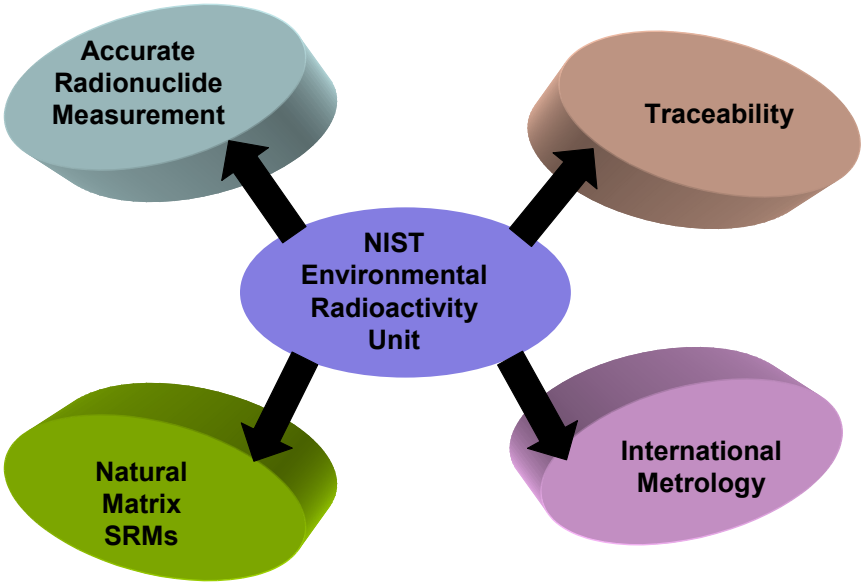
Concentration: 0.25 to 2 or 3 times the PAG (program action guideline)

Funding: DHS -- via ICLN (Integrated Consortium of Laboratory Networks)

Acceptance Criteria: ± 25% except gross alpha/beta in early phase
± 20% for intermediate phase
Uncertainties reported but not used for evaluation

Traceability limits -- combined reported and tester uncertainty with incentive to keep estimated uncertainties reasonable

Summary


Accurate Radionuclide Measurement
Traceability
NIST Environmental Radioactivity Unit
Natural Matrix SRMs
International Metrology

NEW BRUNSWICK LABORATORY

High accuracy determination of minor isotopes in uranium and plutonium materials by thermal ionization mass spectrometry

Peter Mason
Reference Materials Program Manager
New Brunswick Laboratory

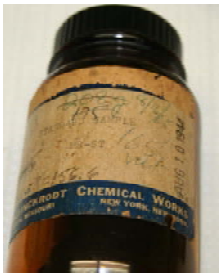
Measurement Evaluation Program Meeting
July 15, 2006
Nashville, TN

Acknowledgements

- Dr. Richard Essex
- Dr. Rebecca Thomas
- Dr. Steven Goldberg
- Dr. Stephan Richter - IRMM

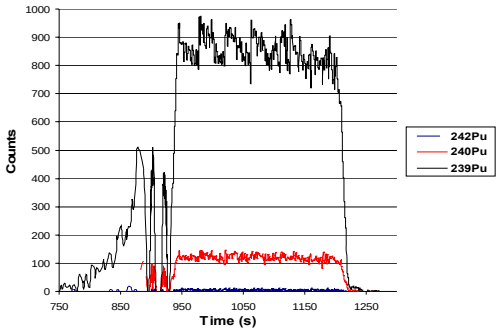
Why better minor isotope characterization?

- **Naval and Commercial Fuel Specifications** (U-233, U-236, Pu)
- **Nuclear Forensics/Nuclear Smuggling** – signatures for history/ID
  - **Reactor Fuel Burnup Monitors and Identification of Reactor Type**
  - **Source Attribution -** Fuel-Related RDDs (Radiological Dispersion Device) and INDs (Improvised Nuclear Device)
  - **Proliferation Indicators** – identify enrichment, processing, or production method
  - **Chronometry** – age of material production or last chemical separation
- **Environmental Monitoring**
  - U/Pu minor isotopes refine pathway transport models
  - identify contaminants in presence of natural U
  - health physics/bio-assay data



How to improve accuracy and sensitivity?

- Modify the Ion Source
- Modify the Detector System
- *Improve Measurement Protocols*



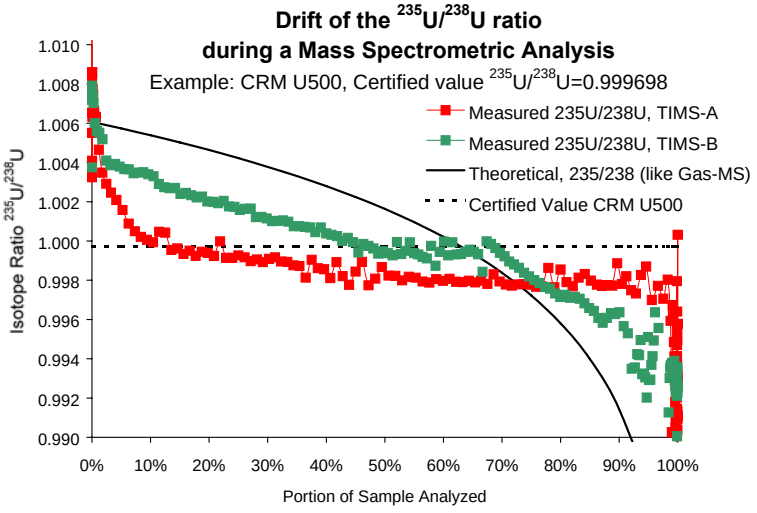
Improved Mass Spectrometric Methods

1. Modified total evaporation
2. High intensity with background correction
3. Advanced ion counting method

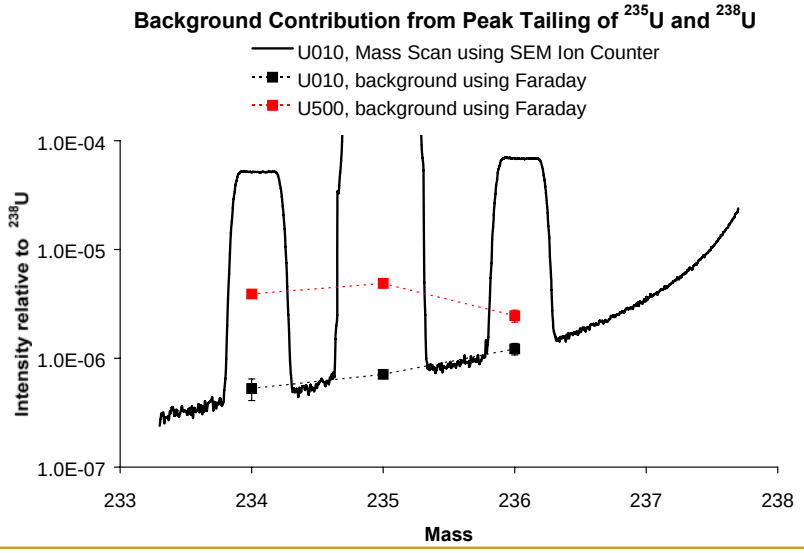
- Above methods take advantage of significant precision/accuracy advantage of total evaporation and/or internal correction

⇨ Advanced methods (and rigor of certification) require extra effort to account for uncertainty contributors

Conventional mass spectrometry limitation: inherent precision limitation



Total Evaporation yields improved precision
Problem: peak tails bias minor ratios



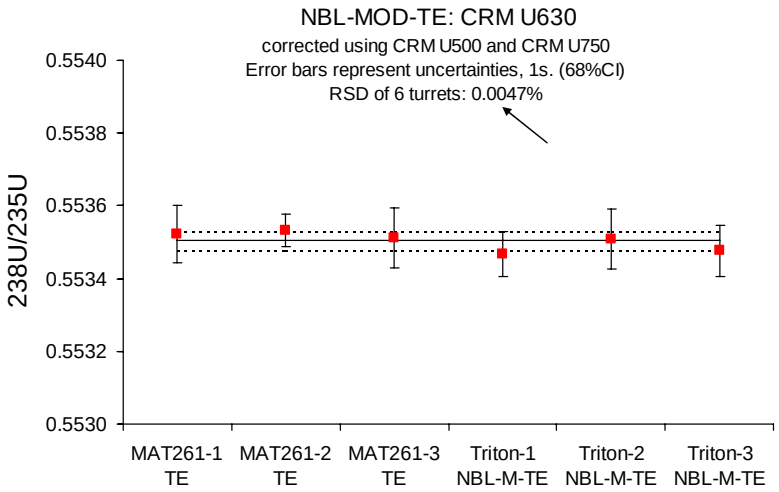
Conventional vs Total Evaporation

- **Conventional Analysis:**
  - **Sample pre-heated (10-40 min) towards target ion beam intensity**
  - **Measurement for a short span of sample**
  - **Periodic background measurement during analysis**
- **Total Evaporation Analysis:**
  - **Sample pre-heated to low intensity for ion beam focussing only**
  - **Measurement *continuously* until sample exhausted**
  - **Two-to-four fold better precision; faster analyses; smaller sample size; less susceptible to interferences**
  - **No background correction – minor isotope data biased**

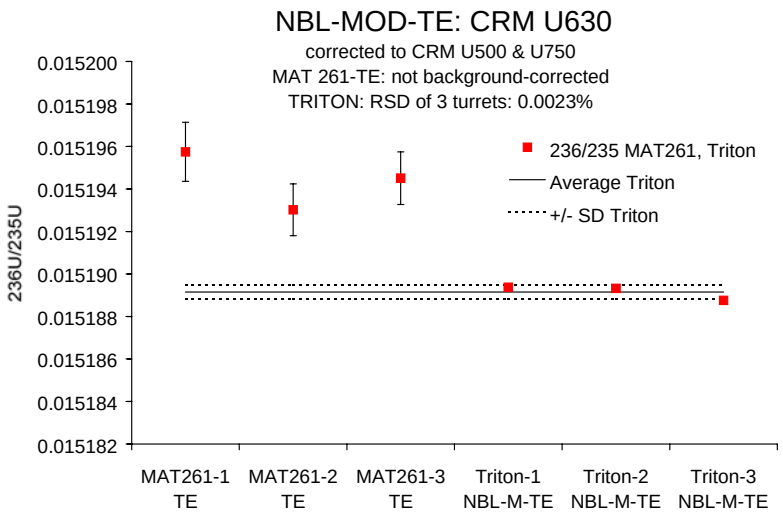
NBL-Modified Total Evaporation

- **NBL-Modified Total Evaporation Analysis:**
  - **Measurement until sample exhausted**
  - **Measurement periodically interrupted to allow background measurement and/or multi-dynamic data acquisition**
  - **Periodic peak centering and focusing also allowed**
- **Best of both worlds:**
  - Improved precision (2-4 fold)
  - Allows for background correction to compensate for peak tailing: More accurate minor ratio data

Modified TE Strength: Minor Ratios



Modified TE Strength: Minor Ratios



High Intensity Method

- New amplifiers and Faraday detectors allow up to 50 V ion beam
- Extremely stable amplifiers and matrix switching minimize detector calibration influence on uncertainty
- Large sample load (5-15 µg vs <1 µg)
- Allows for accurate minor measurements using Faraday detectors only (or SEM for extreme ratios)
- Eliminates or minimizes SEM linearity and SEM/Faraday detector calibrations (e.g. better uncertainties)
- Internal fractionation correction using previously-determined $^{235}U/^{238}U$ ratio

High Intensity Method Example (C129A)

Material:

Isotope:	234	235	236	238
Atom %:	0.005296	0.72087	0.0000097	99.27382
Intensity:	2 mV	291 mV	ND	40 V

Measurement Scheme:

Cycle	L1	C	H1	H3
1	234	235	236	238
2	233.7	234.7	235.7	
3	234.4	235.4	236.4	

High Intensity Method Example (C129A)

Material:

Isotope:	234	235	236	238
Atom %:	0.005296	0.72087	0.0000097	99.27382
Intensity:	2 mV	291 mV	ND	40 V

Measurement Scheme:

Cycle	L1	C	H1	H3
1	234	235	236	238
2	233.7	234.7	235.7	
3	234.4	235.4	236.4	

Advanced Ion Counting Method

- Dynamic ion counting method with:
  - Internal fractionation correction
  - Near-real time SEM/Faraday calibration
  - SEM linearity correction
  - Can be combined with high intensity technique
  - Suited for minor to extreme ratios (10^{-4} to $<10^{-8}$)

Advanced Ion Counting Method

Sample:

- Plutonium metal standard CRM 126-A
- 93.9% ^{239}Pu; 0.01% ^{238}Pu
- Already characterized for ^{239}Pu/^{240}Pu via TE

Approximate Pu ion beam intensities:

^{238}Pu: 70,000 cps (0.05 mV)
^{239}Pu: 7 Volts
^{240}Pu: 400 mV
^{242}Pu: 4 mV = 220,000 cps

NOTE: High intensity would offer no specific benefit:
^{238}Pu max intensity < 0.3 mV

Advanced Ion Counting Method

Peak Jumping Analysis Scheme:

Step	Cup L3	Cup L2	Cup L1	SEM	Cup H1	Cup H2
1					**242**	
2						
3						

Step 1: Acquire ^{242}Pu beam in faraday detector

Advanced Ion Counting Method

Peak Jumping Analysis Scheme:

Step	Cup L3	Cup L2	Cup L1	SEM	Cup H1	Cup H2
1					**242**	
2				**242**		
3						

Step 1: Acquire ^{242}Pu beam in faraday detector
Step 2: Acquire ^{242}Pu beam in ion counter to establish SEM/Faraday cup calibration factor

Advanced Ion Counting Method

Peak Jumping Analysis Scheme:

Step	Cup L3	Cup L2	Cup L1	SEM	Cup H1	Cup H2
1					**242**	
2				**242**		
3				**238**	**239**	**240**

Step 1: Acquire ^{242}Pu beam in faraday detector
Step 2: Acquire ^{242}Pu beam in ion counter to establish SEM/Faraday cup calibration factor
Step 3: Acquire ^{238}Pu intensity and ^{240}Pu/^{239}Pu ratio for mass fractionation correction

Advanced Ion Counting Method

Step	SEM	Cup H1	Cup H2
1		**242 (F_2)**	
2	**242 (I_2)**		
3	**238 (I_8)**	**239 (F_9 & M_o)**	**240 (M_o)**

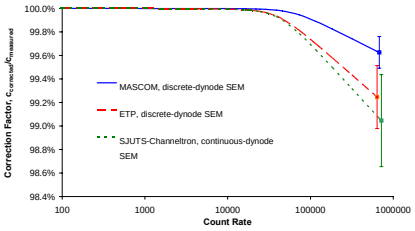
Corrected ^{238}Pu/^{239}Pu: $$[\frac{I_8 / F_9}{I_2 * L / F_2}]*[(M_0 / C)]$$

Where

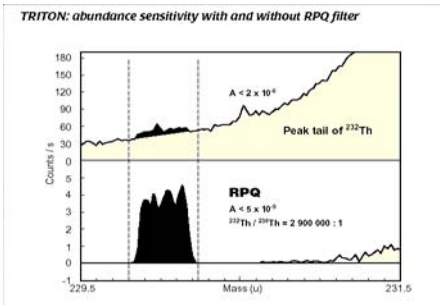
I_8 = measured ^{238}Pu ion intensity in SEM detector
F_9 = measured ^{239}Pu ion intensity in Faraday detector
I_2 = measured ^{242}Pu ion intensity in SEM
L = SEM linearity correction
F_2 = measured ^{242}Pu ion intensity in Faraday detector
M_o = measured ^{240}Pu/^{239}Pu ratio
C = certified value for ^{240}Pu/^{239}Pu ratio

Advanced Ion Counting Method

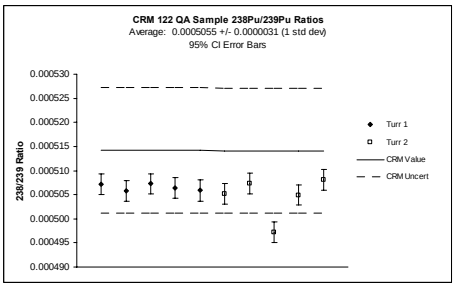
- SEM linearity correction (unique to each SEM)



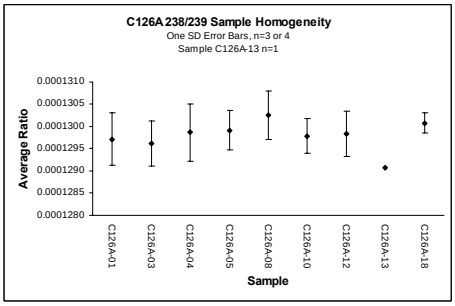
- RPQ to eliminate peak tailing
  - Abundance sensitivity <30 ppb (17 cps at ^{238}Pu)



QA and sample data



Material	238/239	Std Dev	%RSD
CRM 122 QC:	0.0005064	0.0000011	0.22
Metal Sample:	0.00012984	0.00000047	0.36



Conclusion

- NBL has developed and implemented three methods
- Improved precision and accuracy
- Methods are complementary, and are selected based upon sample composition
- Require latest-generation instrumentation
- Uncertainty determinations require extensive knowledge of instrument operation/detector performance

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Measurement Evaluation Program Annual Meeting

Calorimetry Exchange
July 15, 2006
Nashville, TN.

B. Srinivasan

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Calorimetry Exchange: January 2005 – December 2005

Measurement evaluation of Calex 1

- Isotopic abundance of Pu isotopes and ^{241}Am
- Effective specific power (P_{eff})
- Calorimetric power
- Mass of Pu

Working reference material certification of Calex 2

- Pu assay
- Pu isotope abundance
- ^{241}Am abundance
- Mass of Pu

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Participants, measurement methods and analysis schedule

Participants

- Hanford and LLNL participated.
- LANL and SRS did not participate.

Method

- Pu and ^{241}Am isotopes abundance by gamma ray spectrometry
- Calorimetric power by calorimetry

Analysis schedule

- Frequent measurements throughout the year

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Statistical Evaluation

% RD of measurement results with respect to reference values and standard deviations

- Pu isotope abundance
- ^{241}Am abundance
- Calorimetric power
- P_{eff}
- Mass of Pu

Note: P_{eff} is calculated from measurements of isotope abundance and calorimetric power, and mass from calorimetric power and P_{eff}

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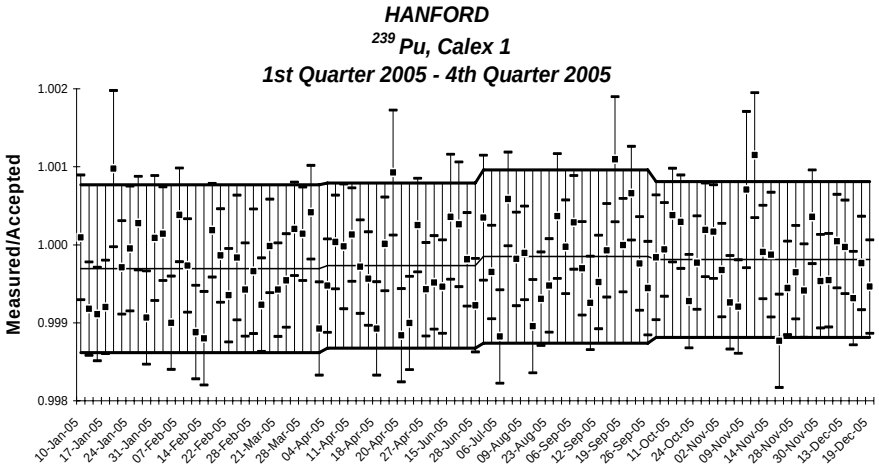
Quarterly Evaluation: an example



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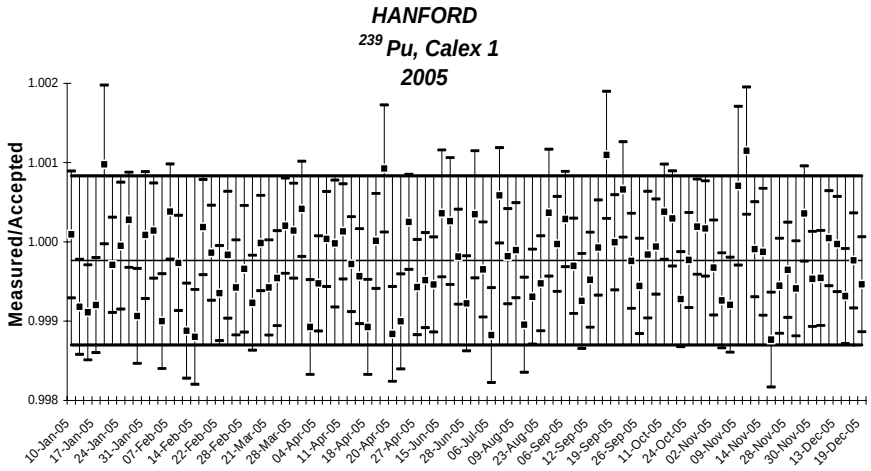
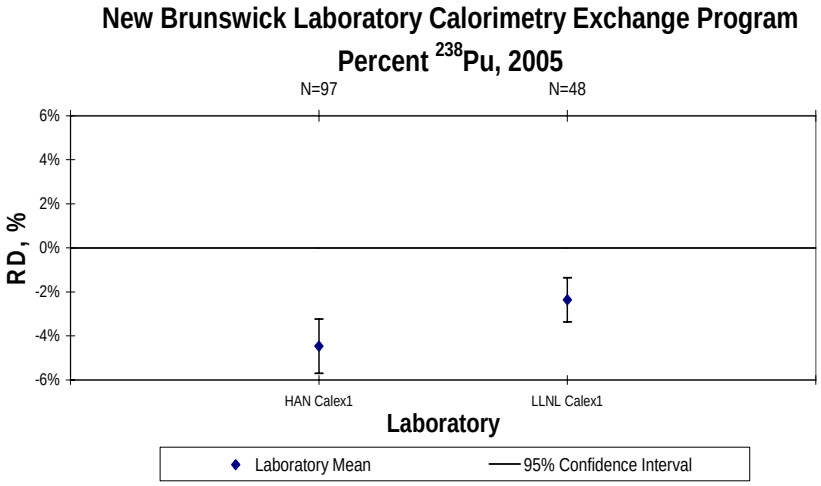
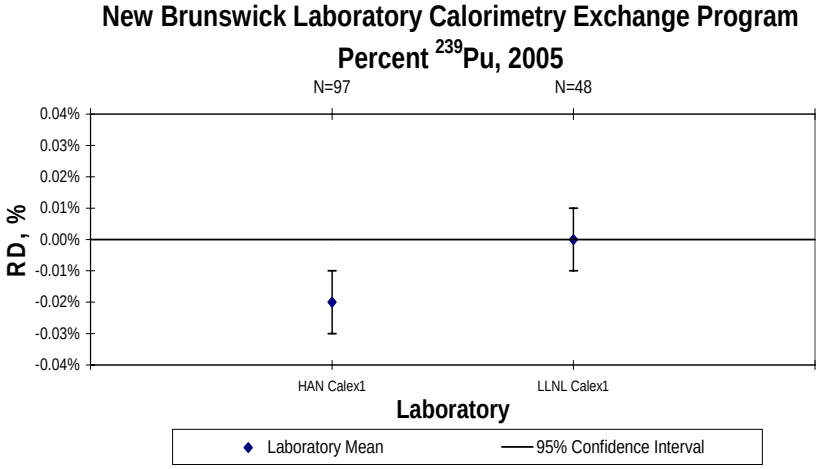
Annual evaluation: an example



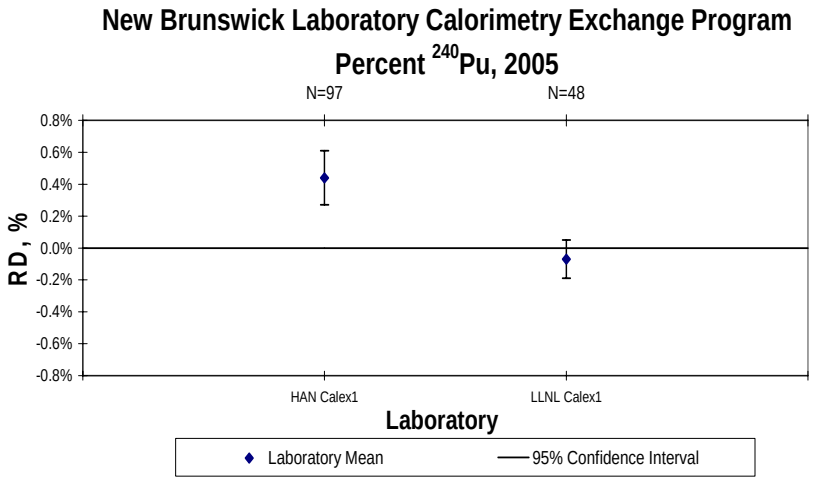
Calex 1: ^{238}Pu evaluation



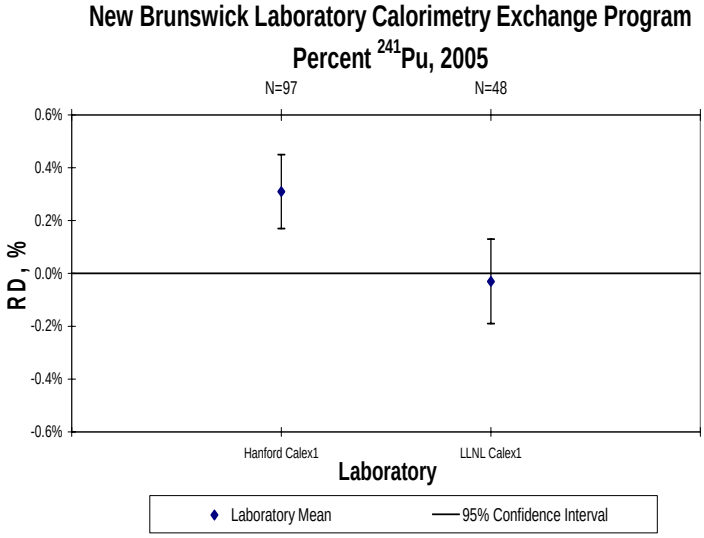
Calex 1: ^{239}Pu evaluation



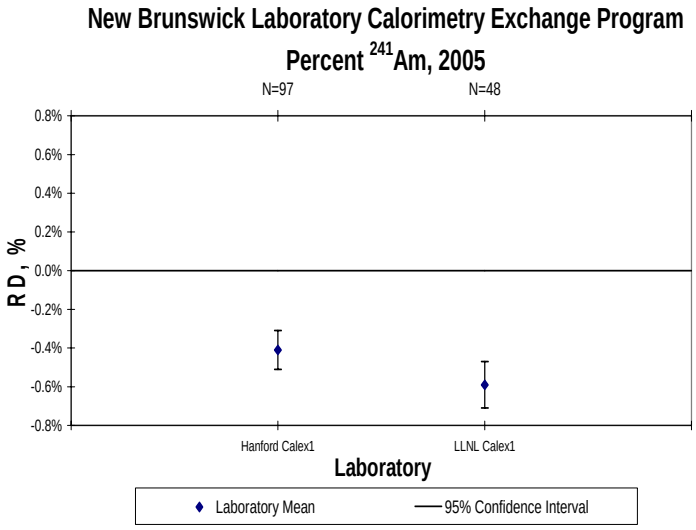
Calex 1: ^{240}Pu evaluation



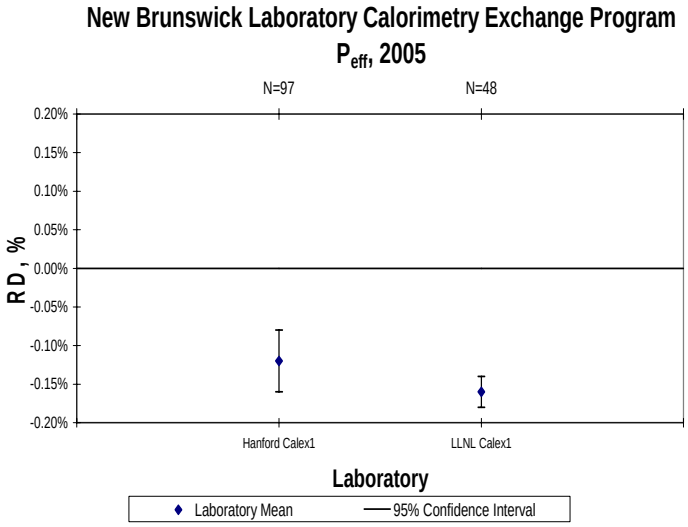
Calex 1: ^{241}Pu evaluation



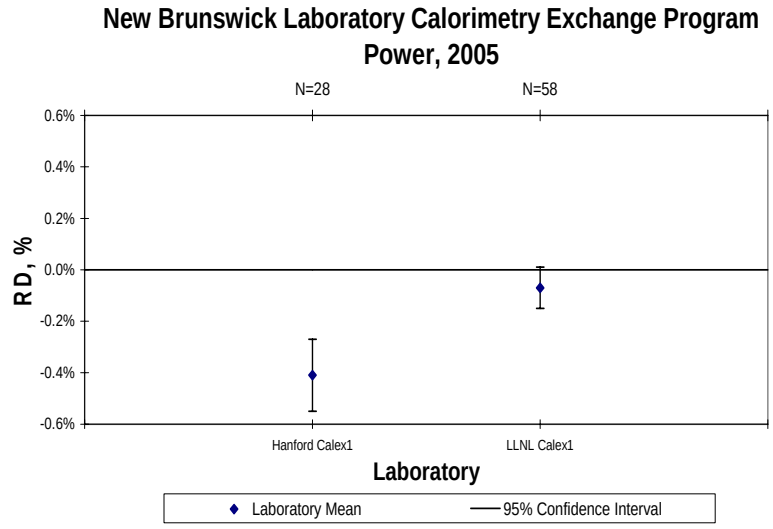
Calex 1: ^{241}Am evaluation



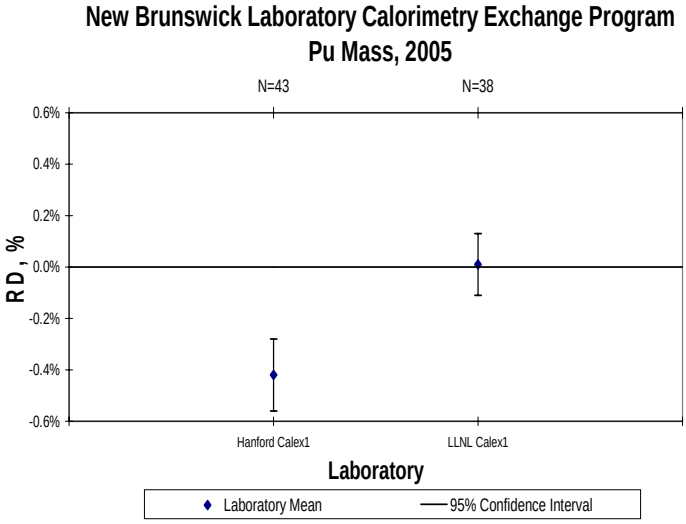
Calex 1: P_{eff} evaluation



Calex 1: Calorimetric power evaluation



Calex 1: Pu mass evaluation



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Calex 1: Evaluation summary

Table 3. Performance evaluation of Calex 1 measurement results fro Hanford and LLNL. The % RDs are shown along with 95 % confidenc intervals (i.e., ± twice the standard uncertainty).

Measured Quantity	% RD	
	Hanford	LLNL
Pu mass	-0.42 ± 0.14	0.01 ± 0.11
Power	-0.41 ± 0.12	-0.07 ± 0.08
P_{eff}	-0.12 ± 0.04	-0.16 ± 0.03
^{238}Pu	-4.46 ± 1.23	-2.36 ± 1.00
^{239}Pu	-0.02 ± 0.01	0.00 ± 0.01
^{240}Pu	0.44 ± 0.17	-0.07 ± 0.12
^{241}Pu	0.31 ± 0.14	-0.03 ± 0.15
^{241}Am	-0.43 ± 0.10	-0.59 ± 0.12

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Calex 2: Working reference material certification

Calex 1	Calex 2
400 g PuO_2; 6 units	2000 g PuO_2 ; 10 units
$^{239}Pu/^{240}Pu = 16.2$	$^{239}Pu/^{240}Pu = 7.2$
Low ^{241}Am	High ^{241}Am
1 watt	6 watt
05/29/1979	07/24/1995

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Calex 2: Moisture content

	NBL	LANL
Moisture (weight %)	0.025	0.026
Std. dev	0.013	0.025
n	4	5
% RD	≡ 0.0	4 %

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Calex 2: Plutonium content (as of 07/24/1995)

	NBL	LANL
Pu (weight %)	87.451	87.711
Std. dev	0.038	0.054
n	10	5
% RD	≡ 0.0	0.3 %

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Calex 2: Plutonium isotope abundance (as of 07/24/1995; all in weight %)

	NBL	LANL	% RD (NBL ≡ 0.0)
^{238}Pu	0.0803	0.0853	6.2%
^{239}Pu	86.5366	86.5304	-0.007%
^{240}Pu	12.1689	12.1691	0.001%
^{241}Pu	1.0074	1.0085	0.11%
^{242}Pu	0.2067	0.2067	0.0 %
Total	100	100	

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Calex 2: ^{241}Am content (as of 07/24/1995)

	NBL	LANL
Am (µg/g Pu)	4730	4780
Std. dev	98	95
n	10	5
% RD	≡ 0.0	1.1 %

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Calex 2: working reference material characterized values

Pu content

- Statistical disagreement between NBL and LANL
- Characterize the Pu content by pooling NBL and LANL results
- Characterized value with expanded uncertainty

  87.60 ± 0.18 g Pu/g sample (as of 7/24/1995)
- Uncertainty estimate may be revised

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Calex 2: working reference material characterized values (continued)

Pu isotopes

- NBL and LANL results in disagreement for ^{238}Pu only
- Characterized isotope abundance same as NBL result (as of 7/24/1995) with expanded uncertainty at 95% C.L.; uncertainty estimate may be revised

Isotope	Wt %	95% C.L.
^{238}Pu	0.08031	0.00056
^{239}Pu	86.5366	0.0050
^{240}Pu	12.1689	0.0022
^{241}Pu	1.0074	0.0018
^{242}Pu	0.2067	0.0006

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Calex 2: working reference material characterized values (continued)

^{241}Am content

- NBL and LANL determinations agree within about 1%; use mean of NBL and LANL values
- Characterized value (as of 7/24/1995) with expanded uncertainty

4755 ± 84 µg ^{241}Am/g of Pu

- Uncertainty estimate may be revised

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Calex 2: working reference material characterized values (continued)

Pu mass

- Pu mass calculated from mass of PuO_2 (2000 g) and Pu content
- Characterized value (as of 7/24/1995) with expanded uncertainty is

1752 ± 4 g Pu

- Uncertainty estimate may be revised

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Calex 2: verification of characterized values

- Calorimeteric power measurement for wattage
  - Two different calorimeters
  - Calibrated using heat source standards

Isotope measurements for P_{eff}
  - FRAM isotope code
  - TRIFID isotope code
  - Mass spectrometer

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Calex 2: verification of characterized values (continued)

- Calorimetric power measurement: 6.2378 ± 0.0045 watt

- P_{eff} from FRAM, TRIFID and mass spec measurements

	FRAM	TRIFID	Mass spec
Peff mw/g Pu	3.564	3.534	3.564
% RD	0.00 %	-0.84 %	≡ 0.00

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Calex 2: verification of characterized values (continued)

Pu mass

- Coulometry

PuO_2 mass X Pu content

- Mass spec

Power/mass spec P_{eff}

- FRAM

Power/FRAM P_{eff}

- TRIFID

Power/TRIFID P_{eff}

Method	Pu mass (g)	% RD
Coulometry	1752.0	≡ 0.00
Mass spec	1750.2	- 0.1 %
FRAM	1750.2	- 0.1 %
TRIFID	1765.2	0.75 %

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Calex 2 working reference material characterization: conclusions

Pu content

- NBL/LANL: 87.60 ± 0.18 g Pu/g
- The uncertainty of 0.2%; it is at least a factor of 2 or 3 higher than expected in coulometry
- Higher uncertainty acceptable for NDA standard (calorimetry/neutron measurements)

Pu isotope abundance

- NBL results from TIMS determination

^{241}Am abundance

- Average from NBL/LANL determinations

Effects of Variations in Half-Lives on Decay-Corrected Characterized Values of Plutonium Standards in Calorimetric Exchange Program

B. Srinivasan, M. Soriano, and W. Losinger
New Brunswick Laboratory

Presented at the 47th INMM Annual Meeting, Nashville, TN, July 2006

Reference Values For CALX Standards

	CALX 1	CALX 2	
Date	5/29/79	7/24/95	
PuO_2 Mass	454.60	2000	g
Pu Concentration	87.819	87.60	wt %
Pu Mass	399.23	1752	g
^{238}Pu	0.0102	0.08031	wt %
^{239}Pu	93.7336	86.5366	wt %
^{240}Pu	5.8560	12.1689	wt %
^{241}Pu	0.3712	1.0074	wt %
^{242}Pu	0.0290	0.2067	wt %
^{241}Am	0.0061	0.4755	g ^{241}Am/g Pu, %
P_{eff}	2.3012	3.564	mW/g
Power	918.71	6244.9	mW

Published Sources of Half Life Values

- ASTM C 1458-00 Test Method (Set A on Charts)
- Nuclear Wallet Cards NuDat 2 2002 (Set B on Charts)
- NuDat 2 2006 (Set C on Charts)
- IUPAC 2001 (Set D on Charts)
- NuBase 2003
- NuBase 2006
- Values used in NBL CALX Program (Set E on Charts)

ASTM C-1458-00 Test Method (First Published 1987)

Isotope	Half Life Value, Yrs	Uncertainty
^{238}Pu	87.74	0.04
^{239}Pu	24119	16
^{240}Pu	6564	11
^{241}Pu	14.348	0.022
^{242}Pu	376300	900
^{241}Am	433.6	1.4

NuDat2 Nuclear Wallet Cards 2002

Isotope	Half Life Value, Yrs	Uncertainty
^{238}Pu	87.7	0.3
^{239}Pu	24110	30
^{240}Pu	6564	11
^{241}Pu	14.29	0.006
242Pu	373300	1200
^{241}Am	432.2	0.7

NuDat2 Nuclear Wallet Cards 2006

Isotope	Half Life Value, Yrs	Uncertainty
^{238}Pu	87.7	0.1
^{239}Pu	24110	30
^{240}Pu	6561	7
^{241}Pu	14.29	0.006
242Pu	375000	2000
^{241}Am	432.2	0.7

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IUPAC 2001

Isotope	Half Life Value, Yrs	Uncertainty
^{238}Pu	87.7	0.1
^{239}Pu	24100	30
^{240}Pu	6560	10
^{241}Pu	14.4	0.1
^{242}Pu	375000	2000
^{241}Am	432.7	0.6

NEW BRUNSWICK LABORATORY

NuBase 2003

Isotope	Half Life Value, Yrs	Uncertainty
^{238}Pu	87.7	0.1
^{239}Pu	24110	30
^{240}Pu	6564	11
^{241}Pu	14.35	0.1
^{242}Pu	375000	2000
^{241}Am	432.2	0.7

NEW BRUNSWICK LABORATORY

NuBase 2006

Isotope	Half Life Value, Yrs	Uncertainty
^{238}Pu	87.7	0.3
^{239}Pu	24110	30
^{240}Pu	6564	11
^{241}Pu	14.35	0.1
^{242}Pu	373300	1200
^{241}Am	432.2	0.7

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Values used in 2005 NBL CALX Program

Isotope	Half Life Value, Yrs
^{238}Pu	87.7
^{239}Pu	24119
^{240}Pu	6563
^{241}Pu	14.35
^{242}Pu	373000
^{241}Am	433

Decay Equations

$\lambda_i = \frac{\ln(2)}{\text{Half Life}_i}$, where Half Life$_i$ is the half life for Plutonium isotope i and i = 238, 239,240, 241, and 242.

$\lambda_{Am} = \frac{\ln(2)}{\text{HalfLife}_{Am}}$, where Half Life$_{Am}$ is the half life for ^{241}Am.

$\text{Den(t)} = \sum_{i=238}^{242} \text{Pu}_i * e^{-\lambda_i * t}$, where t is the elapsed time from initial measurement in the same units as the half lives and Pu$_i$ is the abundance of Plutonium isotope i at initial measurement in weight percent.

Decay Equations (cont.)

$\text{Pu}_i(t) = \frac{\text{Pu}_i * e^{-\lambda_i * t}}{\text{Den(t)}} * 100$, where Pu$_i$(t) is the abundance of Plutonium isotope i at elapsed time t in weight percent.

$^{241}\text{Am(t)} = 100 * \left[{}^{241}\text{Am} * e^{-\lambda_{Am} * t} + {}^{241}\text{Pu} * \frac{\lambda_{241}}{\lambda_{Am} - \lambda_{241}} * (e^{-\lambda_{241} * t} - e^{-\lambda_{Am} * t}) \right] / \text{Den(t)}$, where ^{241}Am is the initial amount of ^{241}Am and ^{241}Am(t) is the amount of ^{241}Am at elapsed time t, both in g ^{241}Am/g Pu, percent.

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Half Life Values Variation, Yrs

Isotope	Minimum	Maximum	Range	Relative Range, %
^{238}Pu	87.7	87.74	0.04	0.046
^{239}Pu	24100	24119	19	0.079
^{240}Pu	6560	6564	4	0.061
^{241}Pu	14.29	14.4	0.11	0.767
^{242}Pu	373000	376300	3300	0.881
^{241}Am	432.2	433.6	1.4	0.323

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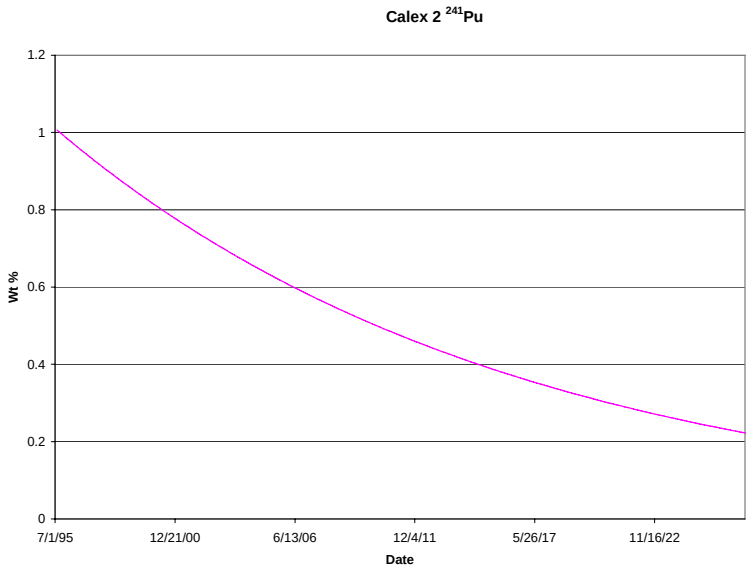
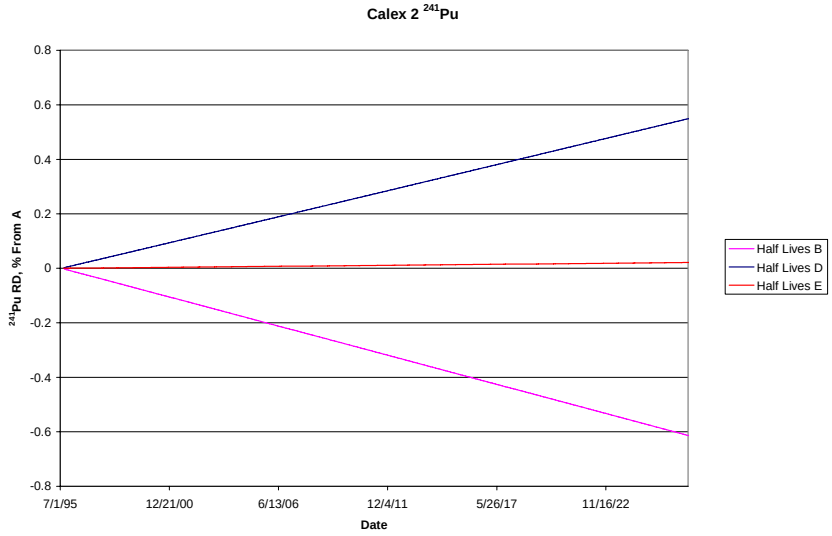
CALX 2 ^{241}Pu over Time



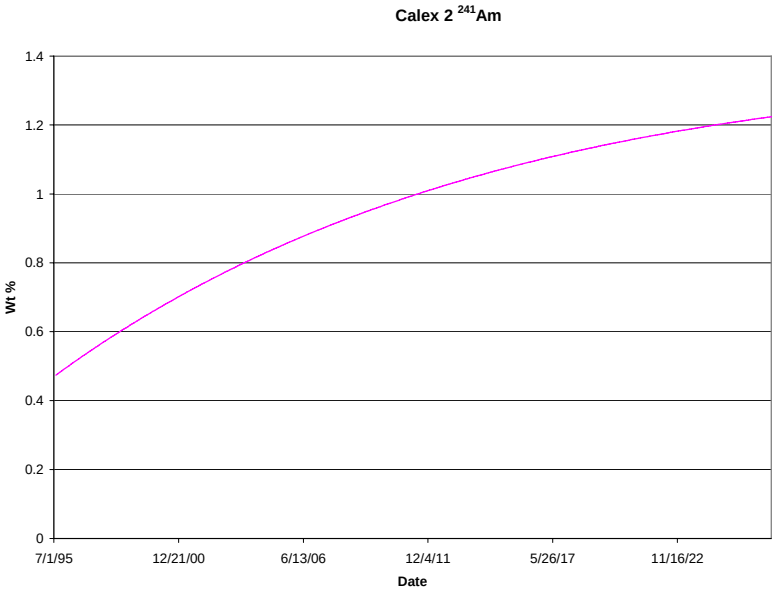
NEW BRUNSWICK LABORATORY

Effects of Different Half Life Values on CALX 2 ^{241}Pu Calculations over Time



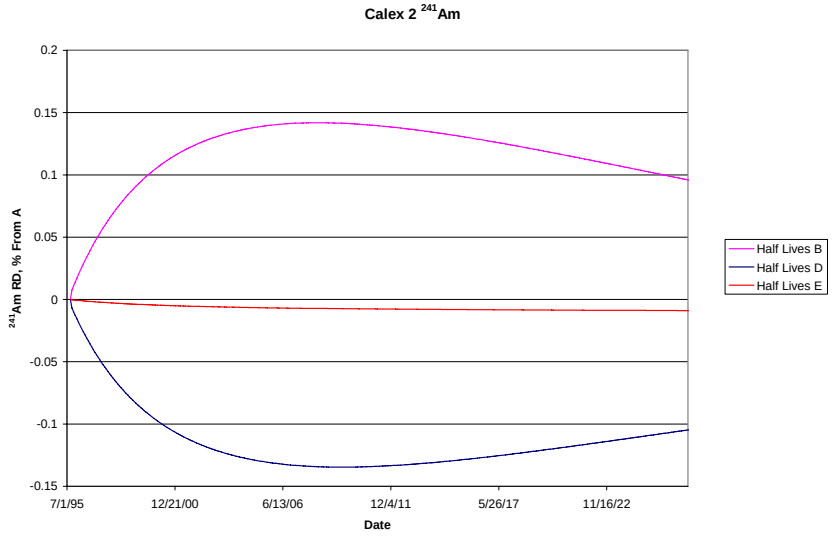
NEW BRUNSWICK LABORATORY

CALX 2 ^{241}Am over Time



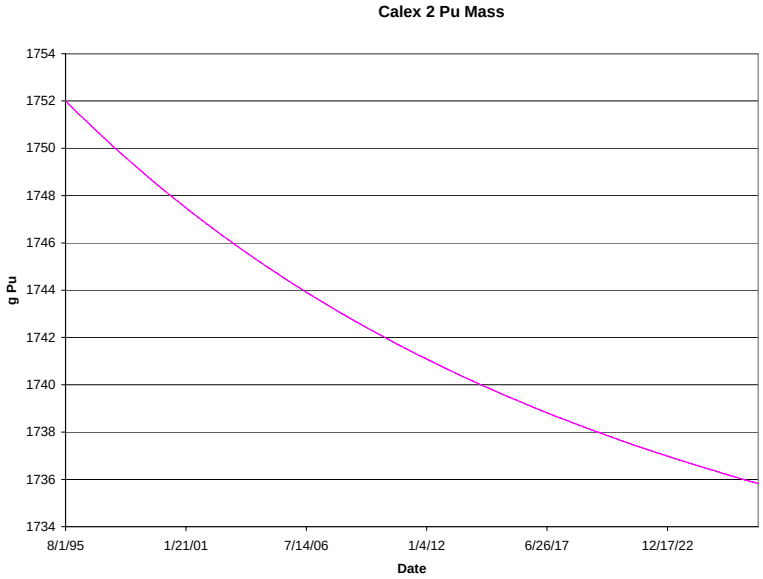
NEW BRUNSWICK LABORATORY

Effects of Different Half Life Values on CALX 2 ^{241}Am Calculations over Time

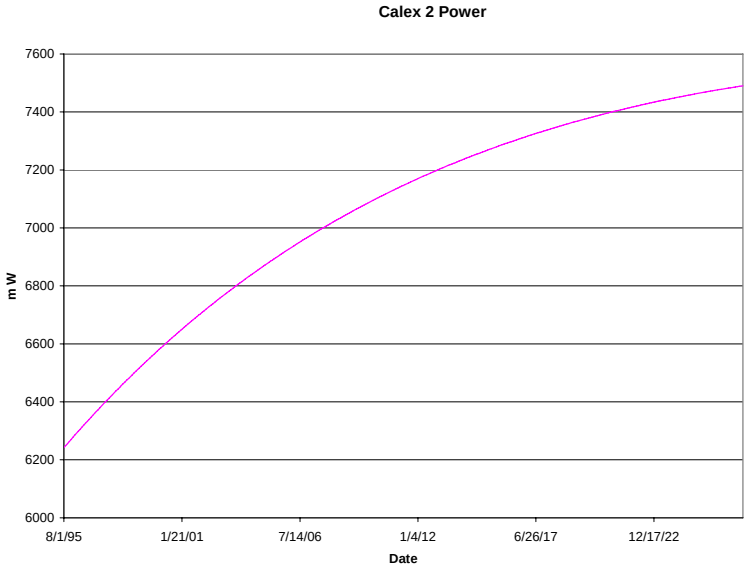


NEW BRUNSWICK LABORATORY

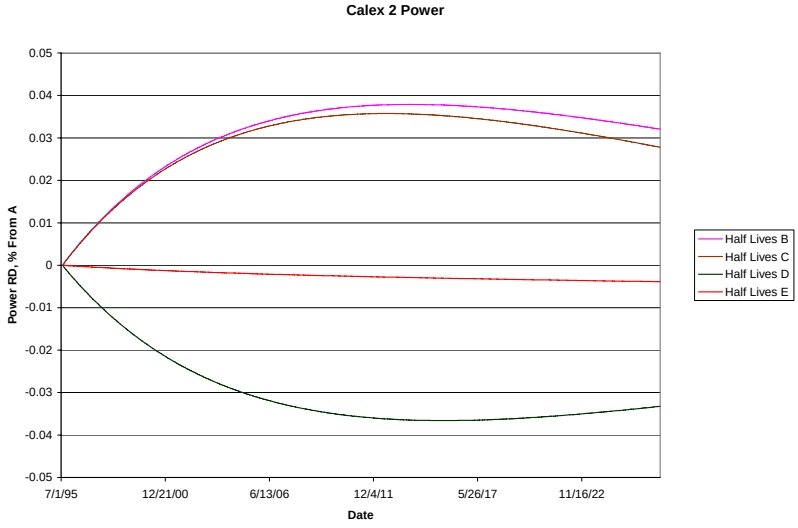
CALX 2 Pu Mass over Time



CALX 2 Power over Time

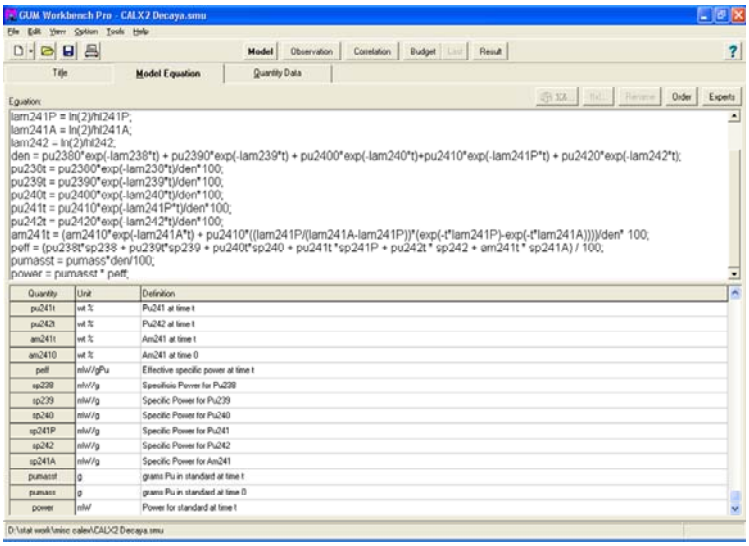


Effects of Different Half Life Values on CALX 2 Power Calculations over Time



NEW BRUNSWICK LABORATORY

GUM Workbench Screen Shots



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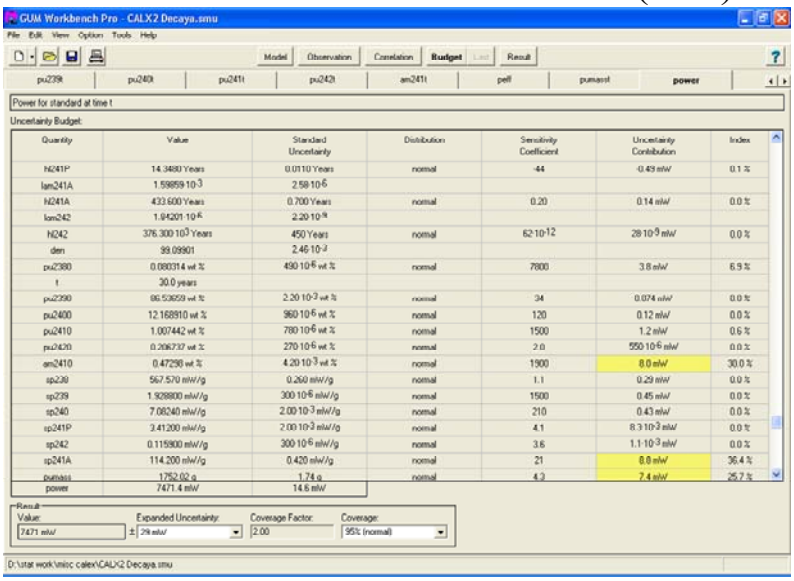
GUM Workbench Screen Shots (cont)



NEW BRUNSWICK LABORATORY

Effects of Parameter Uncertainty on Power Reference Value Uncertainty

	CALX 1	CALX 2
T = 10 Years	**Uncertainty Contributions** Specific Power ^{241}Am 79% Specific Power ^{239}Pu 16% Specific Power ^{240}Pu 3% **Result:** 978.49±0.56 m W	**Uncertainty Contributions** Specific Power ^{241}Am 98% **Result:** 6904±13 m W
T = 30 years	**Uncertainty Contributions** Specific Power ^{241}Am 93% Specific Power ^{239}Pu 5% Specific Power ^{240}Pu 1% **Result:** 1034.05±0.98 m W	**Uncertainty Contributions** Specific Power ^{241}Am 99% **Result:** 7471±18 m W

NEW BRUNSWICK LABORATORY

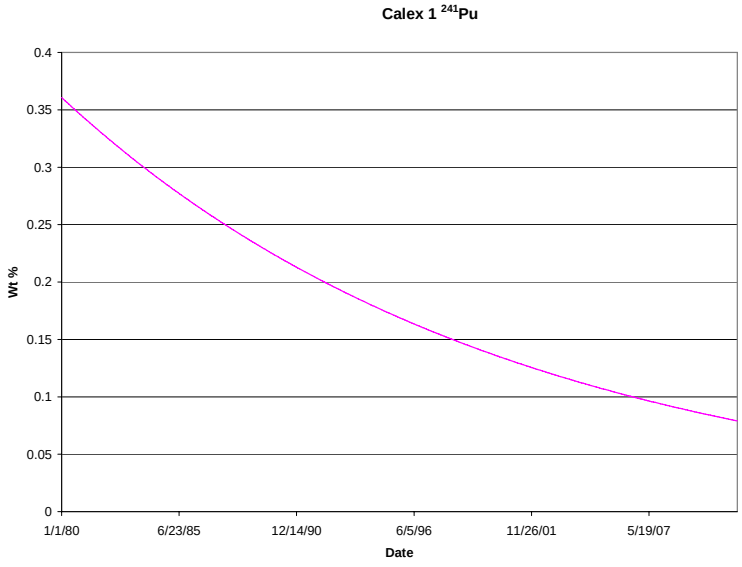
Effects of Measurement & Parameter Uncertainty on Power Reference Value Uncertainty for CALX 2

T = 10 Years	**Uncertainty Contributions** Initial ^{241}Am Value 39% Initial Pu Mass Value 27% Specific Power ^{241}Am 22% Initial ^{238}Pu Value 12% **Result:** 6904±27 m W
T = 30 years	**Uncertainty Contributions** Specific Power ^{241}Am 36% Initial ^{241}Am Value 30% Initial Pu Mass Value 26% Initial ^{238}Pu Value 7% **Result:** 7471±29 m W

Conclusions

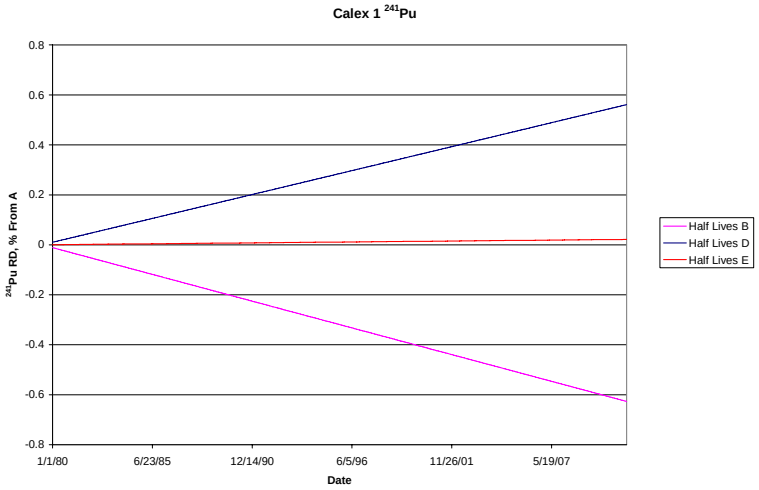
- Varying half life value and associated uncertainties have no significant effect on decay-corrected reference values' uncertainties.
- Uncertainties on isotopic specific power values, primarily ^{241}Am , have a significant effect on the decay-corrected reference values' uncertainties.
- Uncertainty on the initial characterization measurements of values, in particular the ^{241}Am and Pu content, are the major contributors to the decay-corrected reference values' uncertainties.

CALX 1 ^{241}Pu over Time



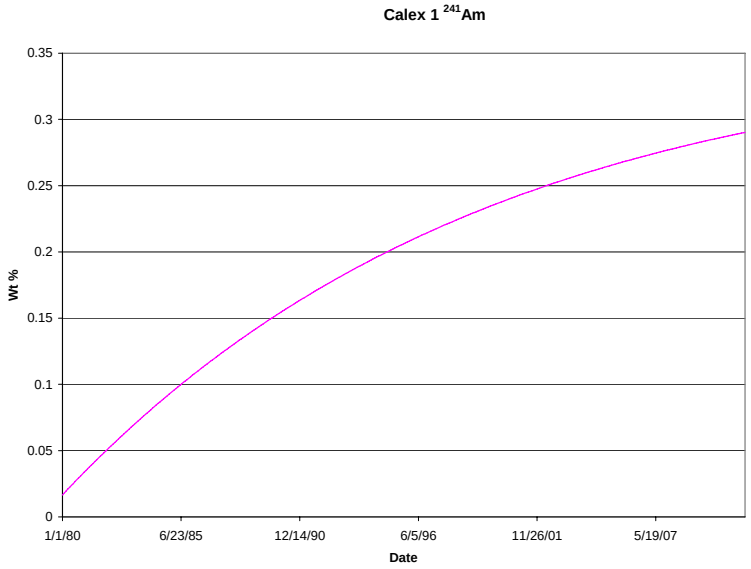
NEW BRUNSWICK LABORATORY

Effects of Different Half Life Values on CALX 1 ^{241}Pu Calculations over Time



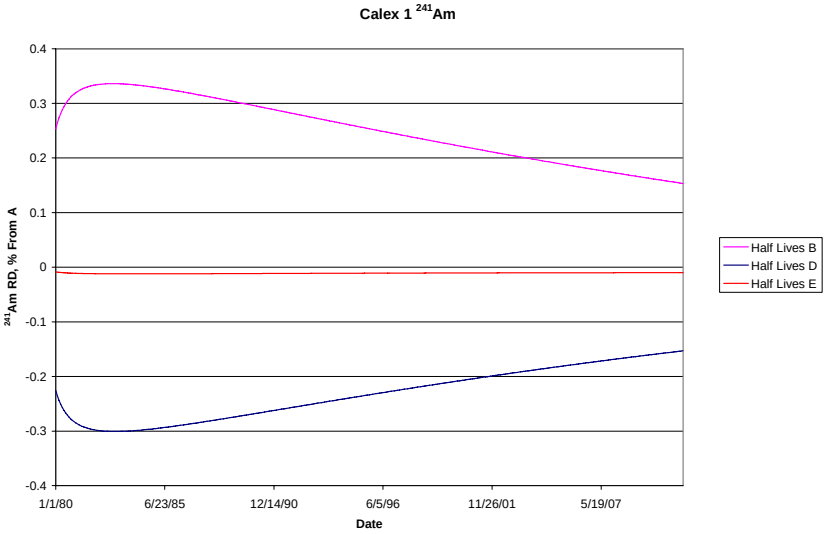
NEW BRUNSWICK LABORATORY

CALX 1 ^{241}Am over Time



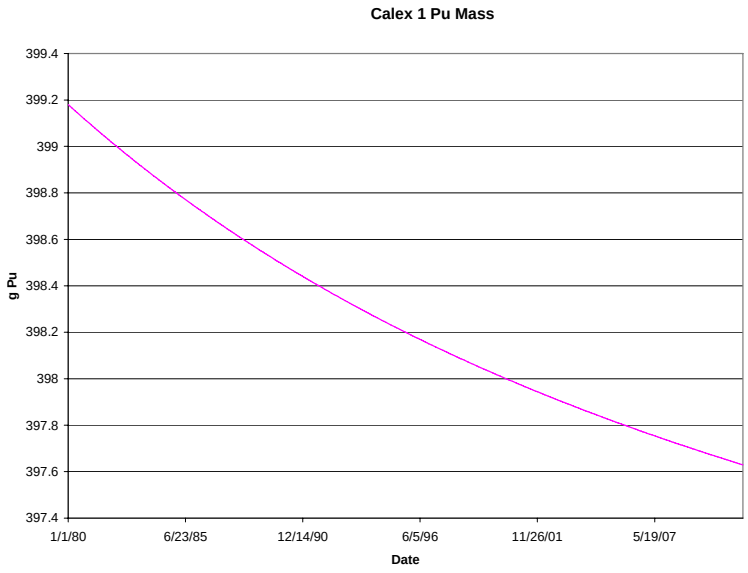
NEW BRUNSWICK LABORATORY

Effects of Different Half Life Values on CALX 1 ^{241}Am Calculations over Time

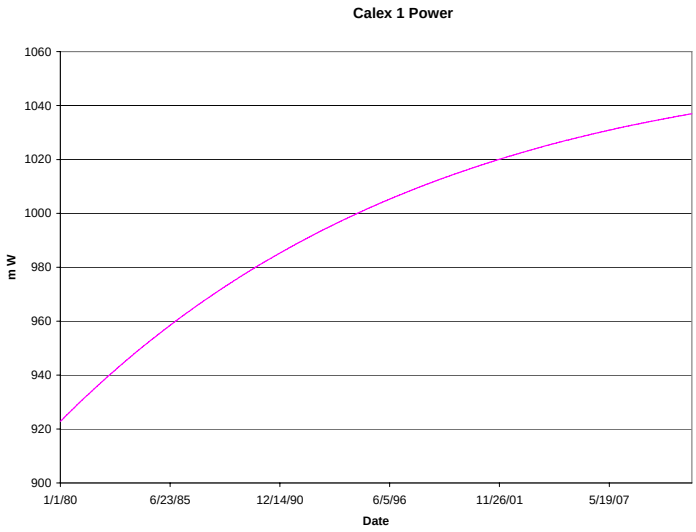


NEW BRUNSWICK LABORATORY

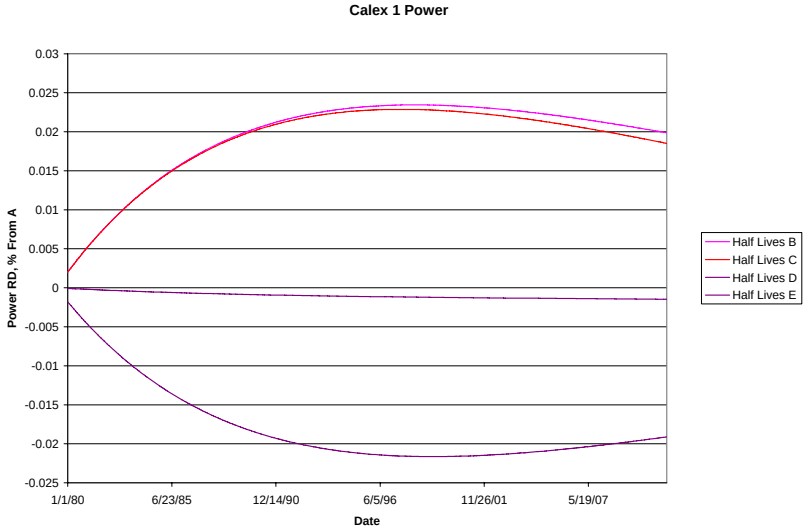
CALX 1 Pu Mass over Time



CALX 1 Power over Time



Effects of Different Half Life Values on CALX 1 Power Calculations over Time



ABSTRACTS OF PRESENTATIONS BY BUD SUMMERS, LLNL

a. LLNL experience with determining uranium isotopic masses in 3013 containers filled with MOx.

LLNL has measured uranium isotopic masses in 3013 containers filled with MOX using three gamma isotopic counters. These containers have significantly more shielding for low energy gammas than typical containers. Information will be presented concerning LLNL experience in measurement precision and accuracy of uranium isotopic masses in the 3013 containers based on historical knowledge of the amount of uranium isotopic mass in these containers.

b. LLNL accuracy/precision of CRM uranium standards in two isotopic counters.

LLNL has measured the uranium isotopic masses in seven CRM uranium standards in two gamma isotopic counters. Information will be presented concerning LLNL experience in measurement precision and accuracy of uranium isotopic mass in these isotopic counters. The LLNL precision and accuracy experience will be compared to analogous results from Hanford.

c. LLNL accuracy/precision of Calex-1 and Calex-2 plutonium standards in three isotopic counters

LLNL has measured the plutonium isotopic masses in Calex-1 and Calex-2 plutonium standards in three gamma isotopic counters. Information will be presented concerning LLNL experience in measurement precision and accuracy of plutonium isotopic mass in these isotopic counters. The LLNL precision and accuracy experience will be compared to analogous results from Hanford.

Some Recent Developments in Nondestructive Assay Technologies

Peter A. Santi
Safeguards Science and Technology Group (N-1)
Los Alamos National Laboratory

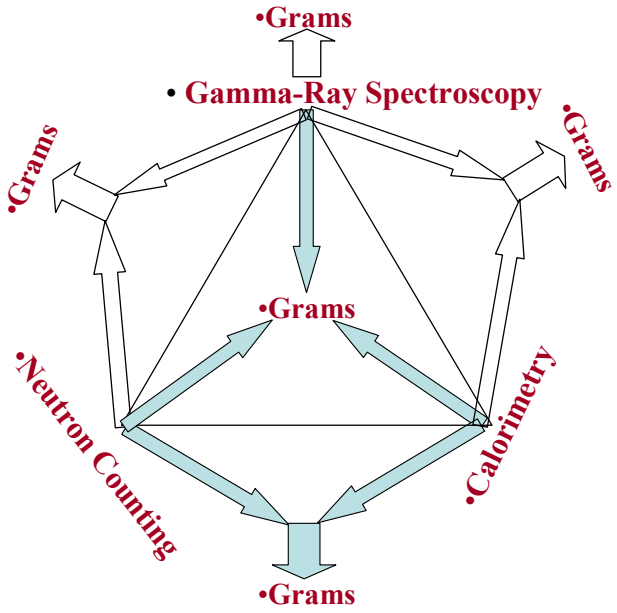
July 15, 2006

LA-UR-06-4844

Outline

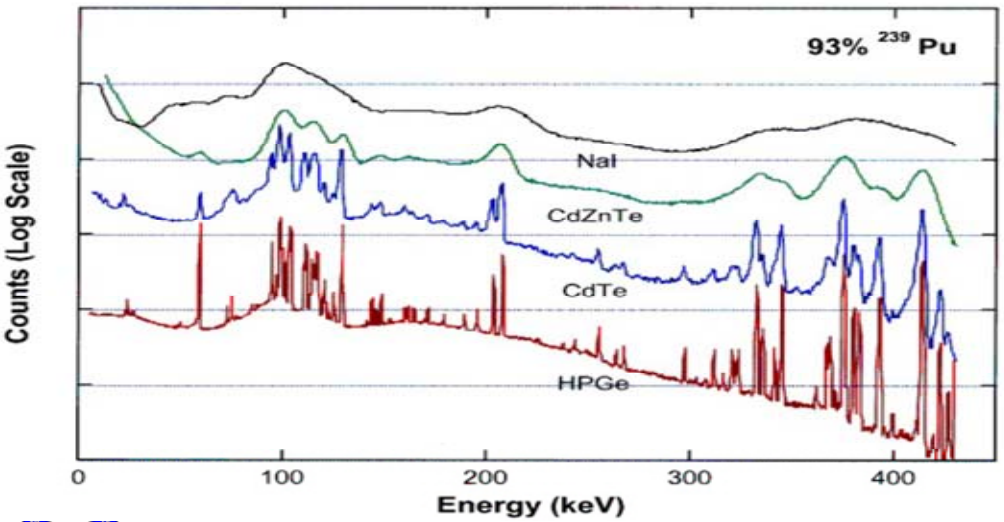
- Three components of Nondestructive Assay: gamma, neutron, and calorimetry
- Recent developments in gamma-ray detector technology
  - Nanocomposite Scintillators
  - μ-calorimetry
- Neutron Multiplicity Counting
  - ENMC
  - LSMC
- Recent work in Calorimetry
  - Modeling of heat flow in calorimeters
  - Improvements in water bath control

NDA of Special Nuclear Material



Importance of Energy Resolution for γ-Ray Spectroscopy

The spectral signature of 93% ^{239}Pu as measured by detectors of different energy resolution



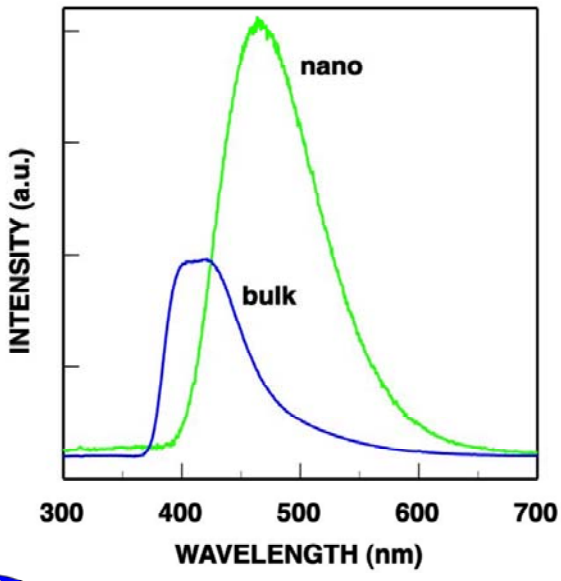
Composite Scintillators for Radiation Detection and Nuclear Spectroscopy*

Edward A. McKigney Rico E. Del Sesto
Luiz G. Jacobsohn Peter A. Santi,
Ross E. Muenchausen Kevin C. Ott
T. Mark McCleskey Bryan L. Bennett
James F. Smith D. Wayne Cooke

LANL

*This work supported by DOE BES, LANL LDRD, LANL TT Tech Maturation Fund and LANL N Division Tech Maturation Fund.

Radioluminescence Light Output

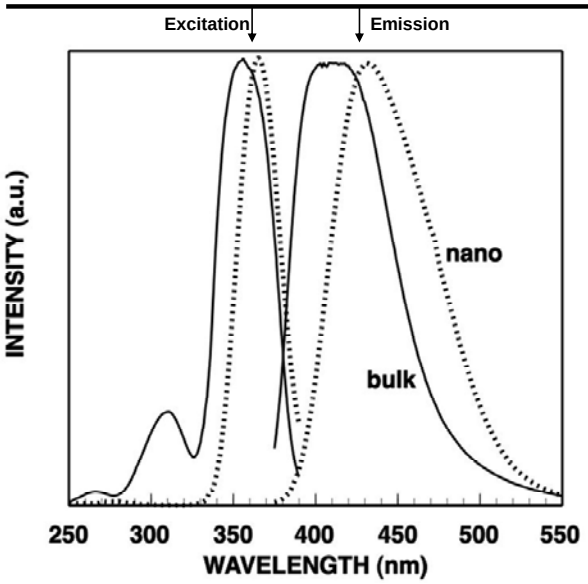


YSO:Ce nanoparticles exhibit higher light output than the bulk powder, under X-ray excitation.

D. W. Cooke, *et al*,
Appl. Phys Lett. 88, 103108 (2006)

Mass normalized radioluminescence of YSO:Ce.

Stokes Shift

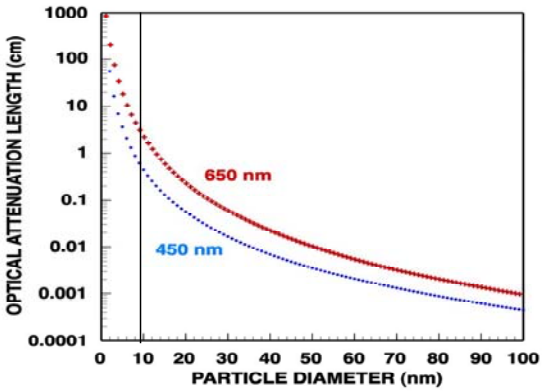


Nanophosphor PLE and PL are shifted with respect to bulk, and the overlap is decreased

D. W. Cooke, *et al*, Appl. Phys Lett. 88, 103108 (2006).

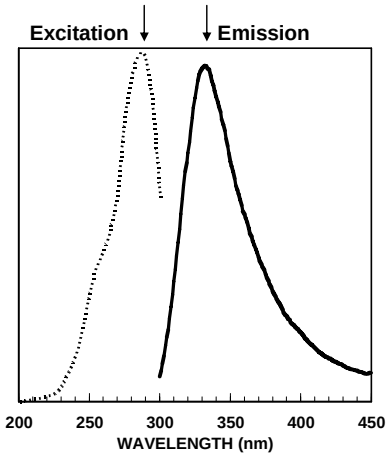
Photoluminescence excitation and emission for bulk and nano YSO:Ce.

LaF_3:Ce Transparent Nanocomposite Scintillator



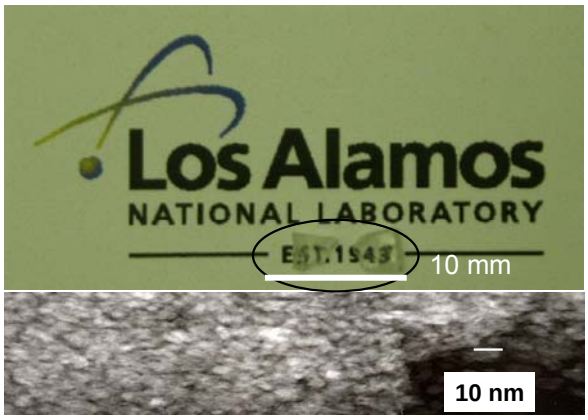
Calculated optical attenuation length vs. particle size.

The solid vertical line indicates the particle diameter cutoff below which transparent composites are expected.



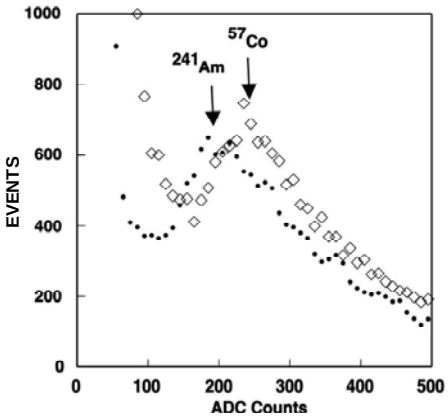
Nanophosphor photoluminescence

LaF_3:Ce Transparent Nanocomposite Scintillator



Transmission electron micrograph showing 10 nm primary particle size.

Events versus ADC counts for a LaF_3:Ce doped sample illuminated by different sources showing photopeak shift.



Work in Progress

- Produce larger scintillating pieces
- Synthesis of nanophosphors of brighter scintillators and fabrication of these into a composite
- Further characterization of nanophosphors
  - absolute light yield
  - linearity of the nanocomposite materials

Microcalorimeter Development for Precision Gamma-Ray Spectroscopy*

LANL

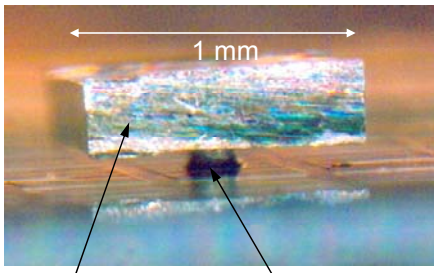
A. Hoover
S. Lamont
M. W. Rabin
C. R. Rudy
M. K. Smith
D. M. Tournear
D. T. Vo

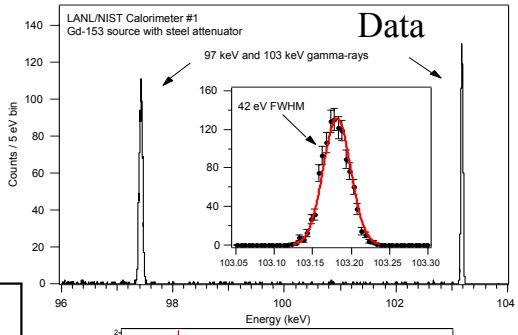
NIST

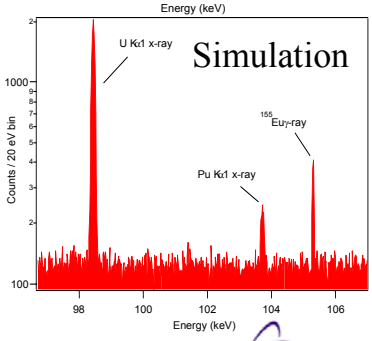
J. N. Ullom
B. L. Zink
J. A. Beall
W. B. Doriese
W.D. Duncan
L. Ferreira
G.C. Hilton
K. D. Irwin
C. D. Reintsema
L. R. Vale

*Sponsored in part by the NIST/EEEL Director's Reserve program, the Department of Energy, Office of Non-Proliferation Research and Development (NA-22), and DCI postdoctoral fellowship

Large Microcalorimeter Arrays



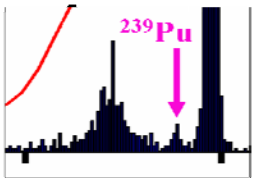




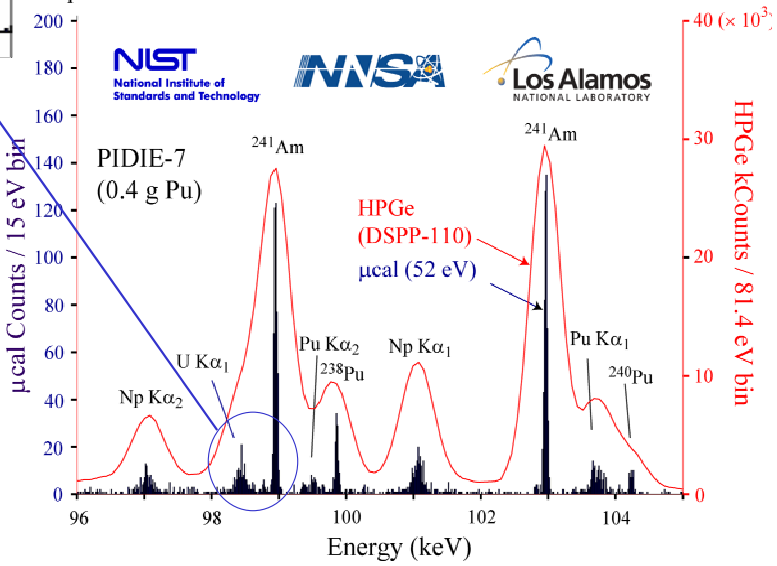
Target Applications:

Nuclear Forensics
Pu isotope analysis
Mass of Pu in Spent Fuel

Measurements of Pu samples

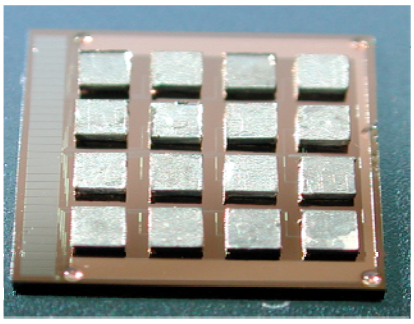


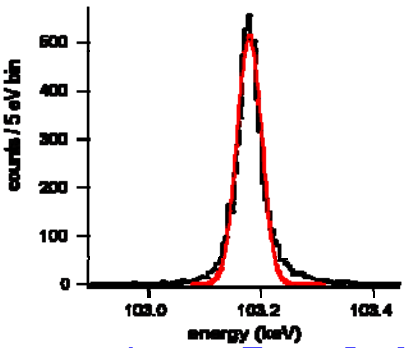
Pu spectra of both 52 eV microcalorimeter and HP Ge detector



13

Recent Results





First Array ***Array Results!***

- First Multiplexed Array
- Best pixel resolution: 27 eV FWHM @ 103 keV
- Combined spectrum from 13 pixels: 50 eV FWHM @ 103 keV

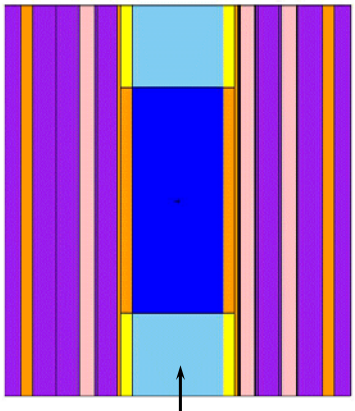
Neutron Multiplicity Counting

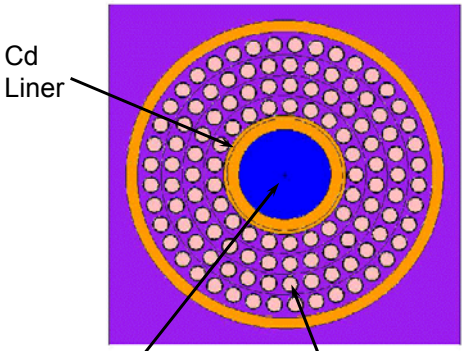
- Neutron multiplicity counting determines mass of special nuclear material (SNM) in an item by converting single neutron (S), double neutron (D), and triple neutron (T) counting rates into $m_{eff,240}$, α, M.
- While neutron multiplicity counting is effective for a wide range of materials, the technique has a reduced precision and accuracy for materials which have a high (α,n) reaction rate (impure items), or for items which have a large leakage multiplication (metals, dense oxides)

Characterizing Secondary Standards using ENMC

Epithermal Neutron Multiplicity Counter (ENMC)

Howard Menlove, James Stewart, et al.





ε = 64% (Pu energy)

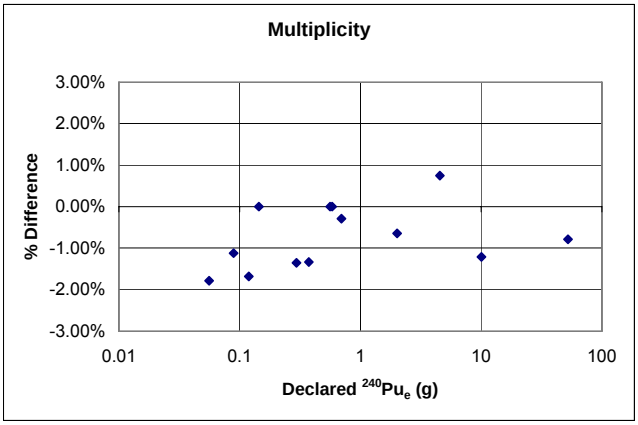
Die-away time = 19.1 μs

Range of Pu Materials Studied

TABLE II. LANL standards for the ENMC calibration

Standard ID	Material	Multiplicity Alpha	Total Pu (g)	Isotopics Date	Pu-239 (g)	Pu-240eff. (g)
FZC-158	Pu-240 oxide	Low (0.169)	0.695	78/12/15	0.006	0.705
P240	Pu-240 oxide	Low (0.184)	55.57	02/12/04	3.22	52.2
646078	MOX pellet	Medium (1.08)	0.8061	91/08/30	0.7128	0.089
646081	MOX pellet	Medium (1.09)	0.5077	91/08/30	0.4490	0.056
646078+081	MOX pellet	Medium (1.08)	1.314	91/08/30	1.1620	0.145
646119	MOX pellet	Medium (0.813)	0.2651	91/08/30	0.2311	0.033
PuOC-1	PuO2	Medium (0.917)	2.002	02/05/23	1.881	0.119
PuOC-2	PuO2	Medium (0.916)	4.971	02/05/23	4.671	0.295
PuOC-3	PuO2	Medium (0.913)	9.935	02/05/23	9.337	0.589
PuF-A1	Pu metal	Low (0.040)	1.765	00/01/01	1.658	0.105
LAO250C10	PuO2	Medium (0.525)	59.84	83/09/09	49.57	9.934

Results



RSD = 0.8%

- ENMC could possibly be used to characterize secondary standards for low multiplication items (MOX, oxides, etc)
- Current ENMC detector parameterization based on low mass items would have a 2-3% accuracy for higher mass items.

Liquid Scintillator Neutron Multiplicity Counter*

Kate Frame, Jonathan Thron, Tim Elmont, Ernst Esch,
Duncan MacArthur, Edward McKigney, Peter Karpius,
Peter Santi, Sy Stange and Morag K. Smith

Fast vs. Thermal neutrons

- No need for moderator
- Coincidence gate < 100 ns (vs ~10-50 μs for thermal neutron multiplicity counters)
- Virtually insensitive to accidental coincidences from high single neutron rates

Ideal for:

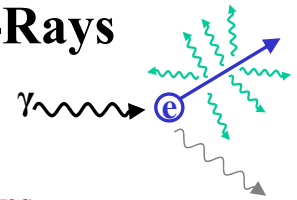
- Pu items with high (α,n)
- HEU active interrogation

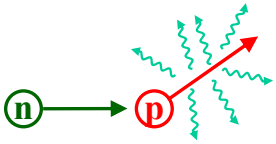
*This work supported by LANL N-Division Program Development and NNSA, Office of Dismantlement and Transparency (NA-241).

Pulse Shape Discrimination (PSD)

Needed to Eliminate Gamma-Rays

Gammas → Compton electrons



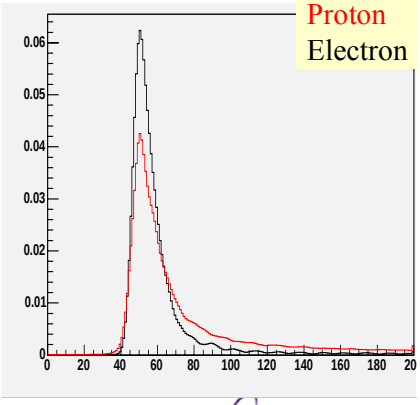


Neutrons → Recoil Protons

Scintillation light depends on ionization density

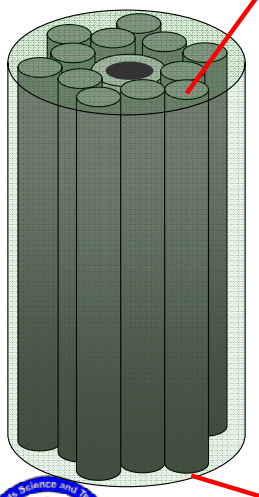
Protons fast component quenched relative to slower components

Pulse Shape Discrimination (PSD) can be used to eliminate gammas



Conceptual LSMC Design

12 Module LSMC



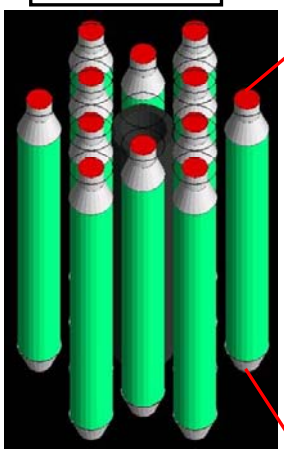
LSMC
- Size – 6-8 inch diameter cavity
- Efficiency – 20-30%
- Coincidence Gate <100ns
- Fast Waveform Digitizer

→PSD and Multiplicity Analysis performed in software

Modules
- 1 m length x 6 cm radius Liquid Scintillator
- Light Guides coupled to PMTs at both ends

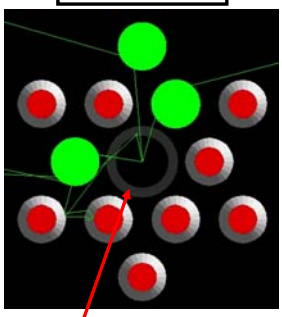
GEANT Modeling of an LSMC

12 modules

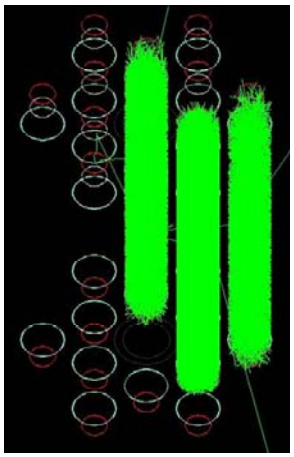


(Al housing not shown)

End View



1 inch (2.5 cm) thick Pb liner

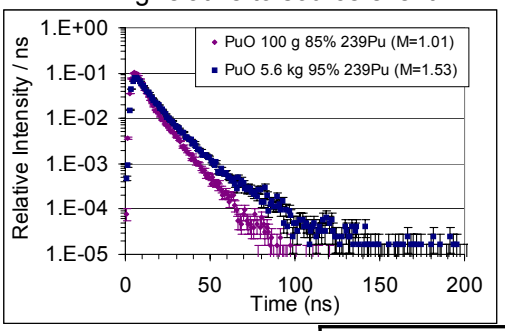


Tracks from a single fission event

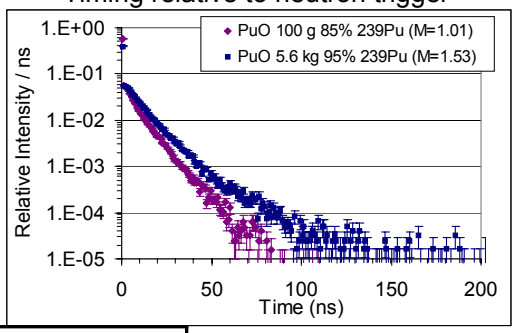
Neutron Timing: PuO

^{240}Pu Spontaneous Fission source Neutron Energy ≥ 500 keV

Timing relative to source event



Timing relative to neutron trigger



Net Multiplication	Time Gate (ns) (99% of total flux)
1.01	33.5
1.11	37.5
1.37	46.5
1.53	53.5

LSMC Status

GEANT simulations to determine performance of various design options for an LSMC module ongoing

Measurements using actual liquid scintilator modules needed to benchmark GEANT results.

Gamma and PSD analysis

Data acquisition electronics development.

For more details, see Abstract #339 to be presented on Monday, July 17 4 PM in Center Room 205

Other Neutron Counting Developments

- Configurable ENMC (see Abstract #307 to be presented on Monday, July 17th at 4:20PM in Center Room 205)
- Neutron Pulse Simulator (see Poster on Abstract #316 on Tuesday, July 18th in Center Room 206)

Calorimetry

- Measures the amount of heat produced in a sample
- Since you can't hide the heat of material, calorimetry is inherently matrix independent (bias-free)
- When combined with gamma-ray spectroscopy, it is the most accurate NDA technique for plutonium
- Is considered the "gold standard" of all of the NDA techniques throughout DOE complex for Pu
- Throughput is an issue due to long measurement times (one to several hours)
- Question often heard from users is "How long will measurements take?"

Heat Flow Calculations for 3013 canisters

Peter A. Santi, and David S. Bracken

The heat equation describing the flow of heat as a function of time is:

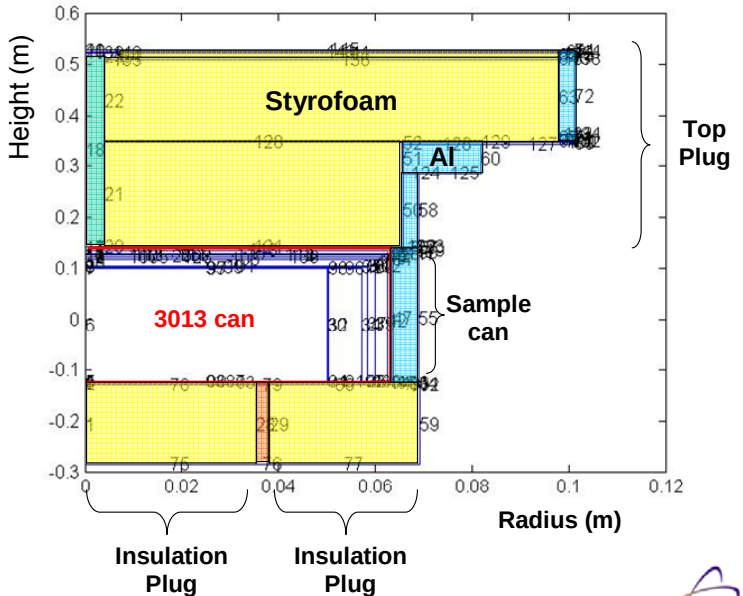
$$\nabla \cdot (k \nabla T) + Q = \rho \cdot C_p \frac{\partial T}{\partial t} \qquad (1)$$

where
- $T(\vec{r},t)$ - temperature of the system (K)
- k - thermal conductivity (W/m*K)
- Q - heat source
- ρ - density (kg/m^3)
- C_p - specific heat capacity (J/kg*K)

Determine which 3013 canister configuration would come to thermal equilibrium the quickest in a gradient calorimeter

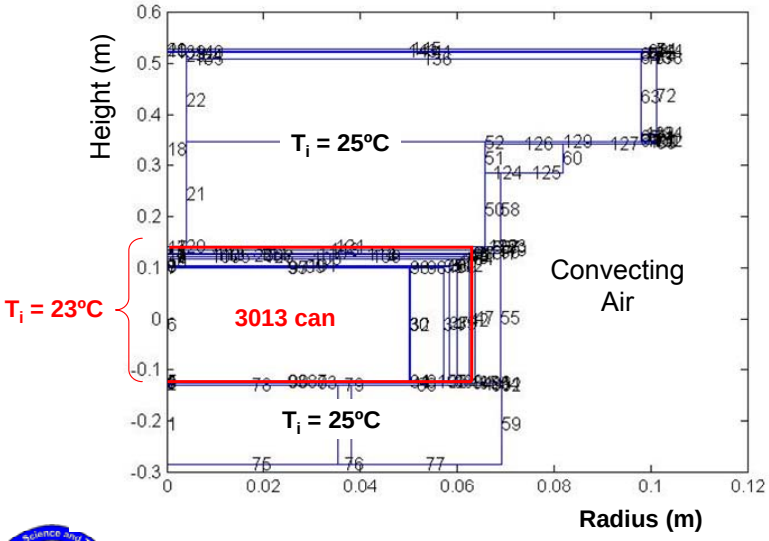
Setup of calculations

LANL Outer / ARIES Inner / ARIES Convenience Can



Initial and Boundary Conditions

LANL Outer / ARIES Inner / ARIES Convenience Can



Time to equilibrium = 395 minutes

Results of 3013 container calculations

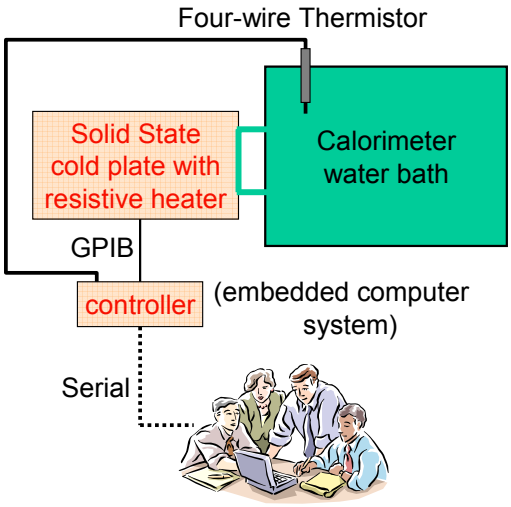
Outer Can	Inner Can	Convenience Can	Relative Difference in Time to Equilibrium	Total Mass of Configuration (g)
LANL	ARIES	ARIES	0.	834.
BNFL	ARIES	ARIES	19.9%	1808.
BNFL	BNFL	BNFL	51.1%	2308.
LANL	BNFL	BNFL	42.3%	1333.
LANL	BNFL	LLNL	1.8%	871.
BNFL	BNFL	LLNL	21.4%	1846.
LANL	SRS BTS	SRS	1.3%	1305.
BNFL	SRS BTS	SRS	21.9%	2280.
BNFL	SRS BTS	Cogema	27.2%	2323.
LANL	ARIES	ARIES	2.3% (0.5 mm air gap)	834.

Green – fastest
Brown – 20-25% increase in time
Red – additional 20-25% increase in time

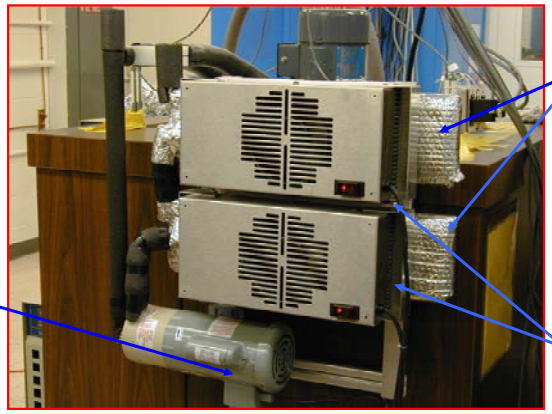
Concept for New Water Bath Control System

Advantages:

- Complete access of all control parameters and data for initial tuning of calorimeter and troubleshooting
- Use of 4-wire isolated temperature probe
- Solid state cooler is essentially a plug and play module
- No use of refrigerant to control temperature



New Water-Bath Control System



- Solid-state cooling plate shown attached to 255 gallon water bath for Twin-Bridge Calorimeter
- Not shown are two 150V Power supplies and controllers for cooling plate, and controlling computer (Mini-PC)
- Average 4 hour standard deviation on Water Bath Temperature is ~ 55 μK

EUROPEAN COMMISSION

JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements

Geel, Belgium

NUSIMEP 5

R. Wellum, L. Benedik, A. Stolarz

http://www.irmm.jrc.be/html/interlaboratory_comparisons/index.htm

NUSIMEP 5 basics

- Continuation of previous NUSIMEP exercises
- Include measurements of radioactivity
- Uranium, plutonium and Cs isotopes
- Levels chosen to allow regular transport

Requests from participants from previous campaigns

NUSIMEP 5 basics

Recognising that we cannot measure and certify in samples of low concentrations we certify 'bulk' materials and dilute and mix with a matrix under carefully controlled conditions

We do not reach the lowest concentration ('conservative approach')

Compromise between realistic materials and level of certification

Responsibilities

- Matrix: cleaning and preparation
  - Anna Stolarz
  - Measurement of residual uranium in the matrix: A. Stolarz, L. Benedik, S. Richter (IDMS/TIMS)
- Uranium:
  - Selection from materials already certified at IRMM (UF_6: J. Truyens, A. Alonso)
  - Dilution and addition to matrix (adjustment for nat U in the matrix)

Responsibilities

- Plutonium: G Sibbens
  - L Benedik separated and prepared Pu, G Sibbens measured alpha spectra to verify material
  - No further isotopic measurements (mass-spec) made on isotopic ratios
  - Both activity ratio 238/(239+240) and isotope ratios separately corrected for decay since certification date and uncertainties included in the final certification

Responsibilites

- Cs gamma ratios: T Altzitzoglou
  - Mixing certified solutions – 2 mixtures
  - Calculating and certifying mixtures
  - Addition to matrix
  - Verification of 134/137 ratio on ampouled materials

Uranium

- Stick with what we know best: prepare dilute solutions of uranium with very well specified isotopics with enrichments between depleted and low enriched
- Lower previous requirements regarding minor isotopes
- 5 ppb solutions; 100 ng total

Matrix

- Semi-complex matrix essential (to enforce chemical treatment)
- Saline matrix (‘sea-water’) shown to be very useful (N3, N4)
- Purify the matrix from natural uranium

Plutonium

- Problem of isotopic ratios by mass-spectrometry and activity ratio measurements by alpha spectrometry
- Selected materials previously certified for both at IRMM
- Certification based on previous certificates plus verification measurement of activity by alpha spectrometry

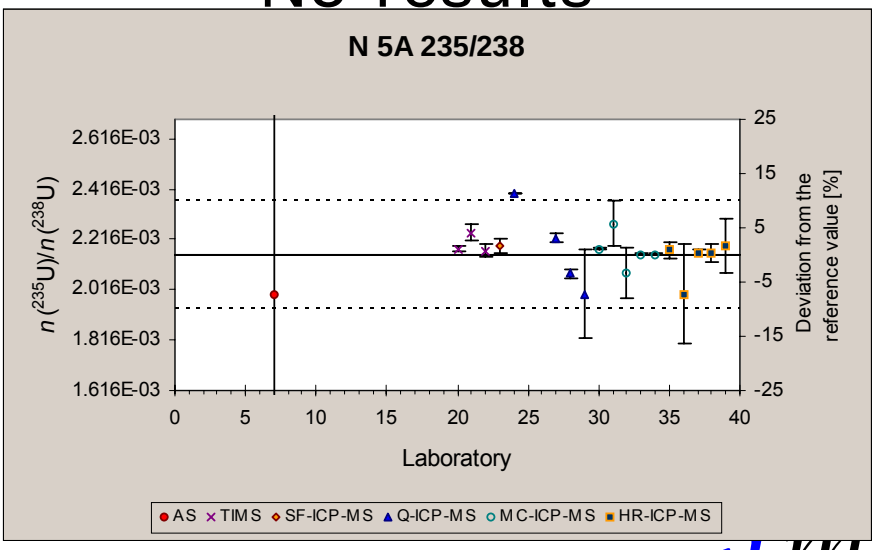
Caesium

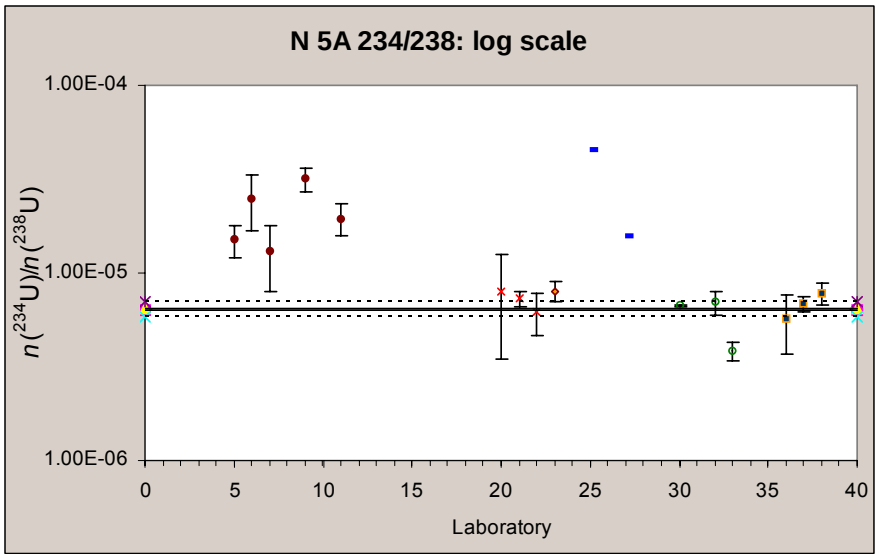
- Certified solutions of ^{134}Cs and ^{137}Cs available
- Mixtures of solutions by weighing
- Verification on mixtures
- Dilution and adding to matrix

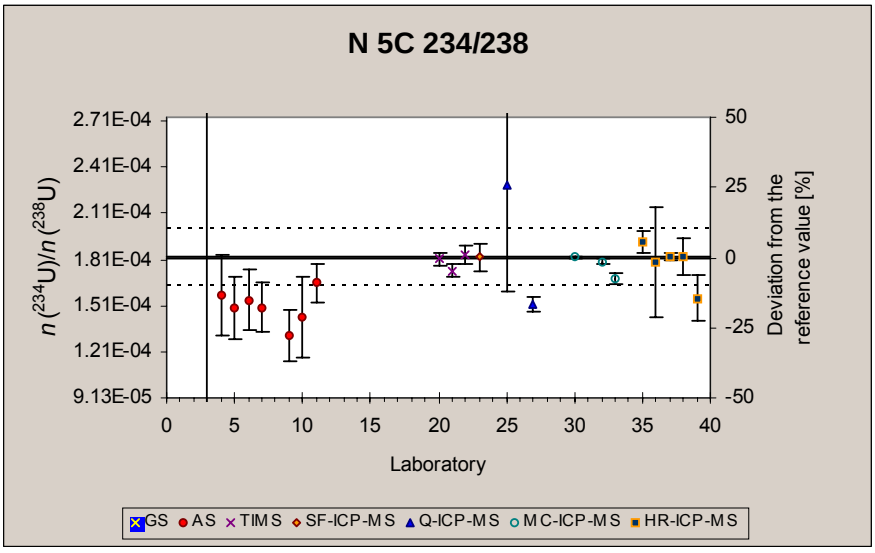
Certification basis

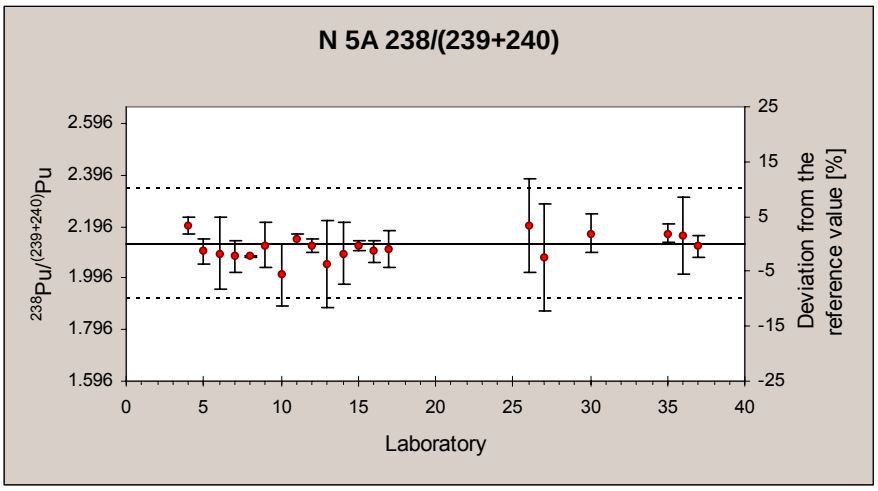
- Uranium: from certificates of isotopic ratios at IRMM and corrected for residual U in matrix soln
- Plutonium: from Euromet exercise certification corrected for decay
- Caesium: from certificates of individual enriched isotope solutions, corrected for decay

N5 results

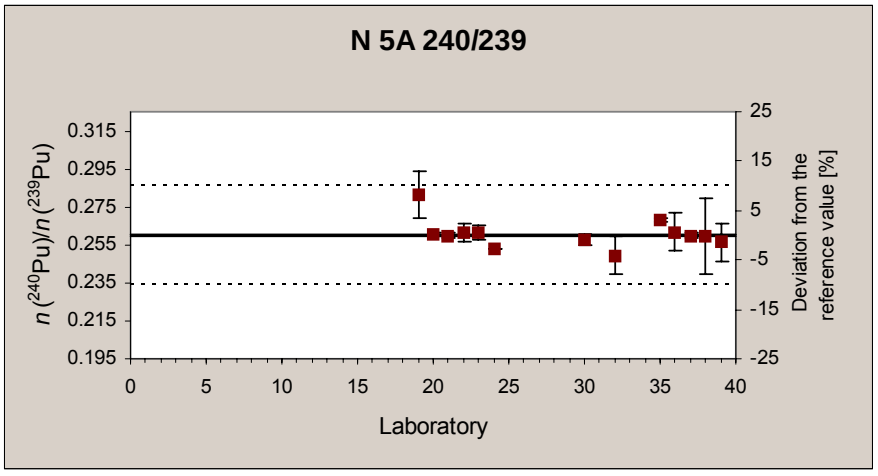



N 5A 234/238: log scale
1.00E-04
1.00E-05
1.00E-06
n(234U)/n(238U)
0
5
10
15
20
25
30
35
40
Laboratory

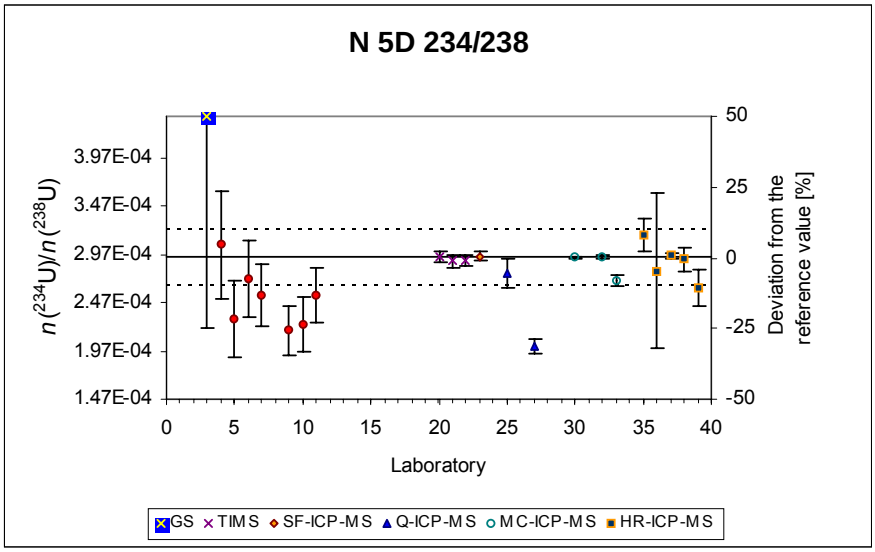

N 5C 234/238
2.71E-04
2.41E-04
2.11E-04
1.81E-04
1.51E-04
1.21E-04
9.13E-05
n(234U)/n(238U)
50
25
0
-25
-50
Deviation from the reference value [%]
0
5
10
15
20
25
30
35
40
Laboratory
GS
AS
TIMS
SF-ICP-MS
Q-ICP-MS
MC-ICP-MS
HR-ICP-MS



NBL/SME July 2006



NBL/SME July 2006



Conclusions

- Mixing 3 elements succeeded
- Good response from participants
- Matrix proven for environmental samples
- Concentrations not realistic yet- maybe never? Some adjustments still to be made
- Some anomalies in results

Anomalies

- Bias on alpha measurements of $^{234}U/^{238}U$ seems to be dependent on 234U abundance
- Very high measurements of ^{242}Pu for ICP-MS not yet explained

Conclusions (2)

- Participants would like lower concentrations:
  - Uranium, to be more realistic
  - Pu because usually much lower activities are measured
  - Cs