NBL-378

U.S. DEPARTMENT OF ENERGY

MEASUREMENT EVALUATION PROGRAM MEETING MINUTES

Marriott Desert Ridge
Phoenix, Arizona.

JULY 9, 2005

NEW BRUNSWICK LABORATORY
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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 Plutonium, Uranium and Special Materials Inventory (SO-20.3). The laboratory was established in 1949 as an analytical chemistry laboratory in New Brunswick in New Jersey to provide support to the Unites 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.

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. The program is divided into two parts: the Safeguards Measurement Evaluation (SME) program and the Calorimetric Exchange (CALEX) Program. The SME program evaluates results from destructive analyses of uranium and plutonium materials, and the CALEX Program evaluates results from non-destructive analyses of plutonium materials only. Until 1996, the CALEX Program was administered by EG&G Mound Applied Technologies; it was transferred to NBL in that year. The ME Program, in the beginning stages, dealt with evaluation of results from destructive analyses measurements only carried out by Department of Energy facilities. Later on, laboratories outside the DOE complex were permitted to join. In the expanded program, as it is organized now, results from both destructive and non-destructive measurements are evaluated. Non-DOE facilities, such as Nuclear Regulatory Commission licensees and international laboratories, participate on cost recovery basis.

The ME program operation distributes different types of well characterized uranium and plutonium materials to the participating laboratories for analyses. The materials are usually made at NBL from existing or newly created reference materials, and are characterized at NBL for elemental content and isotopic abundance. The participants analyze these materials at periodic intervals, and submit the results to NBL for evaluation of accuracy and precision using statistical methods. Evaluation reports are sent to laboratories and their respective oversight organizations/agencies.

Once a year, NBL hosts the ME Program meeting. The meeting is usually held at about the same time and in the same venue as the International Nuclear Material Management (INMM) annual meeting. The 2005 ME Program meeting was held on July 9th, a day prior to the start of the 46th INMM meeting, at the Marriott Desert Ridge in Phoenix, Arizona. The ME Program meeting provides a forum to the program participants and other interested groups to discuss topics related to safeguards nuclear measurements, measurement techniques, inter-laboratory comparison of results, measurement uncertainties, and measurement needs. In the 2005 meeting, results from both SME and CALEX Programs were discussed. In addition, several technical talks, pertinent to measurement technology, were presented. This report represents the meeting minutes.

SYNOPSIS

The morning session started with opening welcome remarks by Jon Neuhoff, Director of NBL. Seven technical talks were presented in this session. Chino Srinivasan of NBL delivered the first talk in this session that dealt with the FY 2004 SME program and some of the problems encountered during the year in operating the program. Andrew Maddison of INL spoke next on a comparative study of results from ICP-MS and TIMS. He expressed an interest in participating in the evaluation of ICP-MS analyses results in addition to TIMS results evaluation. Amy Wong of LANL presented two talks, one dealing with actinide analytical chemistry capabilities at LANL, and the other on the LANL plutonium metal exchange program; the exchange program was originally administered by Rocky Flats. Lav Tandon was scheduled to deliver the plutonium metal exchange talk, but he could not attend. Mika Sumi, a visiting scientist at NBL, gave a talk on the collaborative work between JNC and NBL on the preparation of plutonium reference materials for producing large spikes dried (LSD) for use in IDMS measurements in Japan. Steven Balsley of IAEA spoke on destructive analysis capabilities at the IAEA Safeguards Analytical Laboratory, and on the intention of IAEA to participate in the NBL measurement evaluation program. Steven Goldberg of NBL spoke on uncertainty evaluations, and on ISO guidelines.

The afternoon session started with opening remarks by Lynn Preston of DOE-HQ. Seven technical talks were presented in this session. Chino Srinivasan of NBL delivered the first talk; it dealt with the 2004 CALEX program and on the need to certify the CALEX II material soon. Clifford Rudy of LANL gave an update of calorimetric assay techniques including the use of “multi cal”, a system designed for calorimeters operation. Thomas Sampson of LANL spoke on the need to measure the ^{241}Am content in calorimetric standards accurately and precisely; ^{241}is an important contributor to the heat output of the standards. Peter Santi of LANL gave an account of developments in plutonium measurements by neutron multiplicity measurement technique. Passive and active neutron measurements are becoming increasingly significant in nuclear safeguards. Tracy Dixon of AWE spoke on the NDA techniques used at AWE in support of MC&A measurements. AWE is interested in participating in the NBL measurement evaluation program. Michael Holland of SRS gave a talk on nuclear laboratory design. The concluding talk of the session was given by Peter Mason of NBL, describing the NBL reference material program. Several of the reference materials made in this program serve as starting materials for producing ME Program samples.

ACKNOWLEDGEMENTS

The organizers of the ME Program Meeting acknowledge the help received throughout the year from technical and support personnel in the laboratories participating in the measurement evaluation program. The organizers 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.

AGENDA

9:00 AM	Introductory Remarks on ME Program	Jon Neuhoff, NBL
9:10 AM	FY 2004 SME Program	B. Chino Srinivasan, NBL
9:30 AM	TIMS vs. ICP-MS	Andrew P. Maddison, INL
10:00AM	Pu Standards Exchange Program and Data as it Relates to Manufacturing and Certification	Lav Tandon, LANL
10:30AM	Actinide Analytical Chemistry Capabilities in Support of Nuclear Materials Program	Amy Wong, LANL
11:00AM	Present Status: Collaboration Between NBL and JNC on Preparation of Pu Reference Material	Mika Sumi, JNC and NBL
11:30AM	Nuclear Materials Destructive Analysis at the IAEA Safeguards Analytical Laboratory	Steven D. Balsley, IAEA
12:00PM	Confidence in Measurements	Steven Goldberg, NBL
12:30PM	Lunch	
1:30 PM	Introductory Remarks on NDA	Lynne Preston, DOE
1:40 PM	FY 2004 CALEX Program	B. Chino Srinivasan, NBL
2:00 PM	Calorimetric Assay: Update	Clifford R. Rudy, LANL
2:30 PM	Importance of ^{241}Am Determination in the Characterization of PuO_2 Standards for Calorimetric Assay	Thomas E. Sampson, LANL
3:00 PM	Status of Multiplicity Counting	Peter Santi* and William H. Geist, LANL
3:30 PM	Non-Destructive Assay (NDA) Techniques and Measurements Performed in Support of Nuclear Material Control and Accountancy (NMC&A) at the Atomic Weapons Establishment (AWE)	Tracy Dixon, AWE
4:00 PM	Role of the Chemist in Designing New or Renovated Nuclear Laboratory Facilities	Michael J. Brisson, Michael K. Holland* and Robin H. Young, SRS
4:30 PM	RM Program Status	Peter Mason, NBL

* Presenter

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GRAPHICS USED IN TALKS

The graphics (slides, pictures etc.) used in the presentation of the 2005 ME Program Meeting talks are included in the pages following this page. 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. The page numbers are shown in some of the graphics and not in others. Where shown, they represent the slide numbers for that particular talk only.

FY 2004 NBL Safeguards Measurement Evaluation Program Phoenix, Arizona

July 9, 2005

B. (Chino) Srinivasan

Evaluation Program History

- General Analytical Evaluation (GAE)
  - 1952-1984
  - U.S. Participants (6-9 labs)
  - Uranium measurements only
- Safeguards Analytical Laboratory Evaluation (SALE)
  - 1970-1984
  - U.S. and International (large number)
  - Uranium and plutonium

Evaluation Program History (continued)

- Safeguards Measurement Evaluation Program (SME)
  - 1986 – present
  - U.S. - DOE and NRC labs
  - International laboratories - ABACC and Japan
  - Uranium and plutonium samples
  - Primary goal - individual needs
  - Secondary – comparative study – shipper/receiver

Evaluation Program Samples: Uranium

Uranium Assay

- UNH solution
- UO_2 pellets
- UF_6
- UO_3 powder

Uranium Isotopics

- LEU
- HEU

Evaluation Program Samples: Plutonium

Plutonium Assay

- Dried plutonium sulfate

Plutonium Isotopics

- Low burn-up (rich in ^{239}Pu)
- High burn-up (less rich in ^{239}Pu)

Evaluation Program: Uranium Analyses Methods

Uranium Assay

- D&G titration (dichromate/ceric titrations)
- High precision titration
- IDMS
- X-ray fluorescence

Uranium Isotopics

- TIMS
- ICP/MS

Evaluation Program: Plutonium Analyses Methods

Plutonium Assay

- IDMS

Plutonium Isotopics

- TIMS

Evaluation Program: Frequency

Quarterly analysis of samples

- In duplicate
- Analyze on two different dates
- Submit results for evaluation
- More frequent/less frequent analysis upon request

Results Evaluation

Results entered into FoxPro database

- Checked for entry errors manually
- Want to add electronic transfer of entry into database to avoid typing errors

Results Evaluation (continued)

Statistical evaluation

- Identify outliers
- Calculate % Relative Difference of each result
- Calculate mean % relative difference
- Standard deviation
- Within-day and between-day variation
- 95% C.L. of mean
- Compare with international target values for bias and precision

FY 2004 SME Program

Participants

- Argonne National laboratory – West
- Los Alamos National Laboratory
- New Brunswick Laboratory
- Savannah River Site
- Tokai Safeguards Analytical Laboratory
- Y-12 National Security Complex

FY 2004 SME Program (continued)

Slow progress in FY 2004

- New Program manager (on the job training)
- A-76 Process (time commitment)
- Safety Inspection and Audit (time commitment/stand-down of laboratory work)

FY 2004 SME Program (continued)

Work completed

- FY 2004 results evaluation completed recently
- FY 2005 samples shipped to DOE and NRC recently
- FY 2005 samples to international laboratories will be shipped within the next two months

FY 2004 SME Program Results

Work completed

- FY 2004 results evaluation completed recently
- FY 2005 samples shipped to DOE and NRC recently
- FY 2005 samples to international laboratories will be shipped within the next two months

FY 2004 SME Program: U and Pu Assay

	UNH Solution	UO_2 Pellet	UO_3 Powder	Dried Pu Sulfate
D&G	Yes	Yes	Yes	
HP		Yes		
IDMS	Yes		Yes	Yes
XRF	Yes		Yes	

FY 2004 SME Program: U and Pu isotopics

Uranium

- LEU - TIMS
- HEU - TIMS

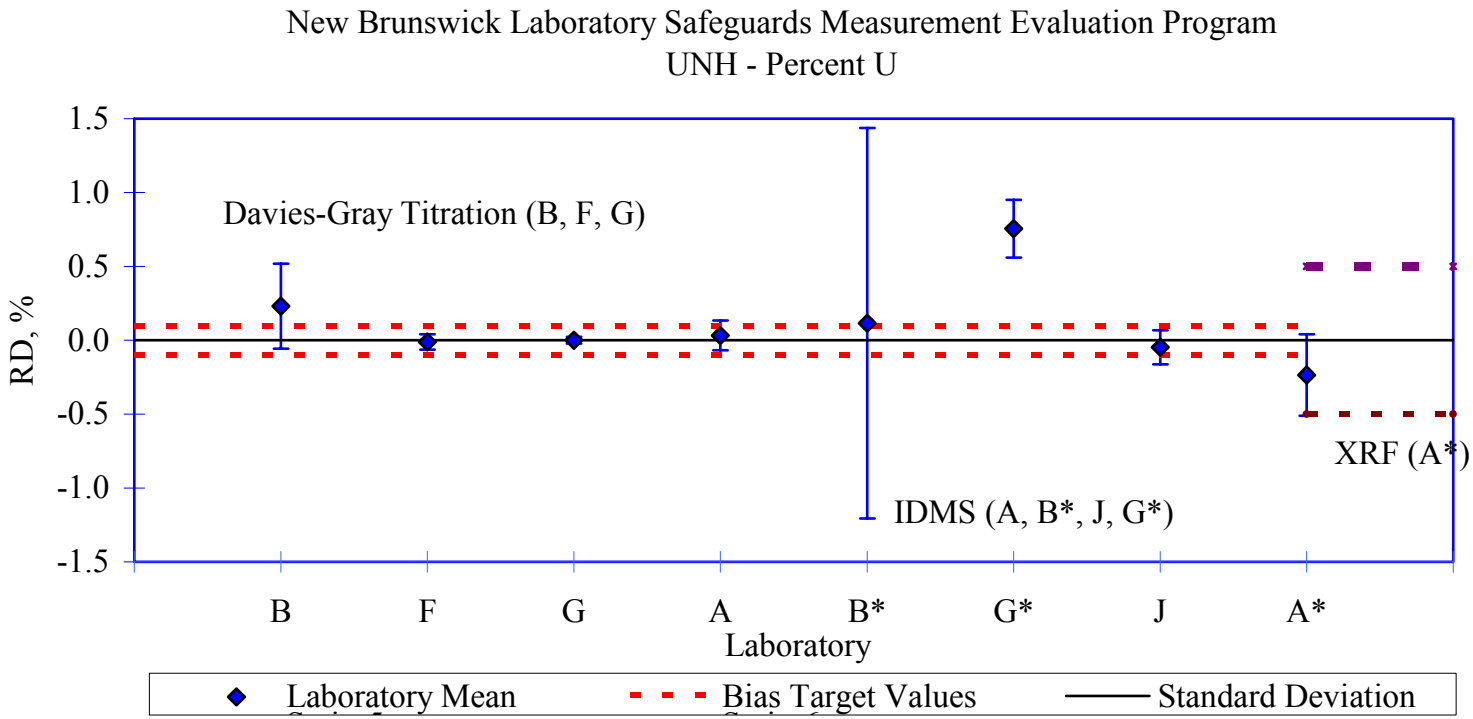
Plutonium

- High Burn-up - TIMS
- Low Burn-up - TIMS

FY 2004 SME Program: UNH Solution Annual Evaluation

Method (B/P)	Lab	Bias ITV	Precision ITV
D&G (0.1%/0.1%)	B	No	No
	F	Yes	Yes
	G	Yes	Yes
IDMS (0.1%/0.15%)	A	Yes	Yes
	B	No	No
	G	No	No
	J	Yes	Yes
XRF (0.5%/0.5%)	A	Yes	Yes

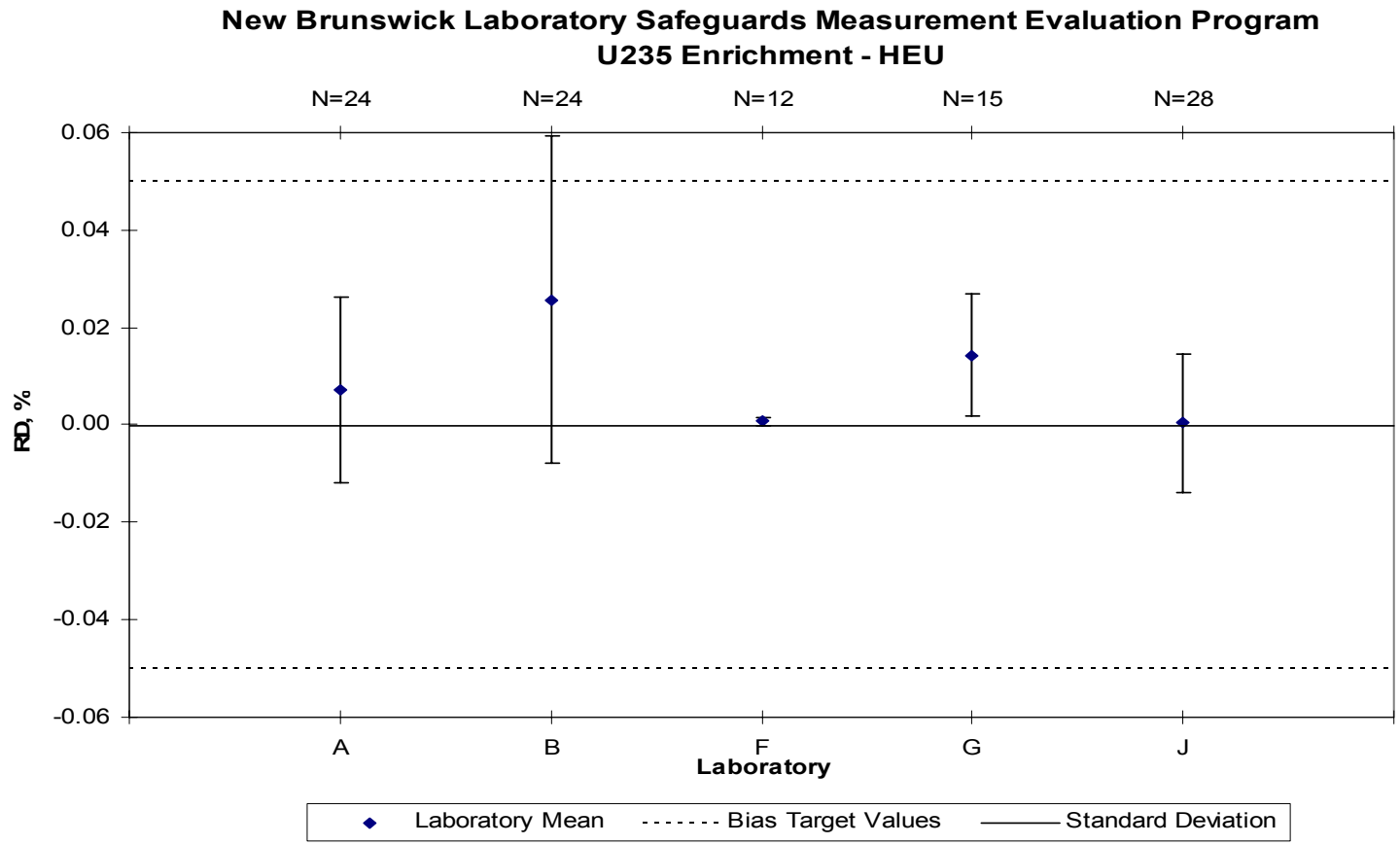
FY 2004 SME Program: UNH Solution Annual Evaluation



FY 2004 SME Program: HEU Isotopic Annual Evaluation

Method (B/P)	Lab	Bias ITV	Precision ITV
TIMS (0.05%/0.05%)	A	Yes	Yes
	B	Yes	Yes
	F	Yes	Yes
	G	Yes	Yes
	J	Yes	Yes

FY 2004 SME Program: HEU Isotopic Annual Evaluation



FY 2004 SME Program: Other Materials Annual Evaluation

- UO_2 pellet – U assay
- UO_3 powder – U assay
- LEU – U isotopics
- Pu dried sulfate – Pu assay
- Pu dried sulfate – Pu isotopics (low burn up and high burn up)

FY 2004 SME Program: Conclusions

FY 2004 results evaluation completed

First draft of FY 2004 SME report ready

Final report will be distributed by the end of August 2005

FY 2005 SME Program

- FY 2005 program has late start
- Samples are being shipped now
- Contacts being made to add new participants
  - DOE Cat 1 and Cat 2 facilities
  - More NRC facilities
  - More international laboratories
- Evaluate needs for new SME sample materials

TIMS vs. ICP-MS

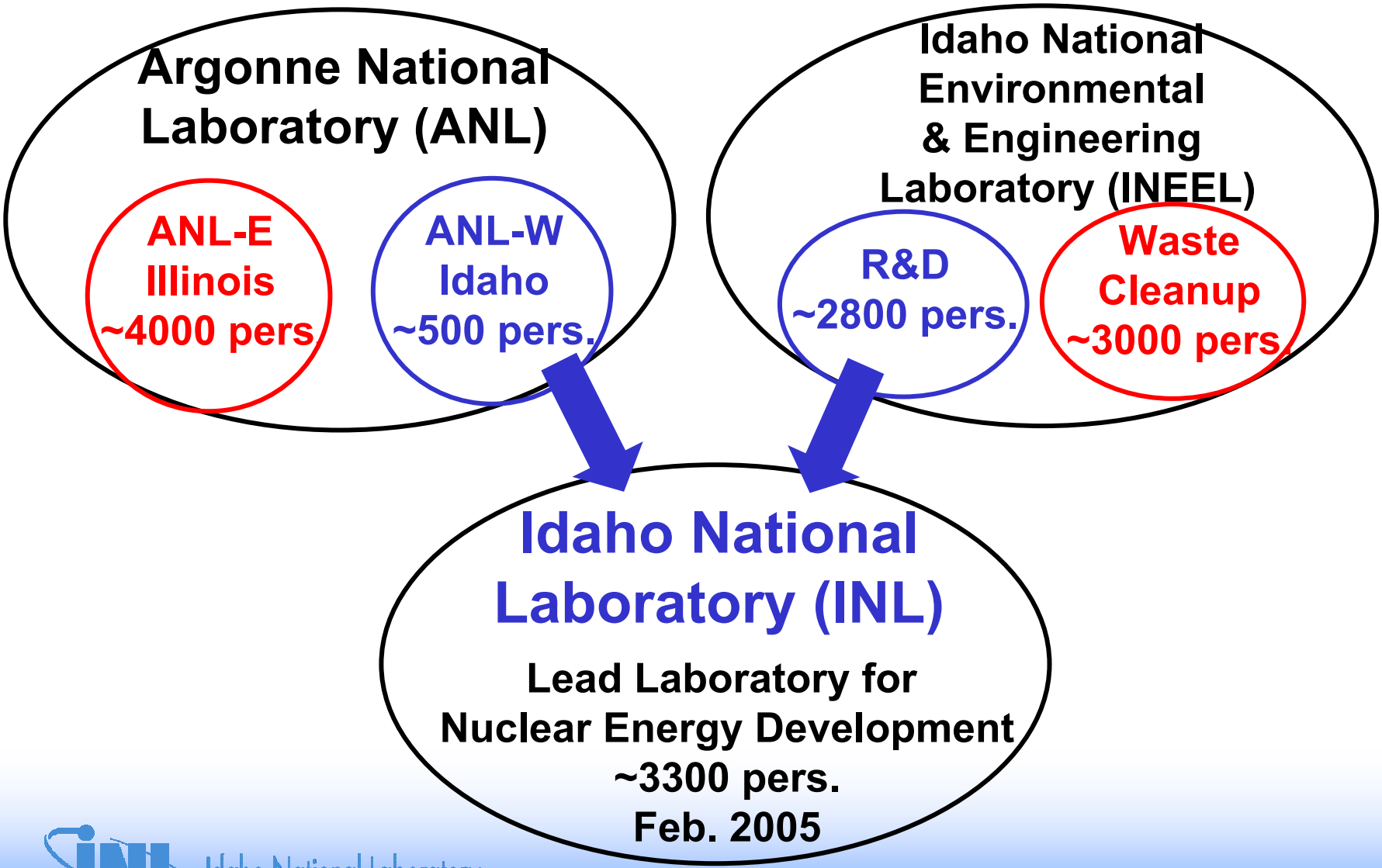
Discussion of work performed at INL-MFC

Andrew P Maddison, Jeffrey Giglio, Dan Cummings and James Sommers - NMCD

July 9, 2005

Idaho National Laboratory

INL Overview



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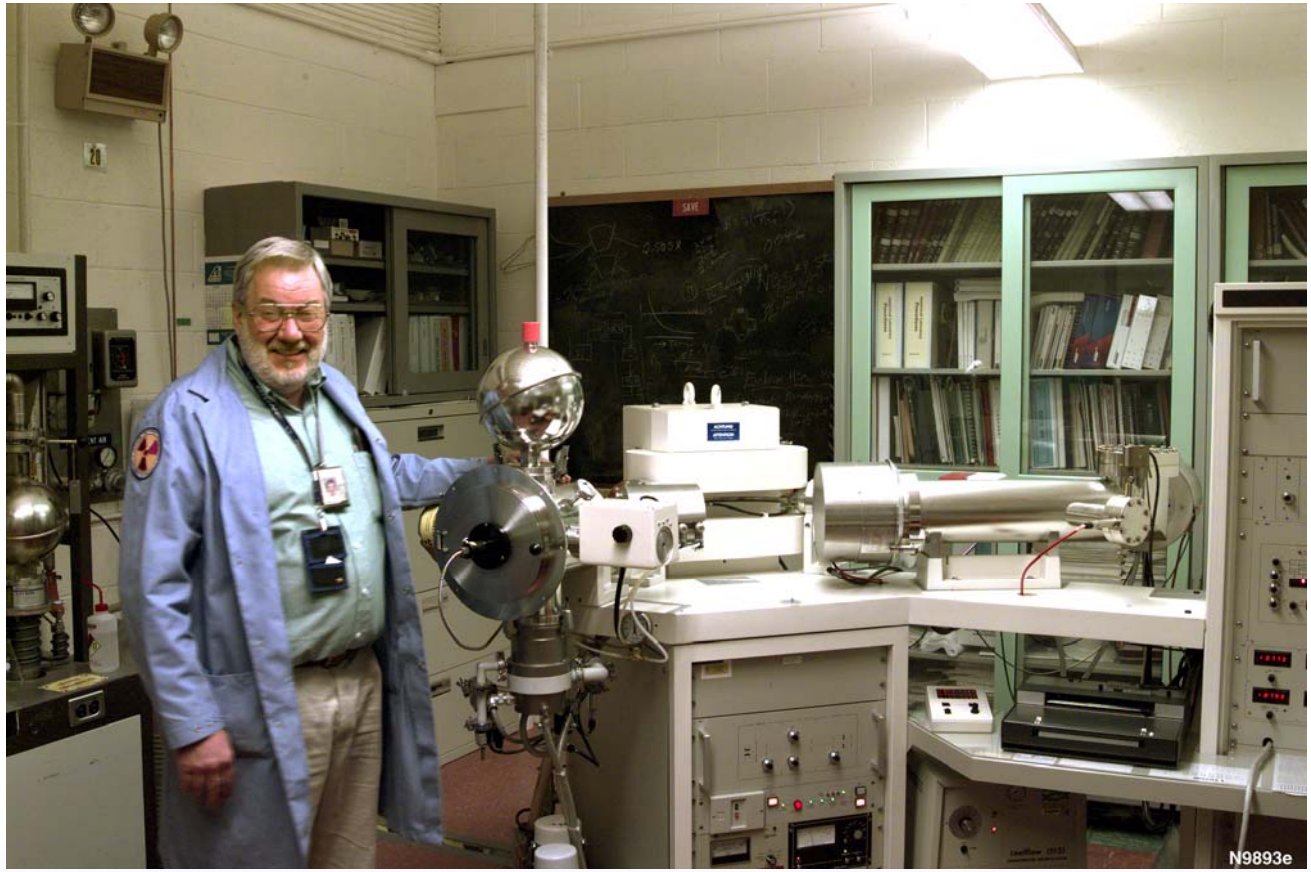
Background

- Multiple sample types are sent to the NMCD for U & Pu analysis
  - Driver Chopper Segments
  - Cladding Hulls
  - LANL Pu Metal Exchange
  - AFCI Metal Fuels
  - Etc…

Background (cont.)

- ICP-MS can be advantageous over TIMS for samples
  - Sampling Error
  - Requested Turnaround
  - Sample Quantity
  - R&D vs. MC&A

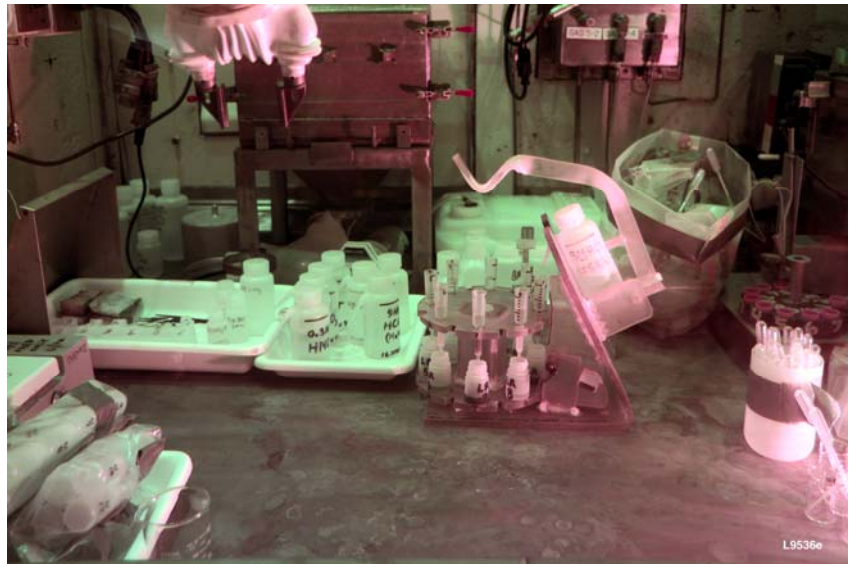
TIMS – Finnegan MAT262



ICP-MS PQ3

Sample Processing - TIMS

- Dilutions
  - U: 1mg or 100ug U-233 Spike (calibrated against CRM 135)
  - Pu: Pu-244 Spike (calibrated against CRM 126) 1ug
- Separations
  - Oxidation state adjustment
  - Initial separation
  - Clean-up separation



Sample Processing - TIMS

- Sample Loading
  - Loading and drying onto Re Filaments
  - Loading of Magazine into Ion Source
  - Re-establish vacuum
- Sample analysis
- Data Reduction

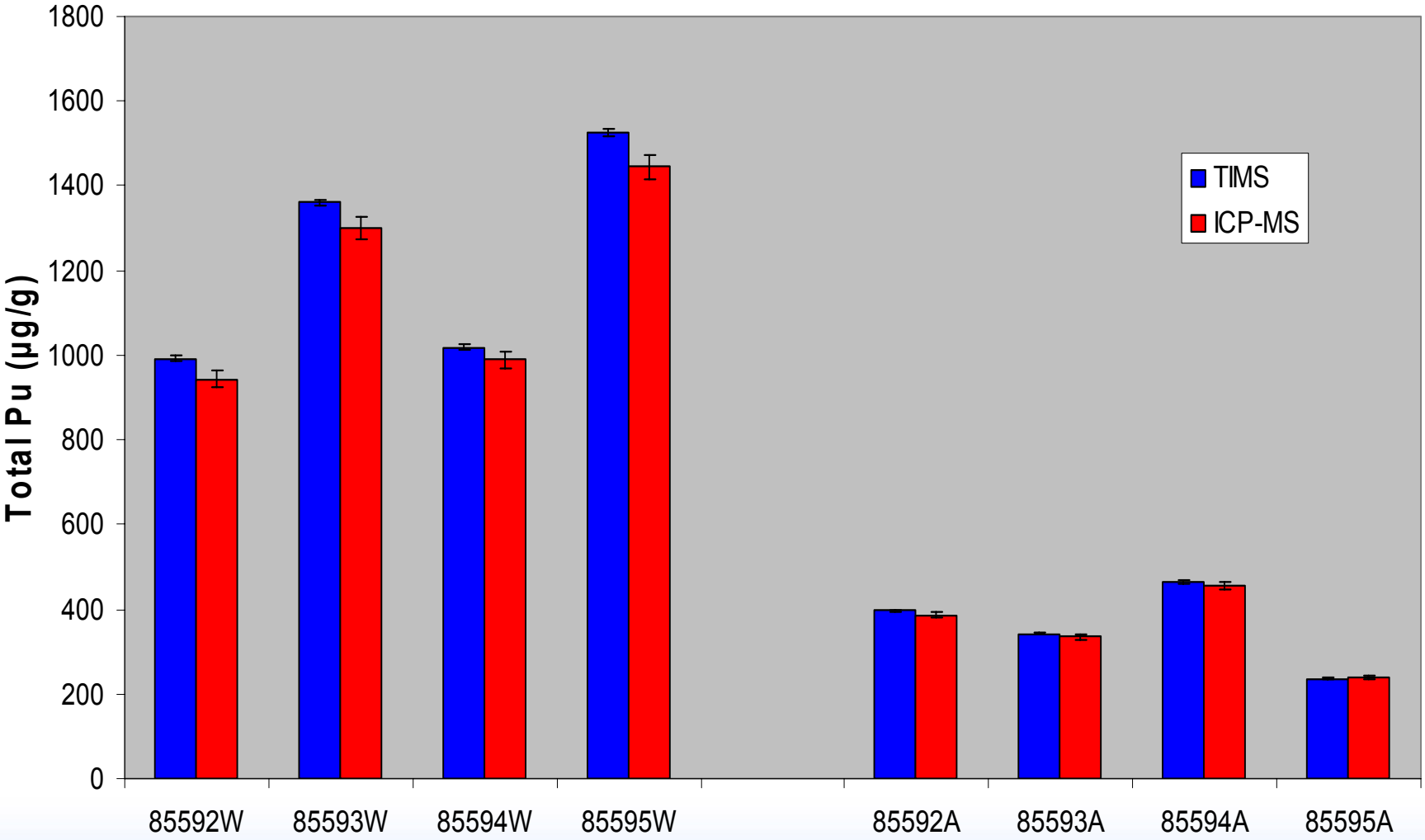
Normal Difficulties Encountered

- TIMS
  - Sample Concentration on Filaments
  - Acid Compatibility
  - Trace elements
- ICS-MS
  - Standards
  - Variation in Sample Delivery
  - Poly-Atomics
    - Hydrides
    - Oxides

Cladding Hulls

- TIMS
  - Dilute and Spike
  - Hot Cell Separation
  - Clean-up
  - TIMS Loading
  - Data Reduction
- ICP-MS
  - Dilute
  - Transfer from Hot Cells
  - Analysis
  - Data Reduction

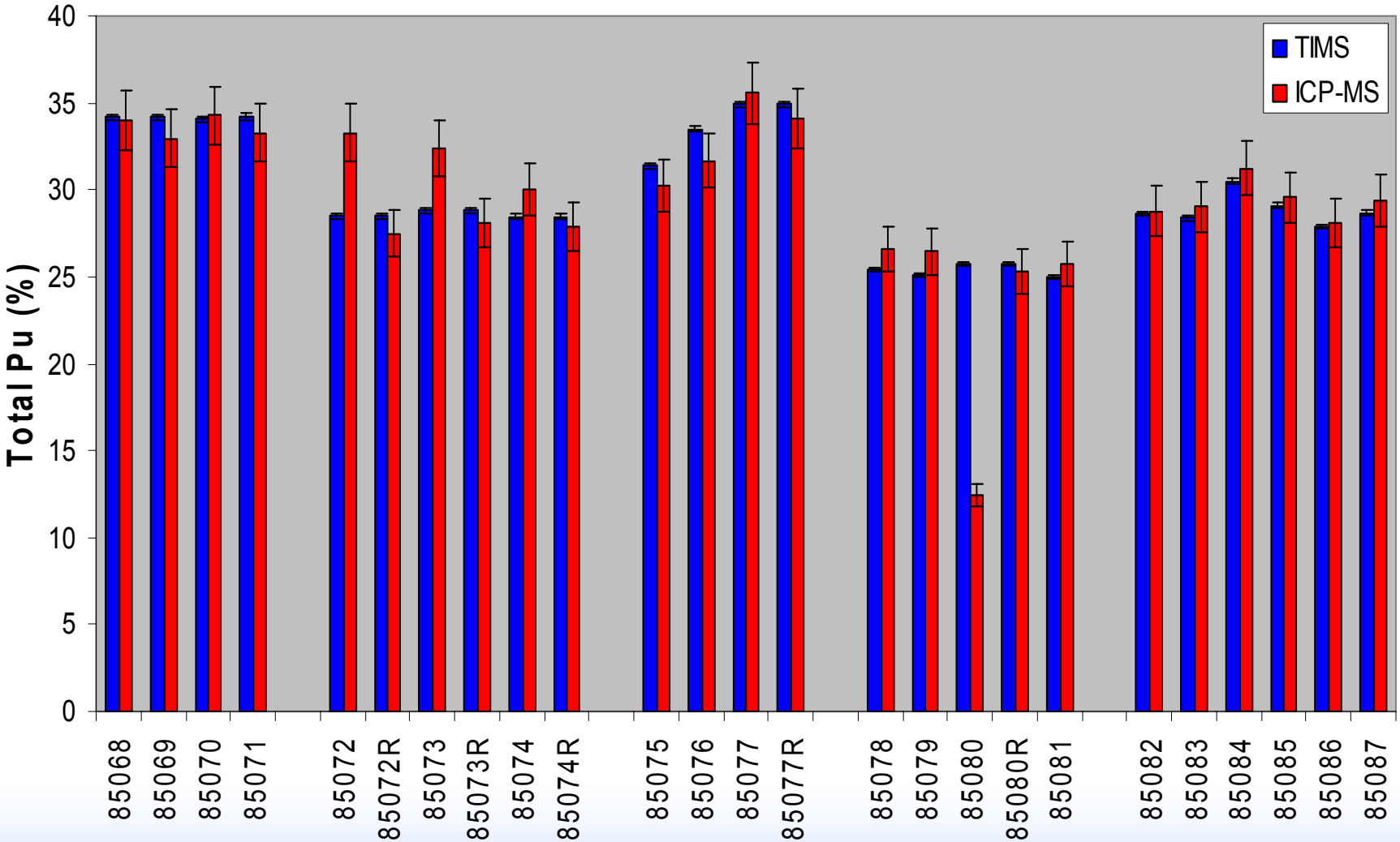
Cladding Hulls



AFCI Metal Fuels

- TIMS
  - Dilute and Spike
  - Glovebox Separations
  - Clean-up
  - TIMS Loading
  - Data Reduction
- ICP-MS
  - Dilutions
  - Micro-column Separation
  - Analyze
  - Data Reduction

AFCI Metal Fuels



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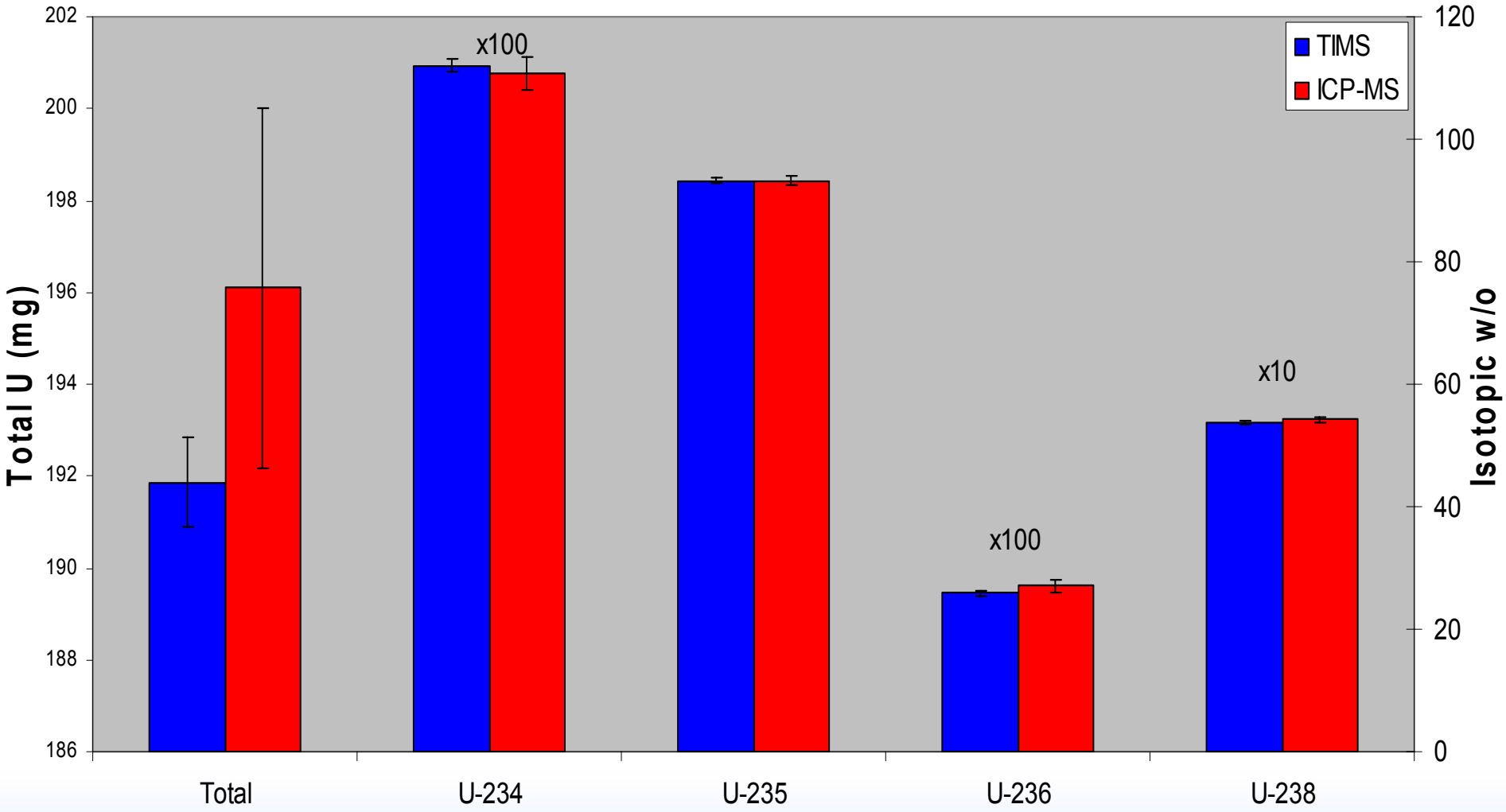
Uranium Sample



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Process Time Comparison

- TIMS
  - Spike Preparation
    - 4hr per 40
  - Sample Preparation
    - 2-3d per 8
  - Loading & Analysis
    - 1-2d per 10
- ICP-MS
  - Dilutions
    - 4hr per 16
  - Analysis
    - 1hr per 16

Summary

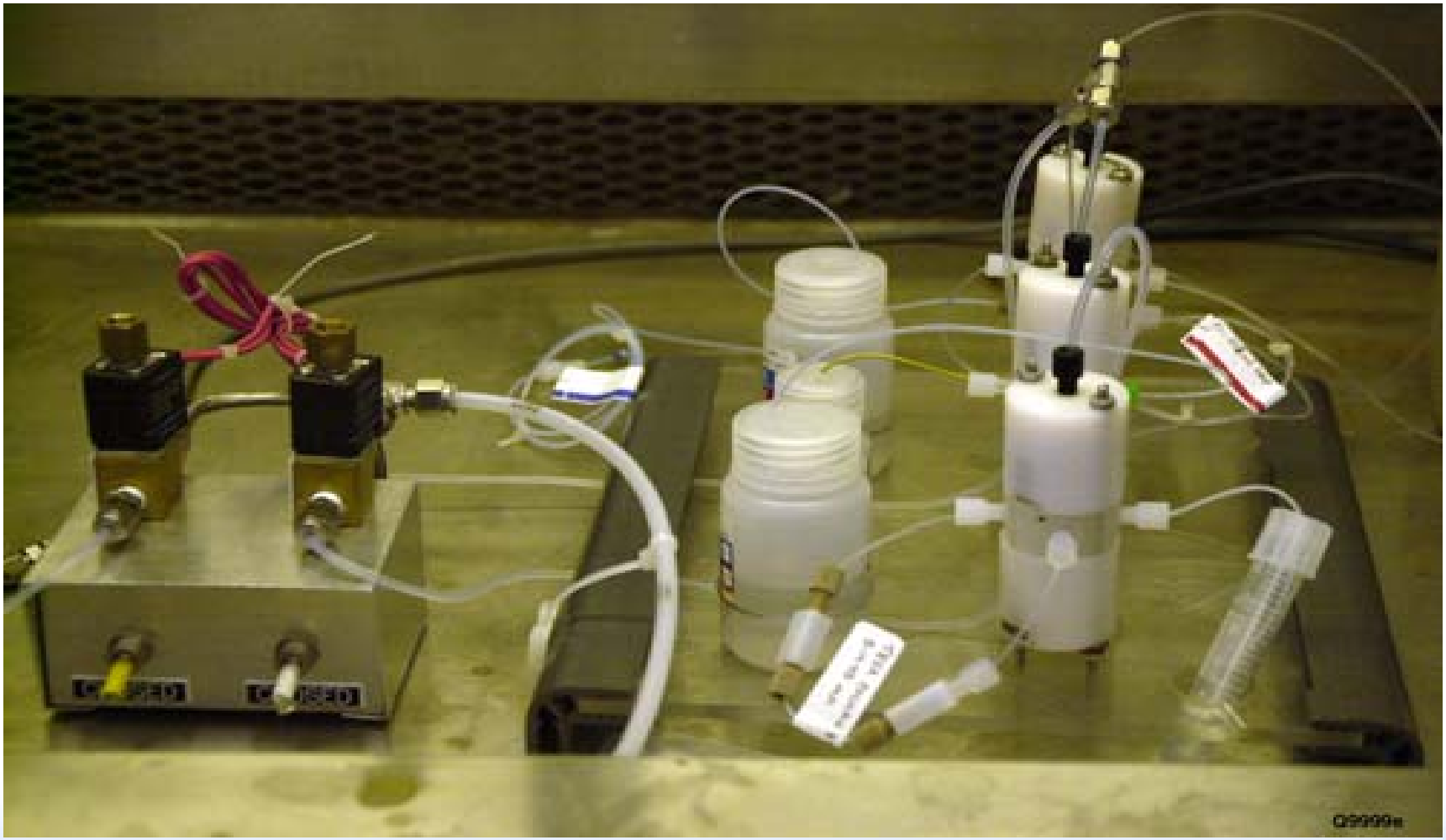
- ICP-MS is giving good results for non MC&A measurements of samples at MFC
- Speed of analysis and cost savings are vastly improved with ICP-MS
- Radiological concerns are minimized with the ICP-MS
- Multiple element analysis can be performed with ICP-MS

ICP-MS advances applied to TIMS

Gas Pressurized Extraction Chromatography System

- **Gas Pressurized Extraction System**
  - **Uses pressurized nitrogen to push solutions through media instead of liquid or gravity**
  - **Advantages:**
    - **Quantitatively recovers liquid put in system**
    - **Tailors column size and resins for varying measurement requirements**
    - **Requires less liquid to complete separation**
    - **Offers faster extraction times**
    - **Has the potential for automated hot cell/glovebox operation**
    - **Can use system for separation or preconcentration experiments**
- **Column Preparation for Pu impurities in U and Am/U impurities in Pu**
  - **Use 3 in. of 1/16 in. O.D. x 0.030 in I.D. Teflon tubing with an internal volume of 0.0347 mL**
  - **Add 0.0771g of TEVA material with frits at end**

Gas Pressurized Extraction Chromatography Set-Up-----Footprint 12 x 18 inches



Initial Characterization of GPEC

- **Recovery of water through system – loop calibration**
  - Sequential injections (0.203 mL aliquots) where run through the system. N=3 **Average = 0.2029 g +/- 0.0017.**

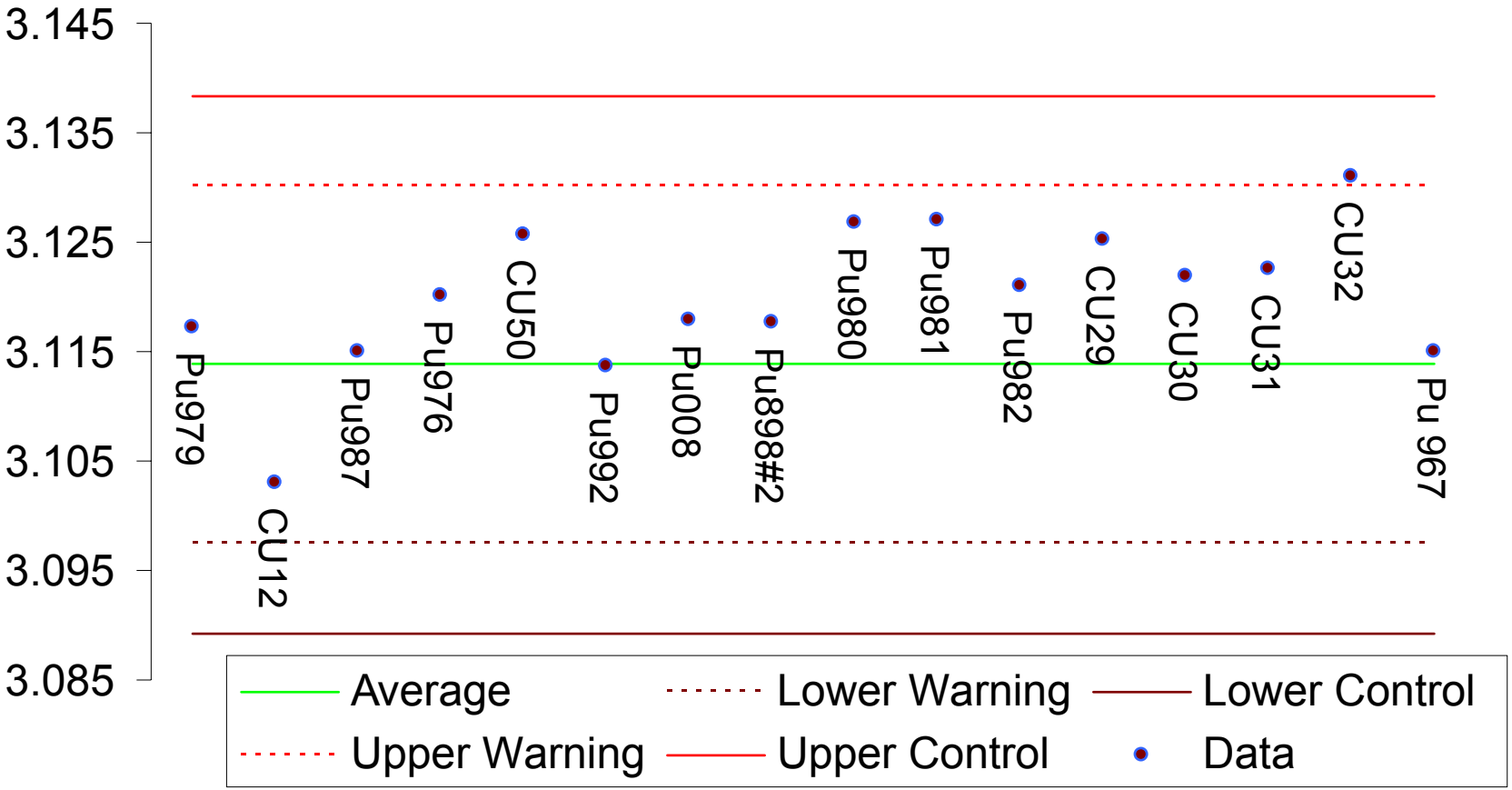
Result: Have an accurate and precise recovery of liquid through system.

- **Pu/U Separation with TEVA Spec Resin**

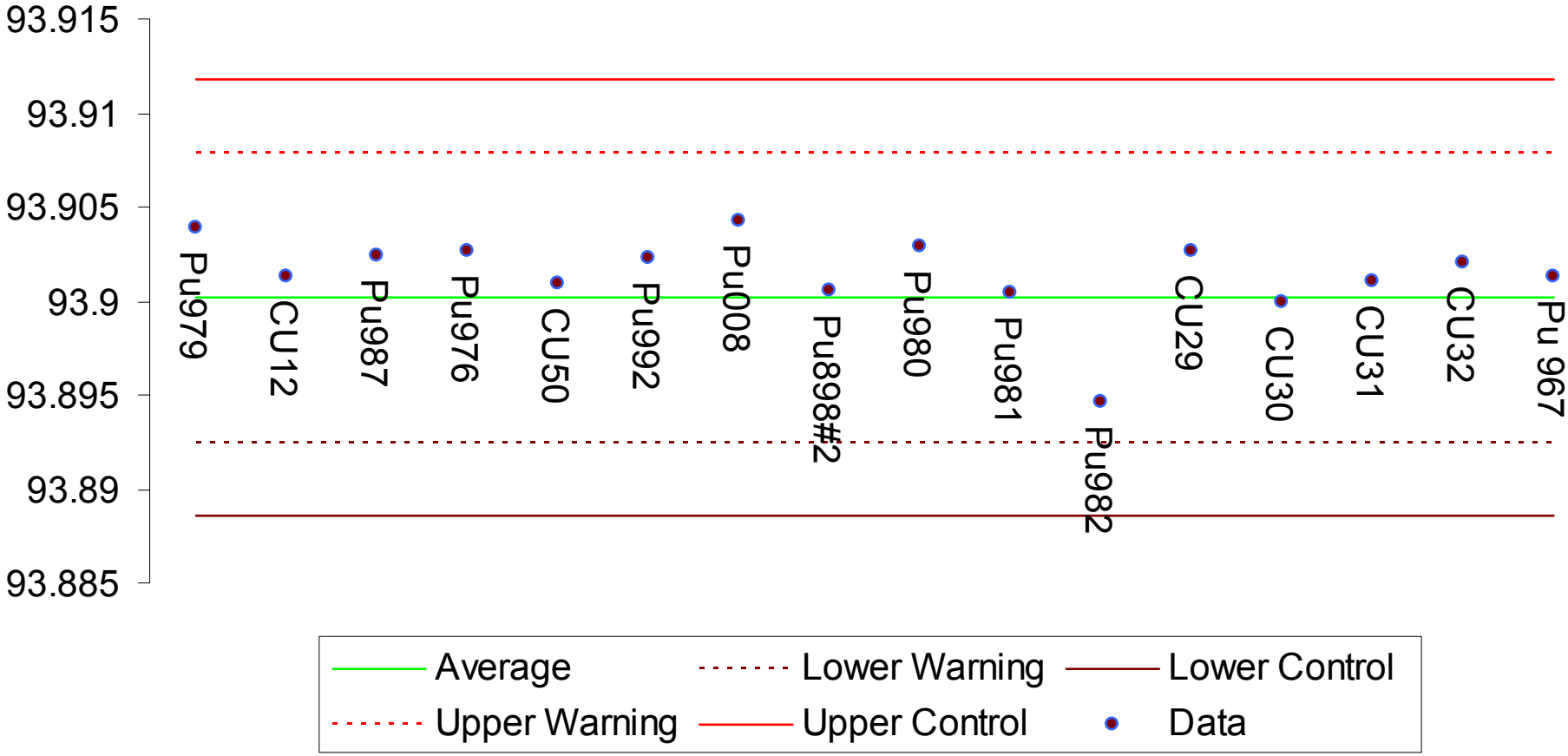
Sample is loaded in *3 M HNO3.* The Am/U fraction is rinsed with one loop of 3 MHNO3, while the Pu is stripped from the column with a 4 % HCl solution.

Run	Pu Measured (ng/mL)	Pu Total (ng) (Recovery %)	U Measured (ng/mL)	U Total (ng) (% Recovery)
1	0.486	1.490 (95.6)	69.7	2101 (104)
2	0.487	1.491 (95.7)	69.4	2092 (103)
3	0.488	1.491 (95.6)	70.0	2114 (104)
Average	0.487 +/- 0.001	1.490 +/- 0.001	69.7 +/- 0.2	2102 +/- 11
Precision		0.5 %		0.5 %

Total Pu using GPEC Separation



Pu-239 using GPEC Separation



Summary

- GPEC System is looking promising for replacing gravity columns for TIMS separation
- Would decrease the time required for separations, saving time and decreasing exposure

Other Application for ICP-MS

- Alpha Spectrometry for low level Pu
- Gamma Spectrometry for Am-241
- Cs/Ba-137
- IDMS for more accurate Pu & U measurement

Acknowledgements

- Michael Michlik
- Jeff Berg
- Jacqueline Fonnesbeck

Plutonium Exchange Program Discussion

Lav Tandon, Judith Eglin, Laurie Walker, Diana Decker, Edward Gonzales, Peggy Gautier, Sarah Michalak, Kevin Kuhn

Measurement Evaluation Program Meeting
Phoenix, Arizona
July 9, 2005
LA-UR-05-5057

Introduction

- **Plutonium Exchange Motivation**

  Outside Influences:

  – Precedent: Rocky Flats Standards Exchange

  – Design Agency Requirement: post-qualification validation of analytical chemistry processes

  Analytical Chemistry:

  – Validation of Analytical Chemistry Methods

  – Identify Potential for Process Improvements

  – New Analytical Chemistry Techniques: Verify measurement performance on characterized plutonium materials

Introduction

- **Plutonium Exchange Approach**

  Comparison of measurement results on the same "standard" plutonium materials from independent laboratories operating independent analytical chemistry methods

  Variability in data set captures inherent biases and uncertainties from multiple measurement methods

Achievements

I - Compilation and validation of FY04 exchange data.

- 2 Los Alamos Reports authored by C-AAC
- 1 Los Alamos Report on statistics authored by D-1

II - Participating laboratories for FY05:

- Memorandum of understanding with the participating DOE laboratories and sub-contracts in place. All budget issues settled

  Argonne (ANL), Argonne-West (ANL-W), Los Alamos (LANL), Livermore (LLNL), New Brunswick (NBL) and Savannah (SRS)

- Memorandum under the auspices JOWOG-22 agreements (Focus Area #22/6/##).

  Atomic Weapons Establishment (AWE) Aldermaston,UK

Achievements

III - FY05 Metal Preparation

- Improvements in metal cutting, plutonium metal packaging, and shipping procedure
- Samples for FY05 cut following improved cutting process
- Shipment status for FY05: external: 3 complete; 2 issues

Achievements

IV - Statistical evaluation of data in collaboration with D-1 for summary reporting to the production and design agencies.

V - Acquisition of two additional materials to be included in the program in FY06.

VI - Casting of two new materials currently underway and characterization of materials to follow.

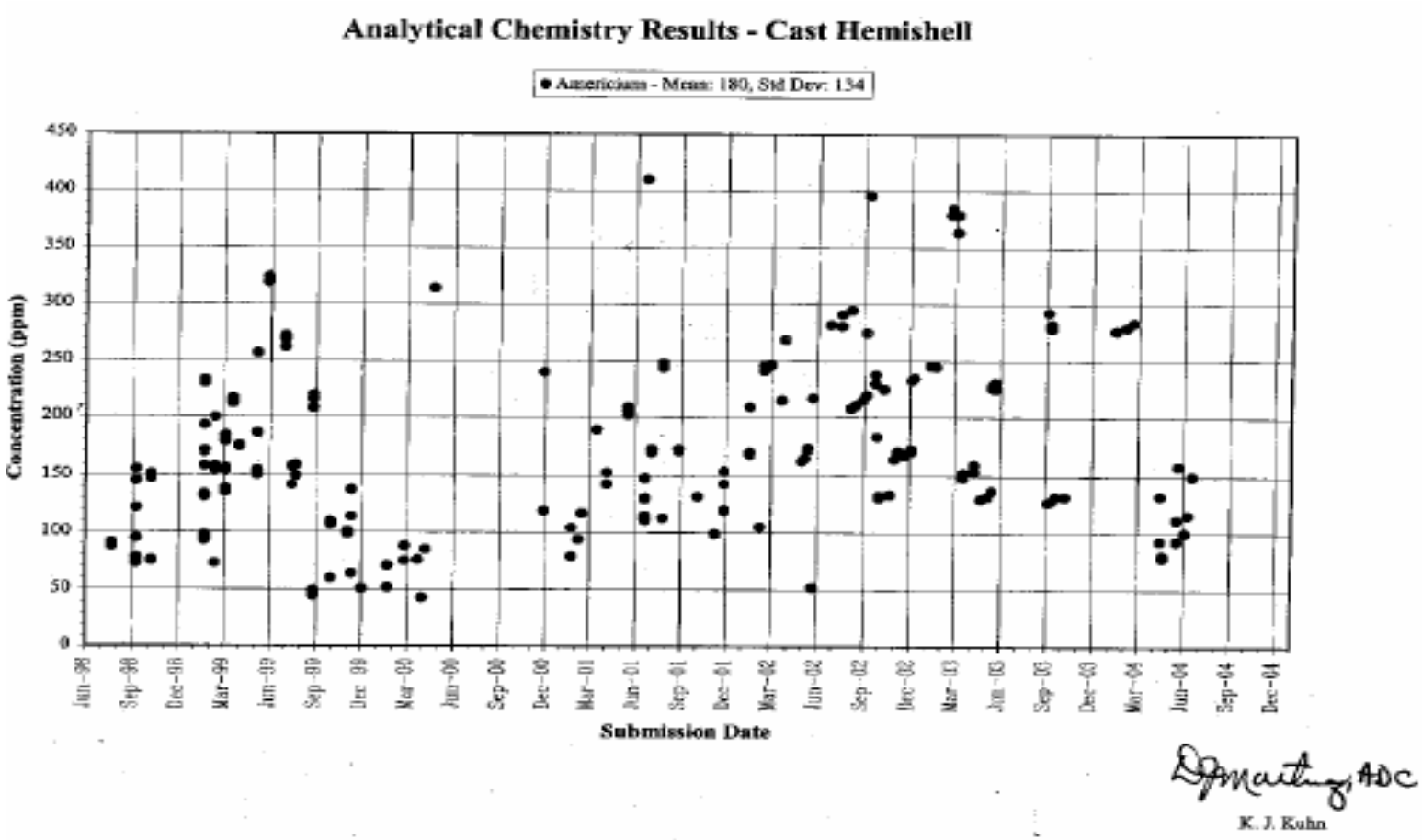
Achievements

- Design of experiments for preliminary testing of materials.
  Two new materials in the program

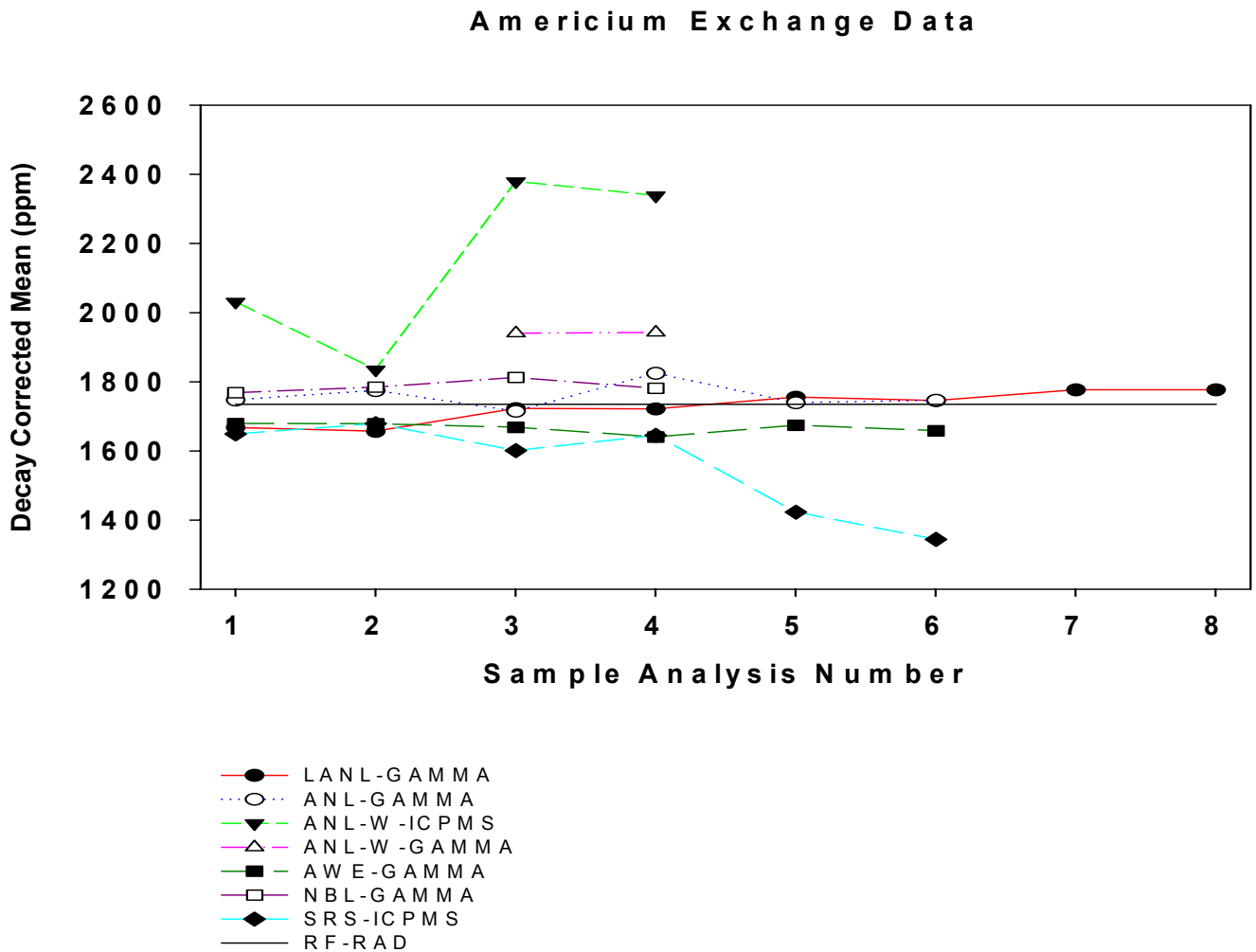
- Materials
  4 Exchange metals used

- Expected Data Set
  Metal N & P (Alpha metals): 4 sets of analytical results
  Metal Q & R (Delta metals): 4 sets of analytical results
  Data sets created for > 40 analytes

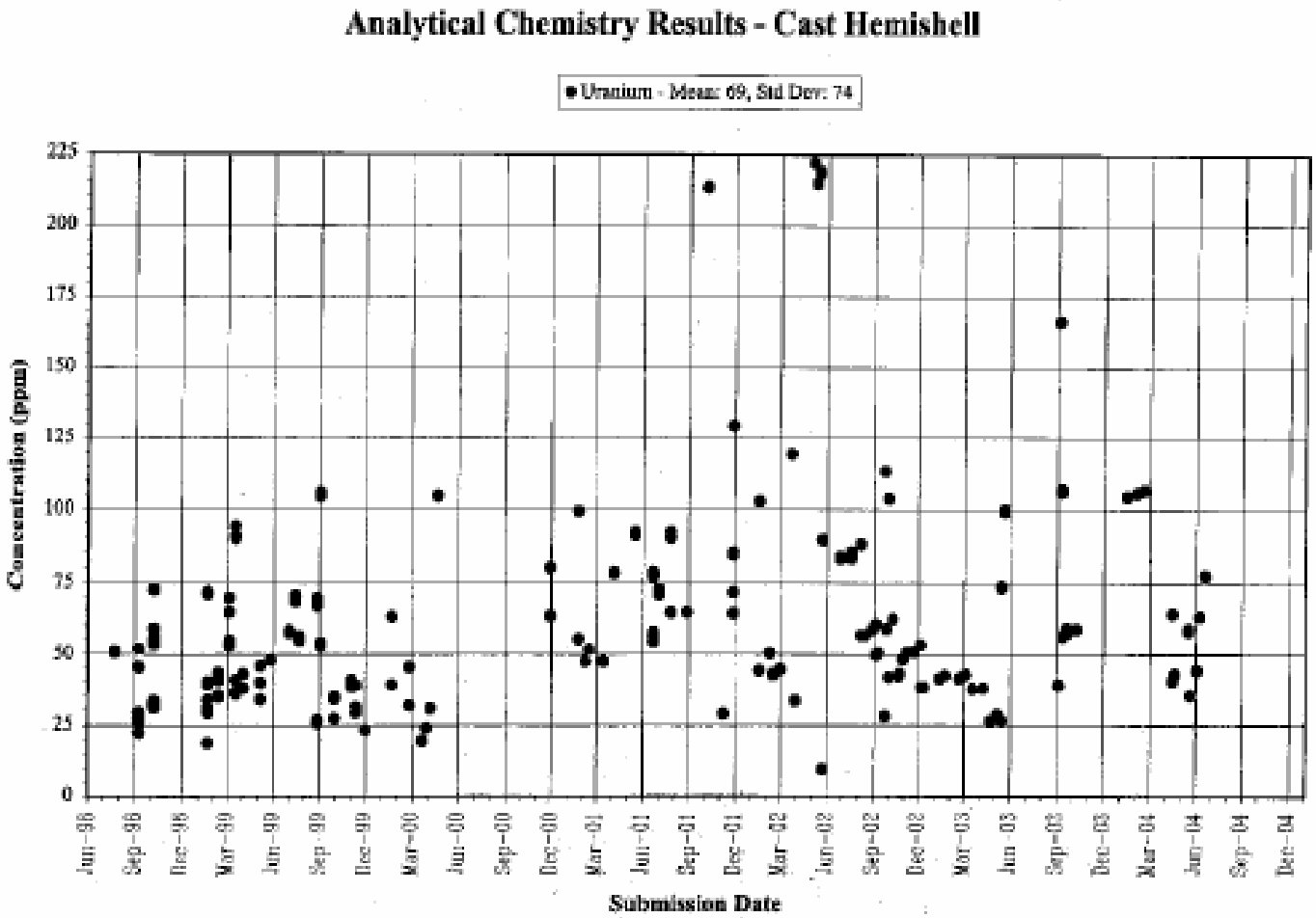
Am Data


Analytical Chemistry Results - Cast Hemishell
Americium - Mean: 180, Std Dev: 134
Concentration (ppm)
0
50
100
150
200
250
300
350
400
450
Jun-98
Sep-98
Dec-98
Mar-99
Jun-99
Sep-99
Dec-99
Mar-00
Jun-00
Sep-00
Dec-00
Mar-01
Jun-01
Sep-01
Dec-01
Mar-02
Jun-02
Sep-02
Dec-02
Mar-03
Jun-03
Sep-03
Dec-03
Mar-04
Jun-04
Sep-04
Dec-04
Submission Date
K. J. Kuhn

Am Exchange Data (Metal A)



U Data


Analytical Chemistry Results - Cast Hemishell
Uranium - Mean: 69, Std Dev: 74
Concentration (ppm)
225
200
175
150
125
100
75
50
25
0
Jun-96
Sep-96
Dec-96
Mar-97
Jun-97
Sep-97
Dec-97
Mar-98
Jun-98
Sep-98
Dec-98
Mar-99
Jun-99
Sep-99
Dec-99
Mar-00
Jun-00
Sep-00
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Mar-01
Jun-01
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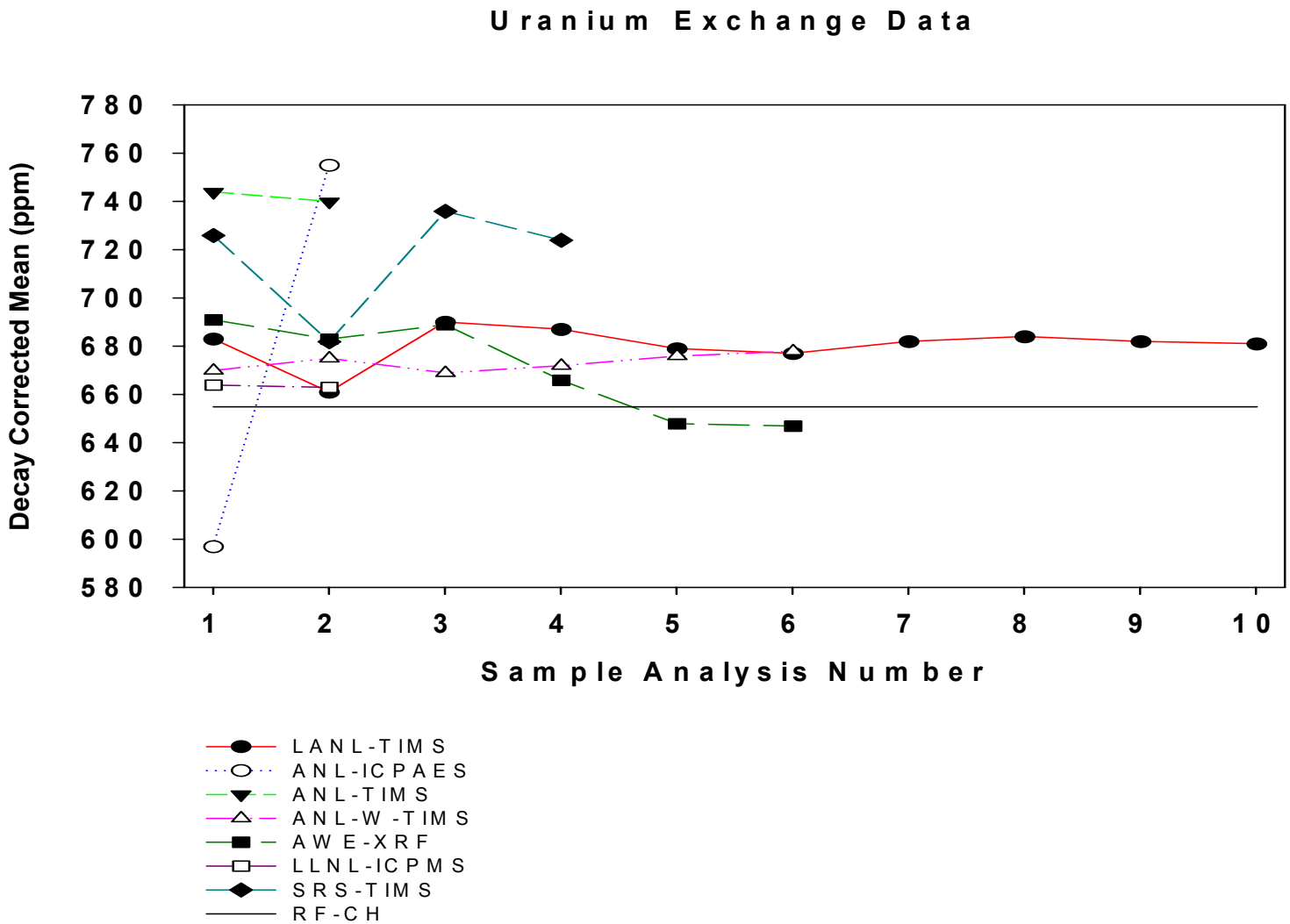
Dec-01
Mar-02
Jun-02
Sep-02
Dec-02
Mar-03
Jun-03
Sep-03
Dec-03
Mar-04
Jun-04
Sep-04
Dec-04
Submission Date

U Exchange Data (Metal B)



Impurity Levels in Metal 465

Impurity	LANL-465 (ppm)	AWE-465 (ppm)
Americium	1600	1586
Uranium Assay	825..0	810.0
Gallium	443.0	479.0
Iron	271.0	203.0
Chromium	217.0	240.0
Nickel	191.0	188.0
Aluminum	173.0	199.0
Carbon	90.0	85.0
Neptunium	91.0	84.0
Silicon	30.0	14.0
Calcium	29.0	33.0
Oxygen	57.0	126.0
Copper	27.6	26.0
Tungsten	17.0	11.0
Tin	16.0	
Manganese	14.8	16.0
Molybdenum	10.6	
Tantalum	29.6	
Zinc	7.0	2.0
Thorium	1.7	
Zirconium	2.7	
Titanium	2.7	2.9
Lead	2.2	
Boron	1.5	3.4
Magnesium	1.5	1.9
Beryllium	0.7	0.2
Cadmium	0.2	
Total	4152.8	4108.5
Average	**4130.7**	
100% - Imp.	**99.587**	

Metal 465

Ratio = Chem Assay/(100%-Impurities)

	4/01	8/01	5/03	5/04
LANL	0.999	0.999	1.001	1.000
ANL-W	0.992	0.988	1.002	0.999
ANL-E	1.003	1.003	0.999	0.984
AWE	0.999	1.001	1.001	
NBL	0.999	0.999	0.999	
SRS			0.999	0.999
RF	1.000			

Ratio = Chem Assay/100%-Impurities (Metal 465)

	4/01	8/01	5/03	5/04
LANL	0.999	0.999	1.001	1.000
ANL-W	0.992	0.988	1.002	0.999
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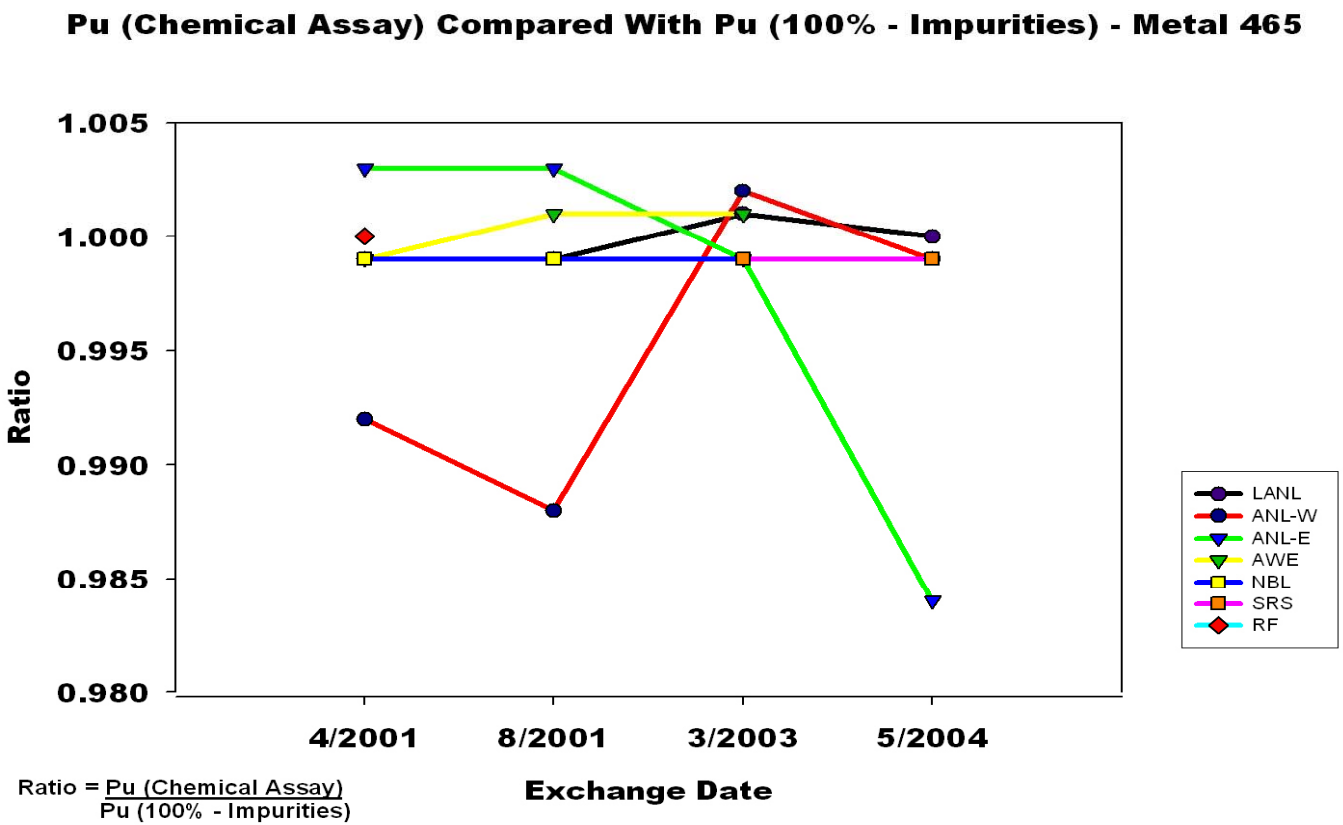
AWE	0.999	1.001	1.001	
NBL	0.999	0.999	0.999	
SRS			0.999	0.999
RF	1.000			

Ratio = Chem Assay/100%-Impurities (Metal 465)



Ratio = $\frac{\text{Pu (Chemical Assay)}}{\text{Pu (100\% - Impurities)}}$

Sample Preparation

Cross Contamination

- Varying levels of impurities within the exchange program
- Separate tools for each metal
- Sample environment and preservation of representative sampling

Other factors

- Sample size and analyte heterogeneity (contribute to precision and MDL)
- Analyte range available to analyst as for Ga and Am
- Method specific requirements
    - Polishing by brush or file; Fresh cuts; Atmosphere; Cleaning; Separations

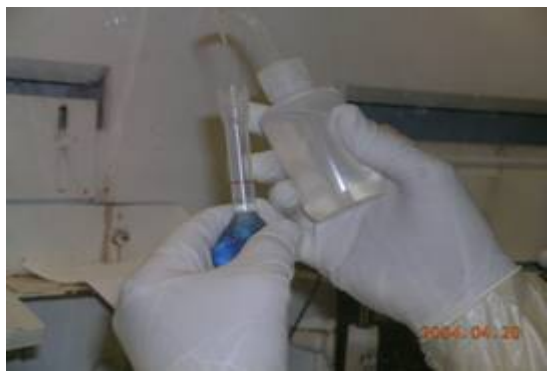
Dirty Dozen Impurities

Top Dozen Impurities	Metal 442	Metal 465	Metal C	Metal D
Decay Products:				
Americium	1440	1600	343	250
Uranium	629	825	94	104
Neptunium	73	91	31	23
Other Elements:				
Iron	223	271	341	29
Gallium	152	442	5186	
Aluminum	125	173		31
Nickel	179	191		
Carbon	61	90	53	
Oxygen	104	57	338	33
Silicon	53	30	11	
Tungsten	14	17	143	
Chromium	78	217	3	4
Total	**3131**	**4004**	**6543**	**474**
Impurities in metal	3172	4131	6556	500
ppm difference	41	127	13	26
Fraction in top 12	**0.9871**	**0.9693**	**0.9980**	**0.9480**

Qualification Activities

Qualification

- 7 Primary processes qualified for QUAL-1.
- 5 Backup methods in various stages of completion currently: New instruments/techniques being brought on-line for: iron analysis, plutonium isotopics, silicon analysis, trace analysis by ICPAES/ICPMS and plutonium assay.



Silicomolybdic acid blue complex & associated spectrophotometer in the open front

Qualification Activities

New ICPAES instrument recently installed for trace metal analysis in Pu matrices

Detection Limits

	New	Old		New	Old
Element	**ug/ml**	**ug/ml**	**Element**	**ug/ml**	**ug/ml**
Aluminum	0.017	0.110	Molybdenum	0.0018	0.029
Boron	0.011	0.005	Nickel	0.0021	0.013
Beryllium	0.0077	0.002	Lead	0.0103	0.078
Calcium	0.016	0.002	Silicon	0.0458	0.115
Cadmium	0.0011	0.006	Tin	0.0037	0.129
Chromium	0.001	0.028	Tantalum	0.029	0.019
Copper	0.002	0.016	Titanium	0.012	0.007
Iron	0.112	0.025	Tungsten	0.0029	0.064
Magnesium	0.0005	0.002	Zinc	0.0018	0.004
Manganese	0.0004	0.001	Zirconium	0.011	0.016

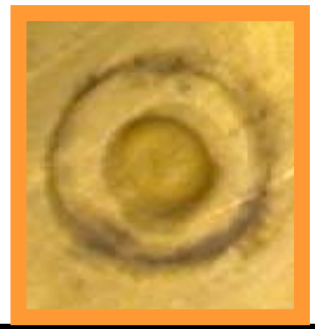
Development Activities

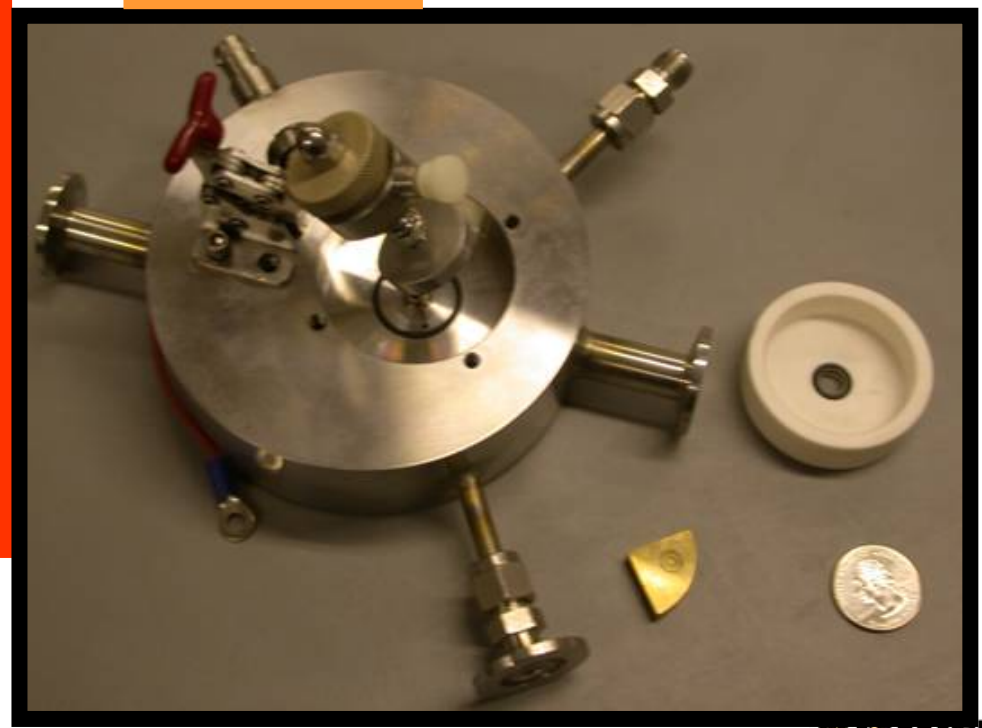
Recent/Current Development Activities

- Scope: To improve processes to address, safety, quality, capacity, and or efficiency of PMCP chemical analysis.
- Examples: NDA for radiochemistry @ TA-55, substitution of non-corrosive reductant, interstitial C & O by LECO, alternate separation chemistry, new gas sampling method, Ga by spotting XRF, Solid metal XRF, & GDMS

Dried Pu spotting technique (analysis by XRF through film)

Development Activities-GDMS





Acknowledgements

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ANL-W: Jacqueline Fonnesbeck
AWE: Terry Piper, Pam Thompson
LLNL: Pat Epperson, Richard Torres
NBL: Chino Srinivasan, Usha Narayanan, Irene Spalleto
SRS: Michael Holland, Pat Nussell
RFP: John Weiss, Bob Leonard

Actinide Analytical Chemistry Capabilities in Support of Nuclear Materials Programs at Los Alamos

Amy S. Wong

Measurement Evaluation Program Meeting

Phoenix, Arizona

July 9, 2005

LA-UR-05-5058

Chemistry Division
Actinide Analytical Chemistry Group (C-AAC)

- Established in 1943 in support of the Manhattan Project
- Currently resides in CMR Wings 3, 5, and 7, and TA55/PF-4 Room 124 (to be relocated to CMRR Facilities in ~2009 and 2014)
- Provides the highest quality actinide analytical services to LANL and external customers
- Our focus is on the analysis of samples in actinide matrices, including determination of the assay and isotopic composition of metals and oxides and trace impurities

Programs Supported

- Pit Manufacturing and Certification Programs (PMCP)
- Pit Surveillance Program
- ^{238}Pu Heat Source Program
- Mixed Oxide (MOX) Fuel Program
- ARIES Disassembly and Conversion Project
- Pu Stabilization and Disposition Project (94-1/00-1)
- Material Identification and Stabilization (MIS) Project

Programs Supported

- Advanced Fuel Cycle Initiative (AFCI) Program
- Jupiter Icy Moons Orbital (JIMO) Project
- TA-18 Move
- CMR Replacement (CMRR) Project
- Support Operations, Maintenance, and D&D Activities in TA-55 and CMR Facilities
- Pu Metal Standard Exchange Program
- Pu Future Conference

Support for Other LANL Programs and Operations

- JOWOG-22
- Department of Homeland Security (DHS) Projects
- Nonproliferation Projects
- Radiation Chemistry Projects
- Research and Development Projects
- Bioassay-LIMS Support

Analysis Capabilities

Assay
Plutonium Assay (includes dissolution, Pu Assay & Fe
Fe (to include dissolution)
Sample Dissolution
U assay by Davies-Gray
Loss of Ignition
Pu-238 assay
Mass Spectrometry
Pu or U isotopics on Metal
Pu or U isotopics on Oxide
Pu or U assay on Metal
Pu or U assay on Oxide
Gallium Analysis
Gas Analysis
Radiochemistry (CMR)
Americium by Gamma Spec
Np on metal
Np on oxide
Am or Pu on metal
Am or Pu on oxide
Am or Pu on liquid
RC- survey
Pu238 - Radiochemistry

Trace Elemental Analysis
ICPAES/-MS for Trace Elements on Metal
ICPAES/-MS for Trace Elements on Oxide
ICPMS - Pu238
DC arc
Low Level Gallium
CVAF-Hg
TCLP
RCRA Analysis of a liquid ICPAES/ICPMS at CMR
Trace Survey of a liquid ICPAES/ICPMS at CMR
Be Analaysis on Smears
Interstitial Analysis
Oxygen
Moisture
Carbon
Hydrogen
Ion Chromatography
Anions (Cl & F)
Anions (S)
Anions (N)
Perchlorates

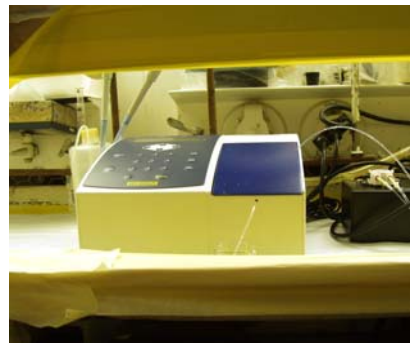
XRF
Gallium Analysis
SemiQuant

TA-55 Capabilities
Waste Analysis (R5-WASTE)
Pu & Am (R5-PUAM)
Pu238 - Radiochemistry
Pu Analysis (TTA Extraction & Am dilution)
RCRA Metals by ICPAES

Future Capabilities at TA-55 PF4
CVAF-Hg
Be Analaysis on Smears
Plutonium Assay
Iron Analysis
Am and Np Analysis on Metal
XRF Gallium Analysis on Metal
Carbon/Oxygen/Nitrogen Analysis
ICP-AES/MS Sample Preparation
Mass Spec Sample Preparation

Pu Assay and Classical Chemistry

- Controlled potential coulometric titration
- Ceric titration - photometric method
- Pu (III) and Pu (IV) spectrophotometric method
- U Assay – Davies Gray using ceric titrant



- Fe determination by spectrophotometry
- Si determination by spectrophotometry
- Loss on Ignition (LOI)
- Free acid determination in Pu containing solutions
- Standard solution preparation

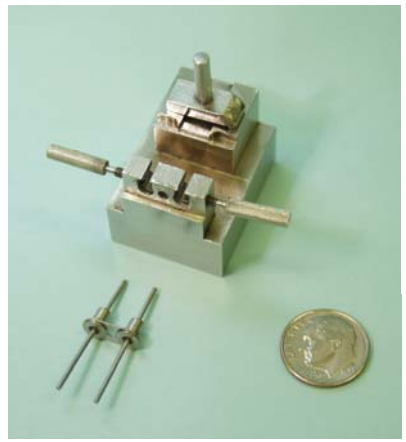
Onsite Analytical Chemistry & Sample Management

- Coordinate sample receiving, shipping, and distribution at TA-55 and CMR
- Pu metal cutting for standard exchange
- Material control and accountability

- Onsite Radiochemistry
  - Sample preparation
  - Gas proportional counter
  - Automatic gamma counter
- Trace metal analysis by ICP-AES
- Solution Assay Instrument Standards

Mass Spectrometry

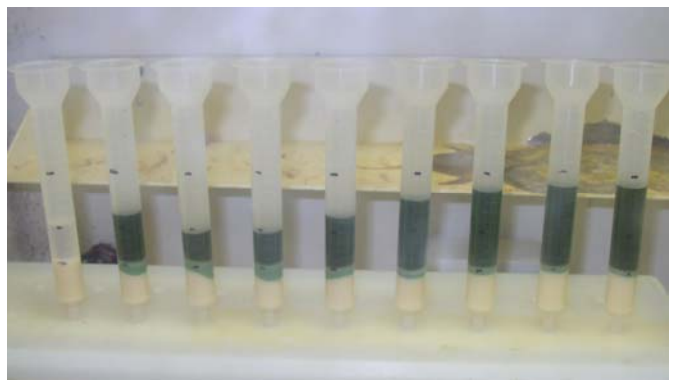
- Thermal Ionization Mass Spectrometry (TIMS) – 2 VG/Fisons + 1 to be procured
  - Pu and U Isotopics
  - Isotope Dilution Mass Spectrometry (IDMS) – high precision assay measurements for Pu, U, Ga, Am
- High Precision Gas Mass Spectrometry – Finnegan-MAT271 high resolution, magnetic sector instrument for measurement of gas compositions from H_2 to Xe (up to mass 150)



Plasma Spectroscopy

Modified JY ICP-AES in a chemical fume hood

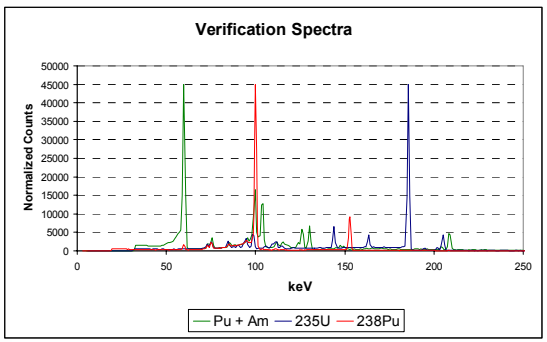
- Sample preparation
- DC Arc – direct current arc emission on solids
- Cold Vapor Atomic Fluorescence for Hg analysis



- Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)
- Inductively Coupled Plasma-Atomic Emission (ICP-AES) Spectrometry

Radiochemistry & Nondestructive Assay

- Radiochemical Separations and Sample Preparation
- Alpha Spectroscopy
- Gamma-Ray Spectroscopy
- Gas Proportional Counters
- Liquid Scintillation Counters
- Automatic Gamma Counters



- Radiation Chemistry
- Nondestructive Assay Standard Fabrication
  - ^{239}Pu, ^{238}Pu, ^{241}Am, ^{235}U, ^{238}Pu
- Forensic Determination - Homeland Security and Nonproliferation

Interstitial Analysis and Ion Chromatography

- By using combustion and inert gas fusion, carbon, oxygen, hydrogen, moisture, and tritium can be determined at trace levels in radioactive and non-radioactive materials.

Installation of new LECO instrument at CMR Wing-7

- Ion chromatographic analysis for fluoride, chloride, nitrite, nitrate, phosphate, sulfate, and oxalate anions
- Perchlorate analysis

X-Ray Fluorescence (XRF) & Diffraction (XRD)

- Wavelength Dispersive X-Ray Fluorescence
  - Elemental scans of liquids and solids for elements present including bulk and trace components
  - Bulk elemental analysis (wt %) and trace elemental analysis (1 to 100's ppm) of solids and liquids
  - Research and development

Fingerprint Detection Technology

MXRF development team: Chris Worley, Sara S. Wiltshire, Thomasin C. Miller, George J. Havrilla and Vahid Majidi

- X-Ray Diffractometer

Participate in the Following Material Exchange and Evaluation Programs

- LANL – Pu metal exchange program with DOE labs
- NBL – Uranium assay and isotopic, UF_6
- JOWOG-22 – Pu and U metal exchange

In planning:

- Gas samples
- PuO_2
- Other non-actinide materials

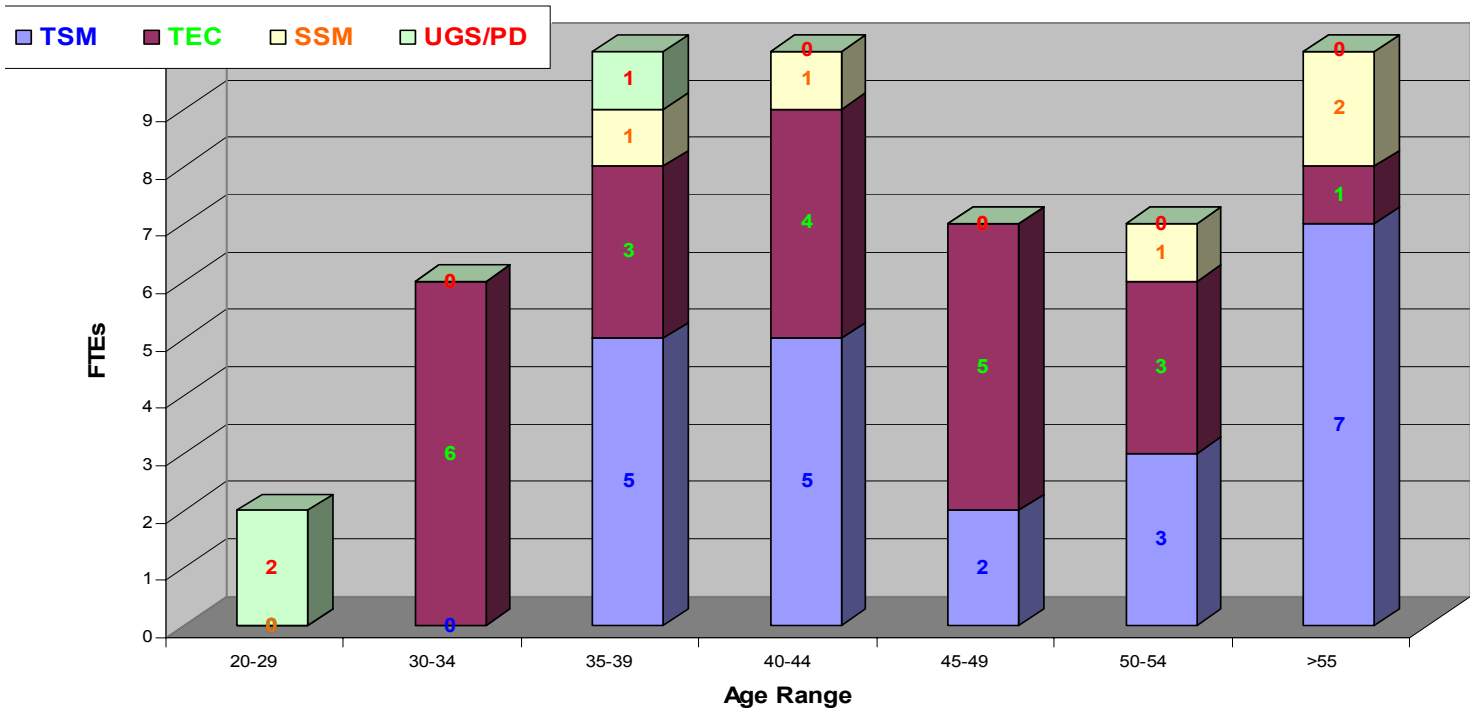
Challenges

- Succession Planning – > 45% TSM are over age 50
  - Two TSM vacancies – one early career and one mid-career
  - Two postdoctoral positions – radiochemistry and general analytical chemistry
- Depth of Qualified Operators
- Loss of Capabilities
- Flat Budget – ~$15 millions annually
  - Do more for less
  - Lean manufacturing and six sigma

C-AAC Group Demographics

July 2005 Update

- Total Personnel: 51 UC + 1 Contractor (25 female; 27 male)
- Education: 14 PhD, 2 MS, 20 BA/BS, 7 assoc., 7 others, 2 UGS



Average: 43.8 years old (UC)

Challenges (cont.)

- Incompatible Sample Analysis on Same Instrument and Sample Preparation Area
  - Isotopic analysis – ^{239}Pu vs ^{238}Pu samples
  - Trace uranium on Pu vs. trace plutonium on U samples
- Aging Instrumentation
- Waste Generation
- Shipping Issues
- Aging CMR Facility – 63 years old facility
  - CMR Replacement – radiological (8.5g ^{239}Pu equivalent) in 2009 and nuclear facility (Cat I/II) in 2014 ?
  - Current CMR authorization basis will expire in 2010
  - Interim Capabilities at TA-55 Plutonium Facility

Development Activities

- Establish Interim Analysis Capabilities at TA-55
  - Open-front hood vs. glovebox operations
  - Co-locate all the Pu metal analysis and sample preparation capabilities in 2,300 ft^2 lab space
- Pu Assay – coulometry, ceric titration, Pu(III), Corpel
- Direct Metal Analysis – x-ray fluorescence and glow-discharge mass spectrometry
- Sample Preparation Improvement – trace elements and Np analysis
- Re-establish NDA techniques
- Smaller footprint for instrumentation and sample preparation area

BACKUP / INFORMATION SLIDES

Analytical Chemistry Support

- Quality Assurance and Quality Control
  - 10CFR830.122 10CFR50 Appendix B
  - DOE Order 414.1A DOE/NNSA QC-1
- Training
- Document Control
- Records Management
- Data Packages
- Laboratory Information Management System (LIMS)
  - Oracle SQL*LIMS
  - Sample/nuclear material tracking & data reporting/management
- Operations Safety Committee

PIÑON Recognition
2002 New Mexico Quality Awards

Present status for the collaboration between NBL and JNC on preparation of Pu reference material

July 9, 2005

JNC

Necessity of Pu reference material preparation in Japan

All accountancy analysis of PFC is performed by IDMS which needs standard material, called spike.

However, Pu reference material have to obtain from foreign producers because Japan has no domestic Pu reference material.

Oversea transportation of plutonium is gradually becoming more difficult

Needs on LSD spike will increase by starting operation of Rokkasho Plants in Japan.

It is important to establish the capability for the preparation of Pu reference materials and associated LSD spike expertise in Japan.

Why has JNC started the study for preparation of Pu reference materials ?

JNC has the MOX scrap powder with proper isotopic composition for LSD spike

Metal content	Pu=1kg	U=7.8kg
Composition	Pu=9.588wt%	U=75.516wt% (MOX)

Isotope composition (wt%) Analysis date：2001/7/23

Pu238	Pu239	Pu240	Pu241	Pu242
0.017	91.336	8.406	0.180	0.058
U234	U235	U236	U238	
0.030	5.827	0.037	94.106	

JNC has the facilities where large amount of plutonium can be handled.

JNC has abundant experience on LSD spike preparation from Pu and/or U metal.

However, JNC has to attain expertise in preparing certified reference materials.

JNC want to develop the scheme for utilizing this MOX as starting material for preparation of Pu reference materials and acquire the expertise needed for certification.

Goal of the study

(1) Preparation of LSD spike from MOX (Short term study)

Establishment of the method for preparing reliable LSD spike from MOX.

(2) Preparation of Pu reference material from MOX (Long term study)

Establish methods for preparation of plutonium reference materials (Feasibility study)

➡ Development of Pu reference material with equivalent uncertainty compared with Pu metal standard

When material should be certified?

(Case 1) Certification of Pu content in MOX ➡ Impossible

No homogeneity of MOX powder

(Case 2) Certification of LSD spike ➡ Difficult

A production batch of LSD spike is about 500 units

⬇

Almost 10 times of certification of LSD spike are required in a year

(Case 3) Certification of Pu nitrate solution obtained from MOX solution ➡ Possible

Advantage ; Large amount of Pu can be certified at a time.
Easy to use, Homogeneity

Disadvantage ; Weight change by evaporation and decomposition of nitric acid during storage

➡ This study involves evaluation of uncertainty with this certification and effect of weight change of the solution

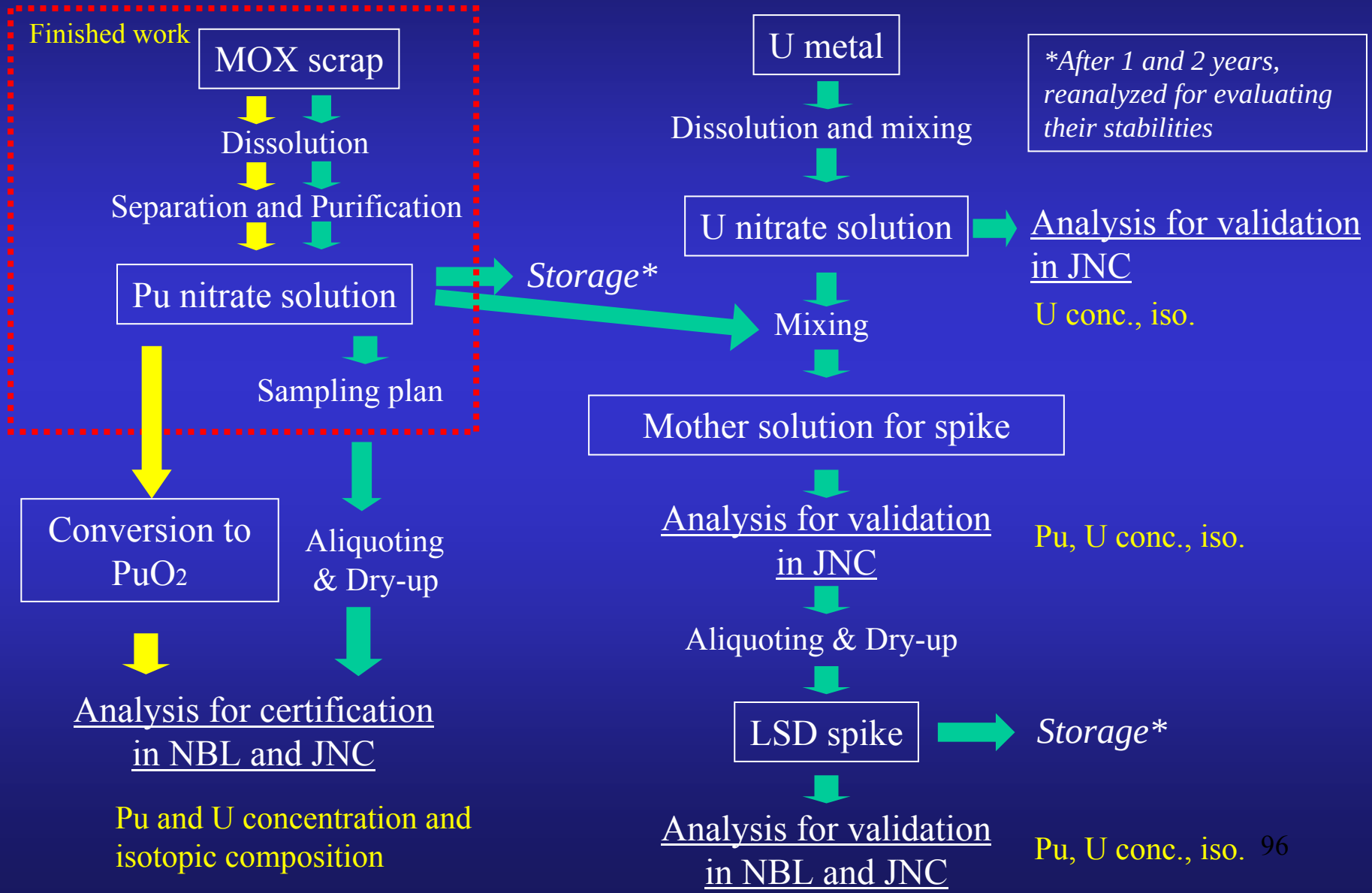
(Case 4) Certification of Pu oxide obtained by conversion of the Pu nitrate solution ➡ Possible

Advantage ; Stability during storage

Disadvantage ; Less solubility

➡ This study involves the evaluation of possibility of usage of PuO_2

The scheme for preparation of LSD spikes; JNC and NBL collaboration



Preparation of Pu nitrate solution from MOX

Period ; From January to October 2004 (10 months)

- Dissolution of MOX scrap powder

Dissolved MOX Scrap ; 190g MOX

Pu ; 9.6% U ; 75.5% Pu239 ; 91.4% U235 ; 5.8%

Major impurities ; Al : 300ppm Mg : 30ppm

Obtained MOX solution ; 620ml of (26gPu+220gU)/L, 4N

- Separation of Pu from MOX solution

3 times ion-exchanges ; Resin used ~ Bio-Rad AG1×8

Eluent for uranium ~ 4~5 N HNO_3

Eluent for plutonium ~ 0.1~0.3N HNO_3 with a few HF

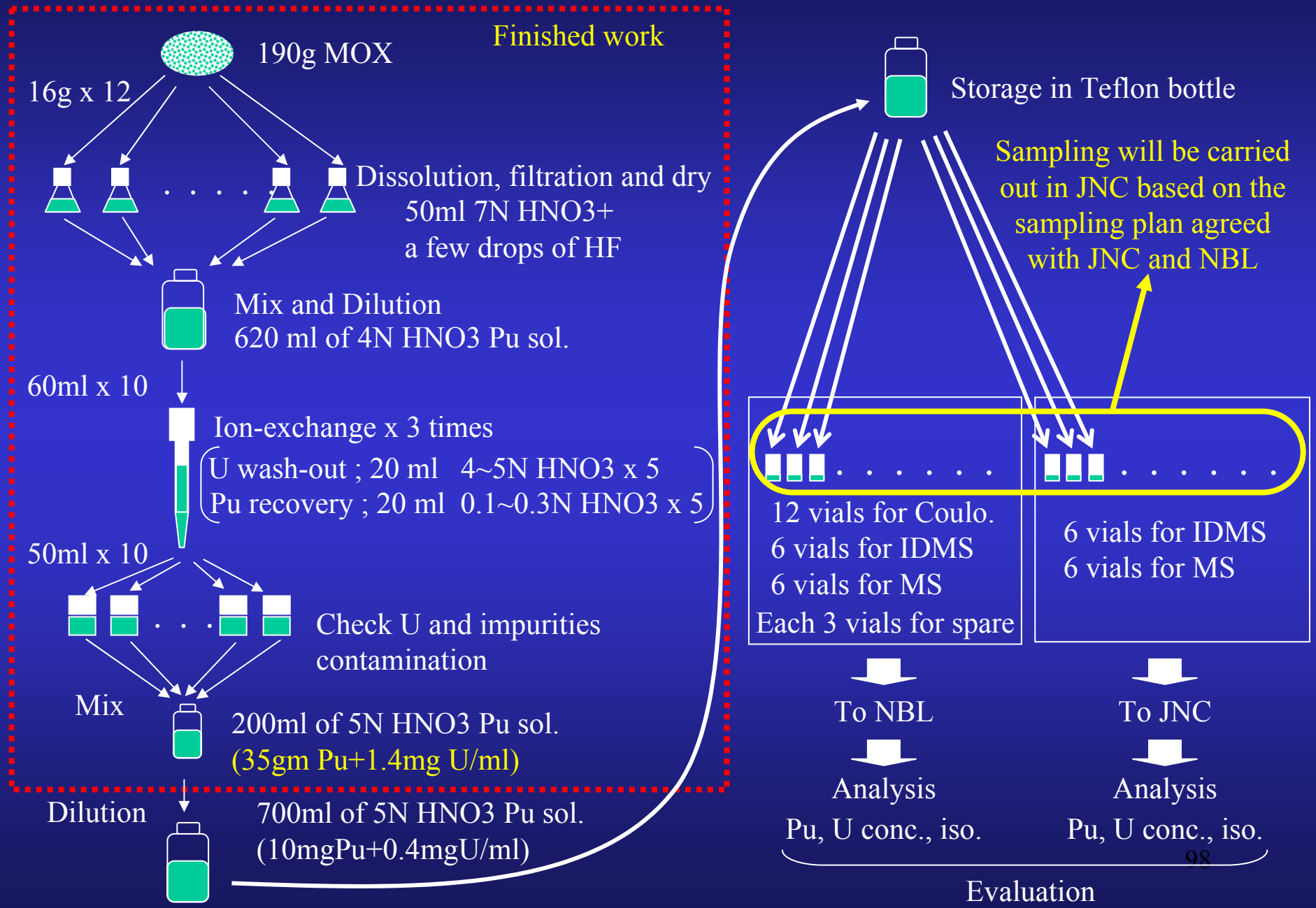
Decontamination factor ; First separation ~ 3 (decantation method)

Second and third separation ~ 70

(usual method (using column))

Obtained Pu solution ; 200ml of (34.6gPu + 1.41gU)/L, 5N

Sampling plan for aliquoting Pu nitrate solution



Issues raised in sampling plan

1. Reagents and apparatus to be used

2. Preparative works

   Cleaning up of working area, vials and bottles

3. Calibration of balances

   Procedures for calibration and simulation

4. Preparation and storage of Pu mother solution

   The procedures for weighing and storing the Pu mother solution

5. Aliquoting

   Procedures for aliquoting including Pu amounts per vial and number of vials to be transported to NBL

6. Drying

   Procedures for drying the solution in vials

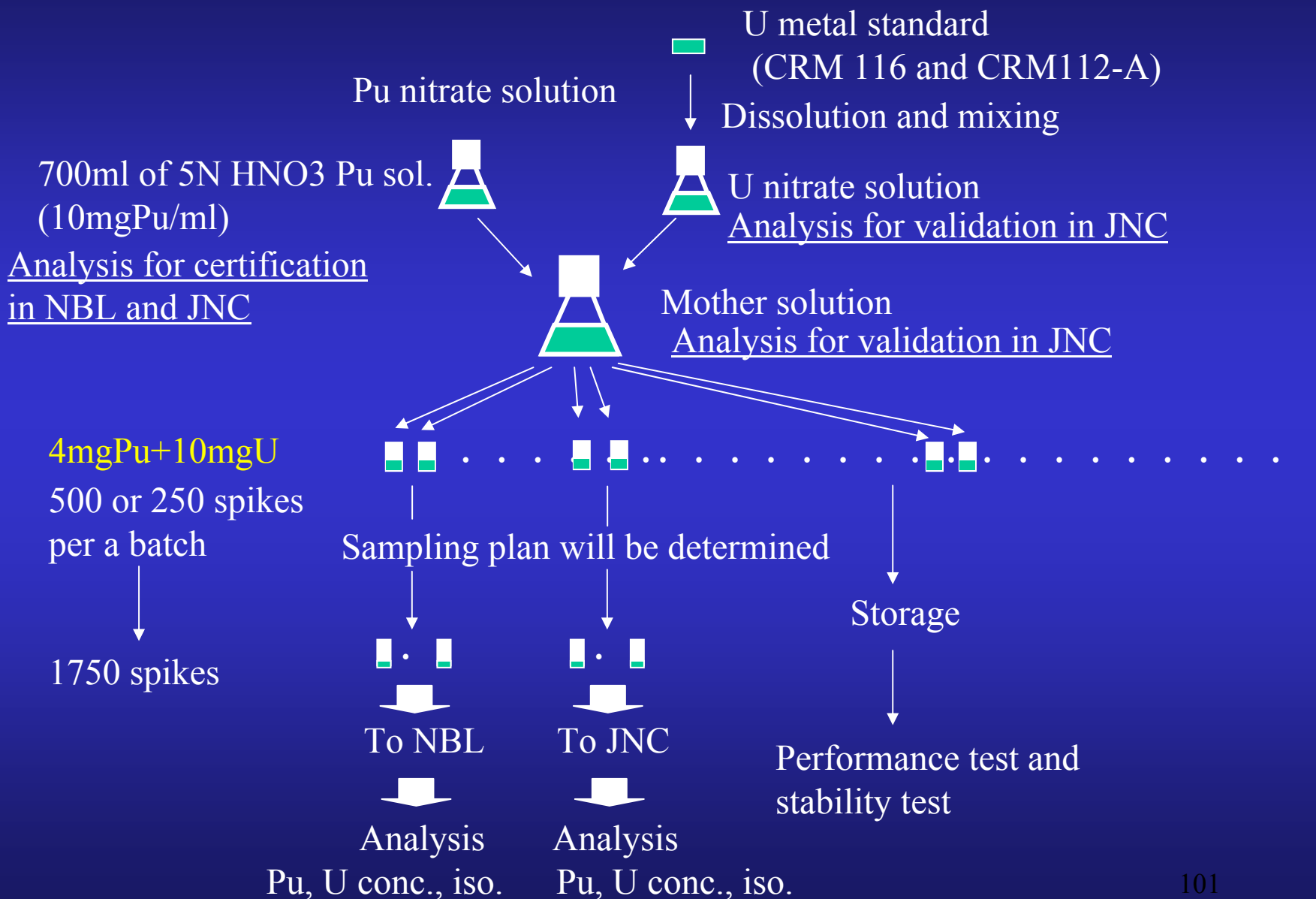
7. Blank measurement

   Blank measurement by IDMS with U233 and Pu242 spikes

Example for sampling manual

	Procedure	Remarks
5. Aliquoting	(1) Preparative works / Clean up surface of the bottle of plutonium mother solution and vials, and operation area. / Calibrate the balances (PR1203 and AG245) according to the chapter 3. / Record time, date, temperature, humidity, and atmospheric pressure. (2) Aliquoting for dilution of the plutonium mother solution / Weigh the bottle of the plutonium mother solution without silicon seal tape using PR1203 and record the weight. Note ; Check the weight change during storage of the solution. / Stir the solution well and keep it gentle for about 15 min. a) For coulometry / Weigh tare of 30ml vial with a cap using AG245 and record the weight. / Open the cap of the vial. / Just after opening the cap of the bottle of Pu mother solution, aliquot about 13g of solution which contains about 130mgPu into the vial using a pipette, and cap the bottle and the vial. / Weigh the mass of the vial with AG245, and record it. Note ; Weighing should be carried out as soon as possible after aliquoting because of minimizing weight change by evaporation. / Weigh the bottle of the plutonium mother solution with PR1203 and record the weight. Note ; Check the no significant difference between weight of the aliquot and weight change of the plutonium mother solution. If the difference is significant, this aliquoting must start over. b) For IDMS and ISO / Weigh tare of 50ml vial with a cap using AG245 and record the weight. / Open the cap of the vial. / Just after open the cap of the bottle, aliquot about 4g of solution which contains about 40mgPu) into the vial, and cap the bottle and the vial. / Weigh the mass of the vial with a cap using AG245, and record it. Note ; Weighing should be carried out as soon as possible after aliquoting because of minimizing weight change by evaporation. / Weigh the the bottle of the plutonium mother solution with PR1203 and record the weight. Note ; Check the no significant difference between weight of the aliquot and weight change of the plutonium mother solution before and after the aliquoting. If the difference is significant, this aliquoting must start over.	Coulometry A total of 12 samples, each sample containing between 8-10mg plutonium, are required. Each sample must have an accurate, well-established weight that is measured using a high quality analytical balance and mass standards traceable to the international measurement base. IDMS A total of 6 samples, each containing 1mg +- 0.1 Pu, are required. Each sample must have an accurate, well-established weight that is measured using a high quality analytical balance and mass standards traceable to the international measurement base. Isotopes A total of 6 samples, each containing 1mg +- 0.1 Pu, are required

Scheme for preparation of LSD spike



Status on preparation of LSD spikes

- Preparation of Pu nitrate solution
- Sampling plan for aliquoting Pu nitrate solution

➡ Finished

- Transportation of Pu samples to NBL

➡ Shipping procedure for of Pu samples

- Analysis of Pu nitrate solution
- Analysis of mother solution for spike preparation for validation
- Preparation of LSD spikes
- Transportation of LSD spikes to NBL
- Analysis of LSD spikes

➡ Works in 2005 JFY

Problems encountered in past study

- Contamination of uranium in Pu nitrate solution
- Long time consuming for separation of Pu from MOX

➡ JNC examines optimization of Pu separation and purification procedure.

-Optimization of length of ion-exchange column
-Rough separation of Pu and U by mild dissolution of MOX at the first step of separations

The MOX may be produced by mixing mechanically with PuO_2 and UO_x

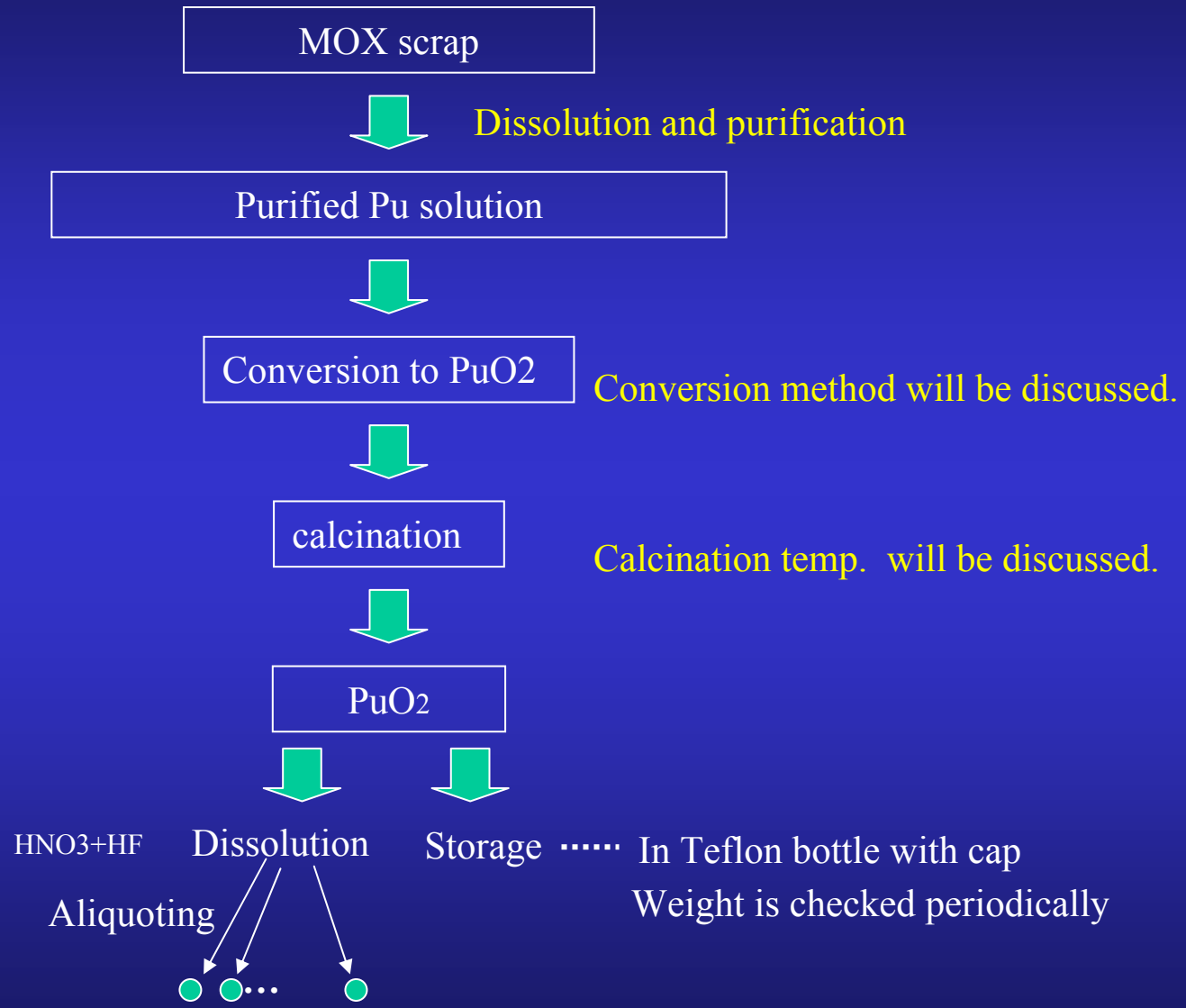
➡ By short time dissolution with diluted HNO3, UOx may dissolve selectively.
Under examination

- Transportation of Pu samples from JNC to NBL

➡ Less experience of export of nuclear material from Japan to foreign country

Long time consuming than expected

Plan for preparation of plutonium oxide



Plan in 2005 JFY

JNC

(Study for LSD spike)

1) Taking samples from Pu nitrate solution
2) Transportation of the Pu samples to NBL
3) Analysis of Pu samples
4) Preparation of LSD spikes
5) Transportation of LSD spikes to NBL
6) Analysis of LSD spikes

(Study for preparation of Pu oxide)

1) Preparation of purified Pu nitrate solution from MOX scrap
2) Conversion of the purified Pu solution to PuO2

NBL

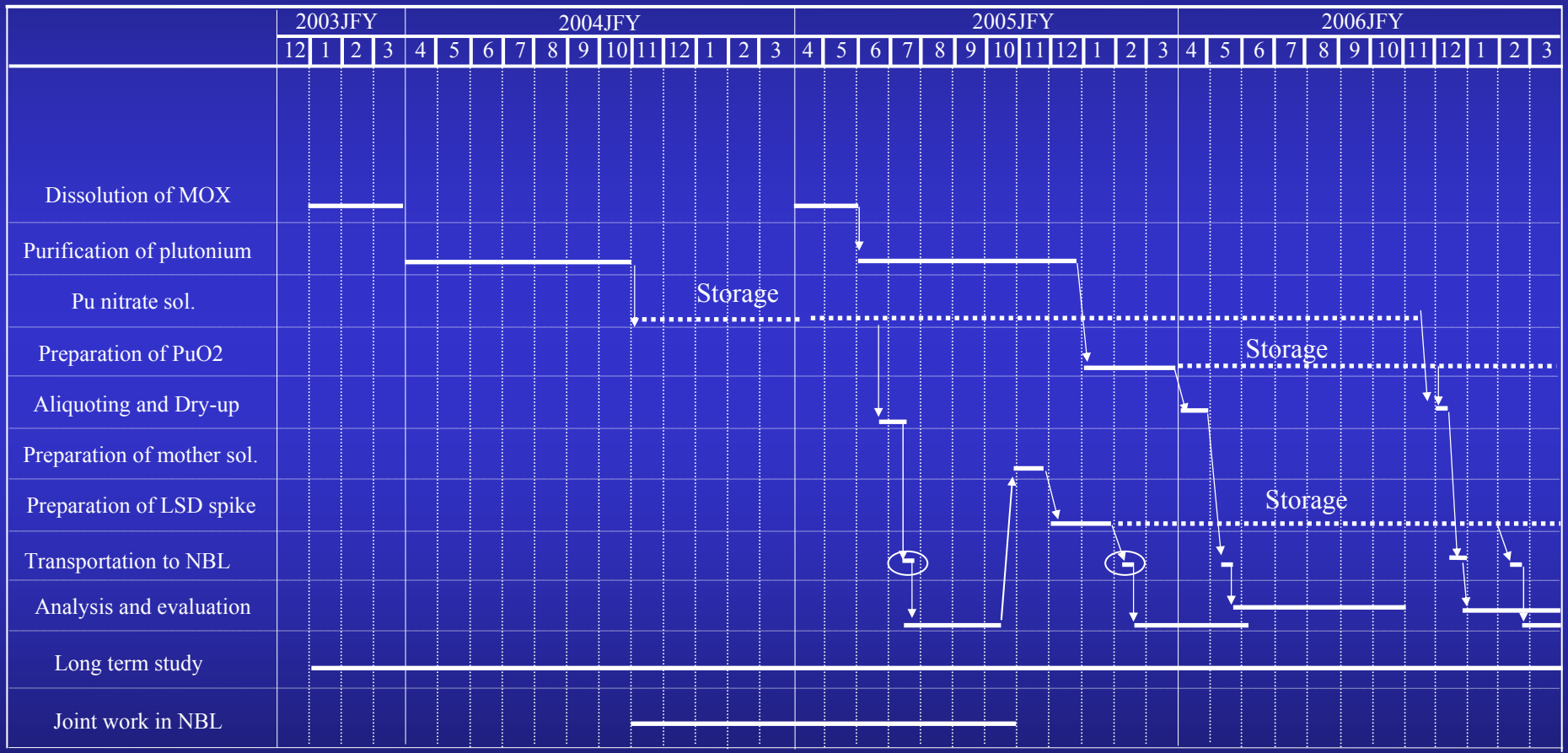
(Study for LSD spike)

1) Analysis of the Pu samples and evaluation of analytical results
2) Analysis of LSD spikes and evaluation of analytical results

(Long term study)

1) Study for domestic preparation of certified reference material in Japan
2) Improvement of knowledge and skills of PFC's staff

Schedule for the study



Summary

JNC has started collaborative work with NBL on the preparation of Pu reference materials and associated LSD spikes.

- MOX is used as starting material of LSD spikes.

- Pu solution obtained by ion-exchange of MOX solution is certified and used as mother solution for preparation of LSD spikes.

  ⇨ Preparation of the Pu solution has finished. Aliquots of the solution will be transported to NBL for analysis for certification within next several months

- After certification of the Pu solution, LSD spikes are prepared and validated.

- PuO_2 converted from the Pu solution is examined as another candidate of starting material of LSD spikes. Conversion method is now under consideration.

⇩

By establishing and expertise the preparation method of LSD spikes from MOX in this study, concern about procurement of them needed for operation of nuclear fuel plants in Japan may be reduced.

Nuclear Materials DA at the Safeguards Analytical Laboratory (SAL)

Steve Balsley

http://www.iaea.org/OurWork/ST/NA/NAAL/sal/salmain.php

IAEA
International Atomic Energy Agency

IAEA Major Program 4
Nuclear Verification

- **Objective**
  To provide credible assurance to the international community that nuclear materials and other items placed under safeguards are not diverted or misused and, for States with comprehensive safeguards agreements in force, to provide credible assurance as to the absence of undeclared nuclear material and activities for States as a whole.
- **Outcome**
  Ability to detect the diversion or misuse of nuclear material and other items placed under safeguards and, where appropriate, any undeclared nuclear material and activities.

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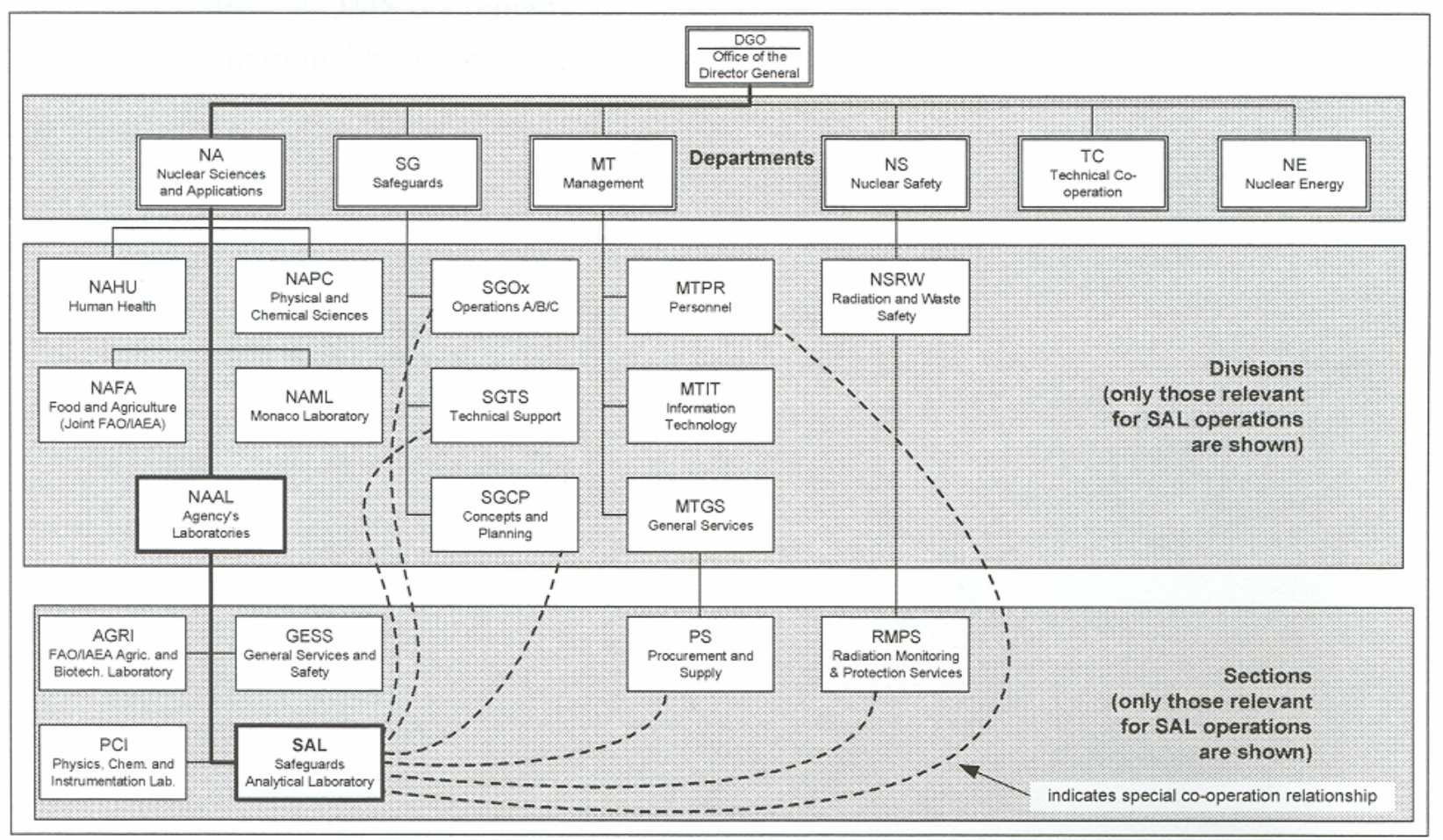
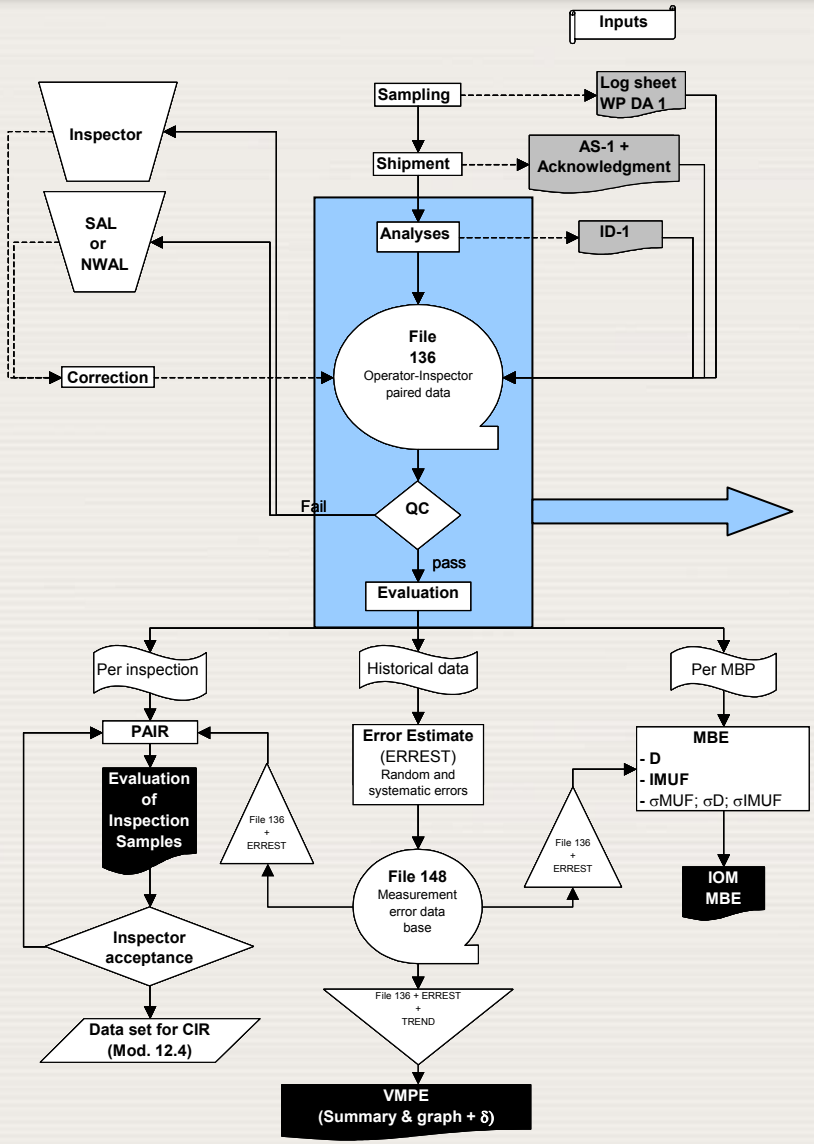
Organizational Structure

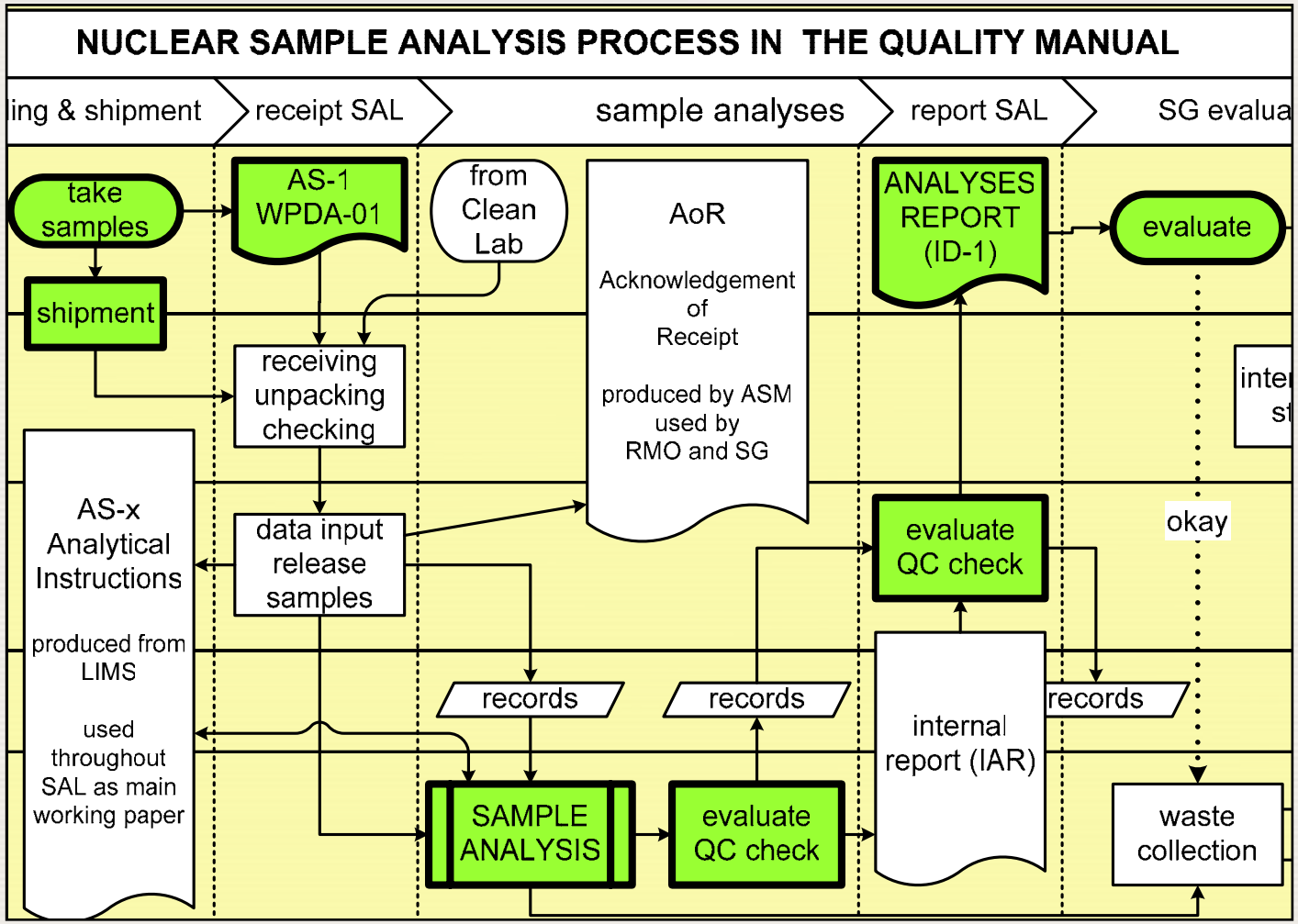


DA Information Processing @ IAEA



Next Slide…

DA Sample & Info Flow in SAL



Nuclear Sample Types & Techniques

Category	Components	Validated Techniques	Combined Std Uncertainty (1s) (1)	Remarks
Spent fuel	U, Pu elemental	IDMS, HKED	ITV2000	
	U, Pu isotopics	TIMS	ITV2000	
	Np, Am (ANM)	TRU/TEVA separation alpha-spectrometry	5%	(Other Alternative methods applicable)
	Cm	Direct alpha-spectrometry	5 - 10% (2)	For Pu/Cm (in-situ neutron measurement)
HALW	U, Pu elemental	IDMS Spectrophotometry (Pu)	5%	
	U, Pu isotopics	TIMS	ITV2000	
	Np, Am (ANM)	TRU/TEVA separation alpha-spectrometry	5 - 10% (2)	(Other alternatives)
	Cm	Direct alpha-spectrometry	5 - 10% (2)	For Pu/Cm (in-situ neutron measurement)
U Product, U process stream (Oxide, UNH, metal, alloy yellow-cake etc)	U elemental	DG-Titration IDMS, Gravimetry	ITV2000	
	U isotopic	TIMS, HRGS	ITV2000	
	Impurities (3) (other elements)	ICPMS, WDXRF	5 - 10% (2)	(Other alternative methods applicable)
U-Th Product	U / Th elementals	DG titration + Gravimetry, HKED	ITV2000 (U) 0.2% (Th)	Th also possible by complexometric titration
	U isotopics	TIMS	ITV2000	
U Fluoride	U elemental	DG-Titration IDMS, Gravimetry	ITV2000	
	U isotopic	TIMS, HRGS	ITV2000	
	Impurities (3) (other elements)	ICPMS, WDXRF	5 - 10% (2)	(Other alternative methods applicable)
U Ore	U and other elementals (3)	XRF, HKED	5%	(Other alternative methods applicable)

Analytical Techniques

	Random, Relative %	Systematic, Relative %
^{235}U by Mass Spectrometry e.g. 1-2% enriched	0.05 (0.1)	0.05 (0.1)
^{235}U By Gamma Spectrometry	0.15	0.15
U by Titration	0.08 (0.1)	0.1 (0.1)
U by Gravimetry	0.05 (0.05)	0.05 (0.05)
U by IDMS	0.1 (0.2)	0.1 (0.2)
Pu by Titration	0.08 (0.1)	0.1 (0.1)
Pu by Coulometry	0.05 (0.1)	0.1 (0.1)
Pu by IDMS	0.1 (0.2)	0.1 (0.2)

Nuclear Chemistry Labs @ SAL

- Uranium Laboratory
  - Samples only containing U
  - Davies & Gray titration (main method)
- Plutonium Laboratory
  - Samples containing Pu and Pu+U
  - IDMS
  - Coulometry (+ spectrophotometry for Fe)
- Input Laboratory
  - Samples containing fission products
  - IDMS

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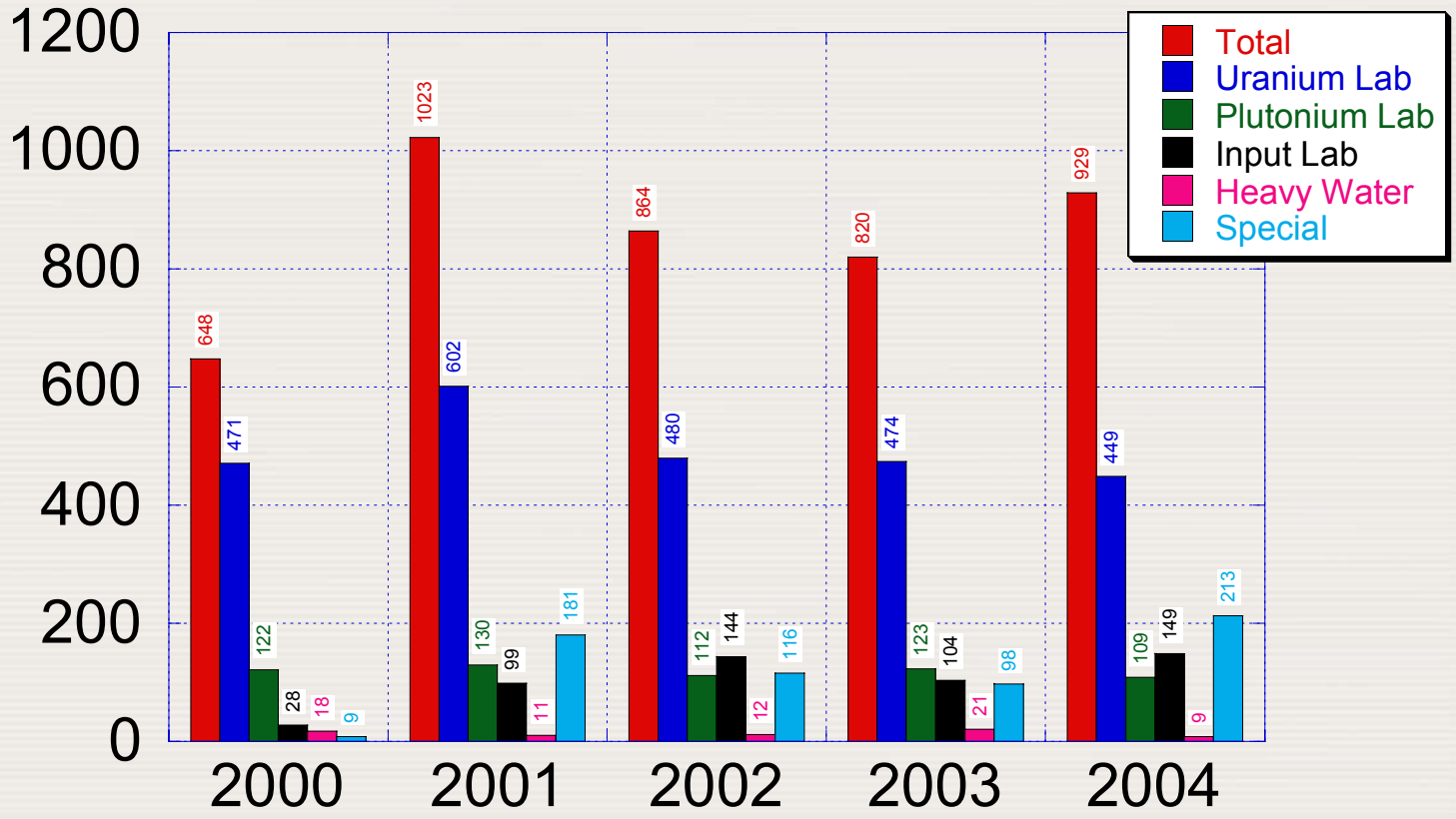
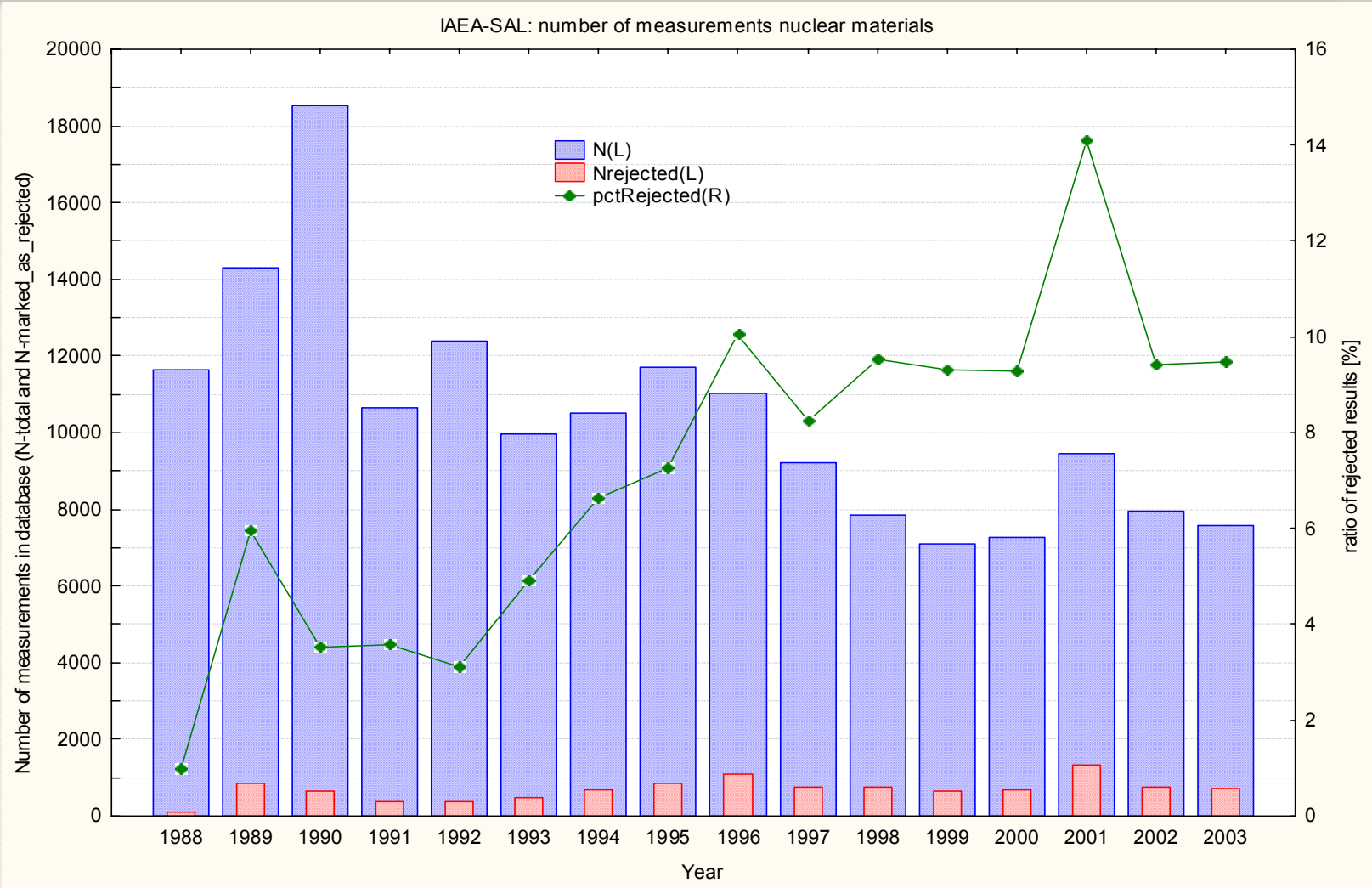
Inspection DA Samples @ SAL



Number of DA Measurements



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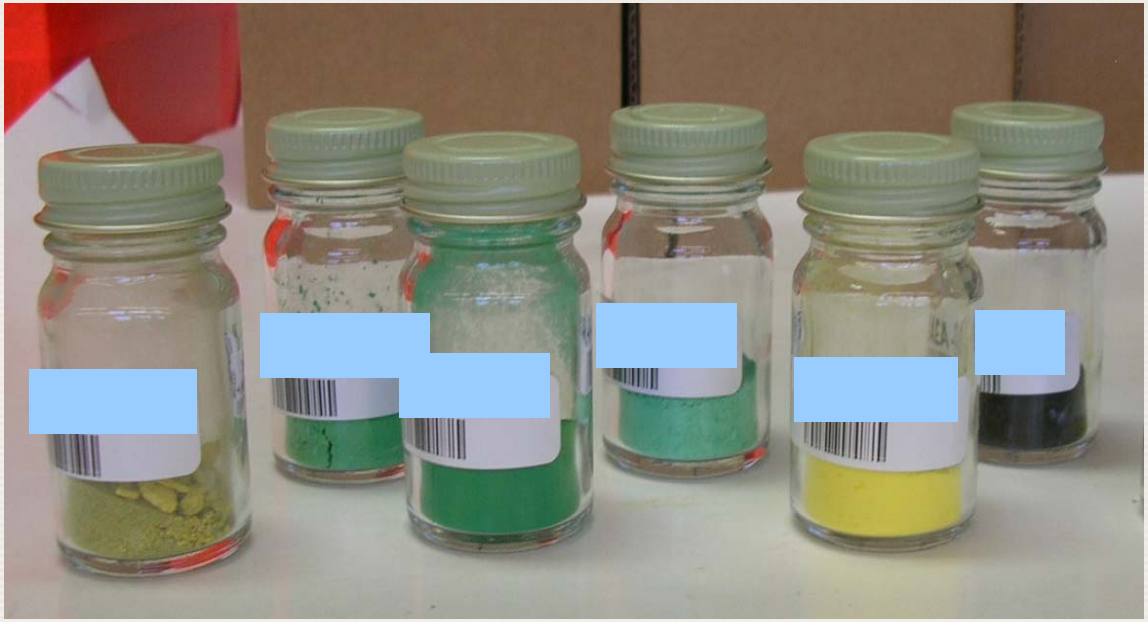
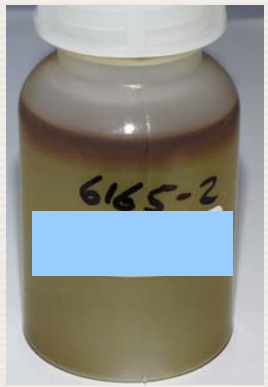
Uranium Laboratory

- Davis & Gray titration, LSD spike preparation.
- Received 449 regular inspection samples in 2004 (UNH, UO2 pellets, UO_3 powder, U metal, UF_6, UF_4, etc.).
- Received 208 “special-mission” samples (e.g., coal) in 2004.

Examples of Special Samples





Plutonium Laboratory

- IDMS & Coulometry for Pu
- Chemical separation of U & Pu for IDMS
- Spectrophotometric determination of Fe for Coulometric correction of Pu.
- Received 109 regular inspection and 5 “special-mission” samples in 2004.

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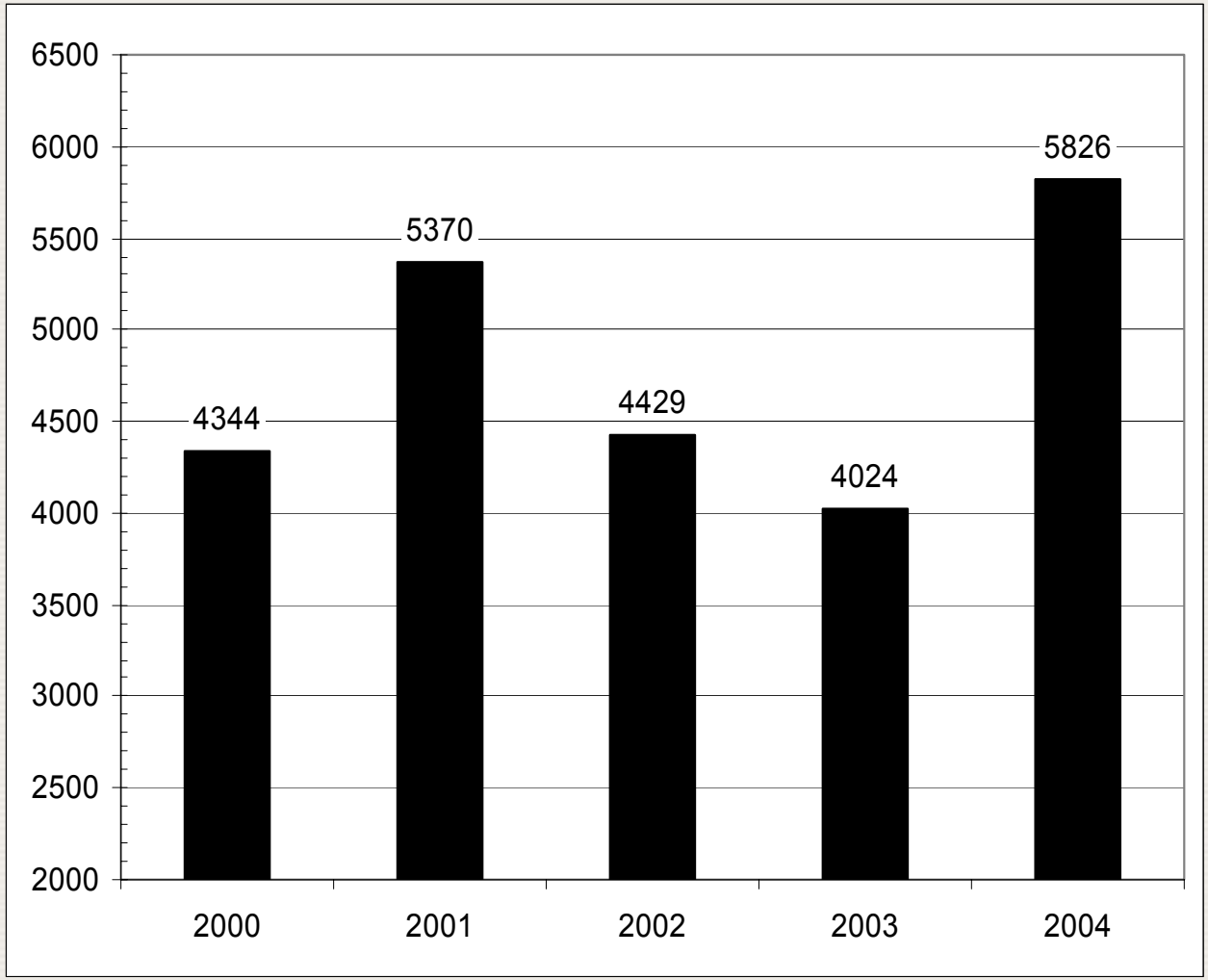
Input Laboratory

- 100-150 Spent Fuel and High-Active Waste samples annually.
- IDMS
- Production of HAW spikes for Japan.
- Special sample work (e.g., Chernobyl unit 4)

SAL DA TIMS Measurements



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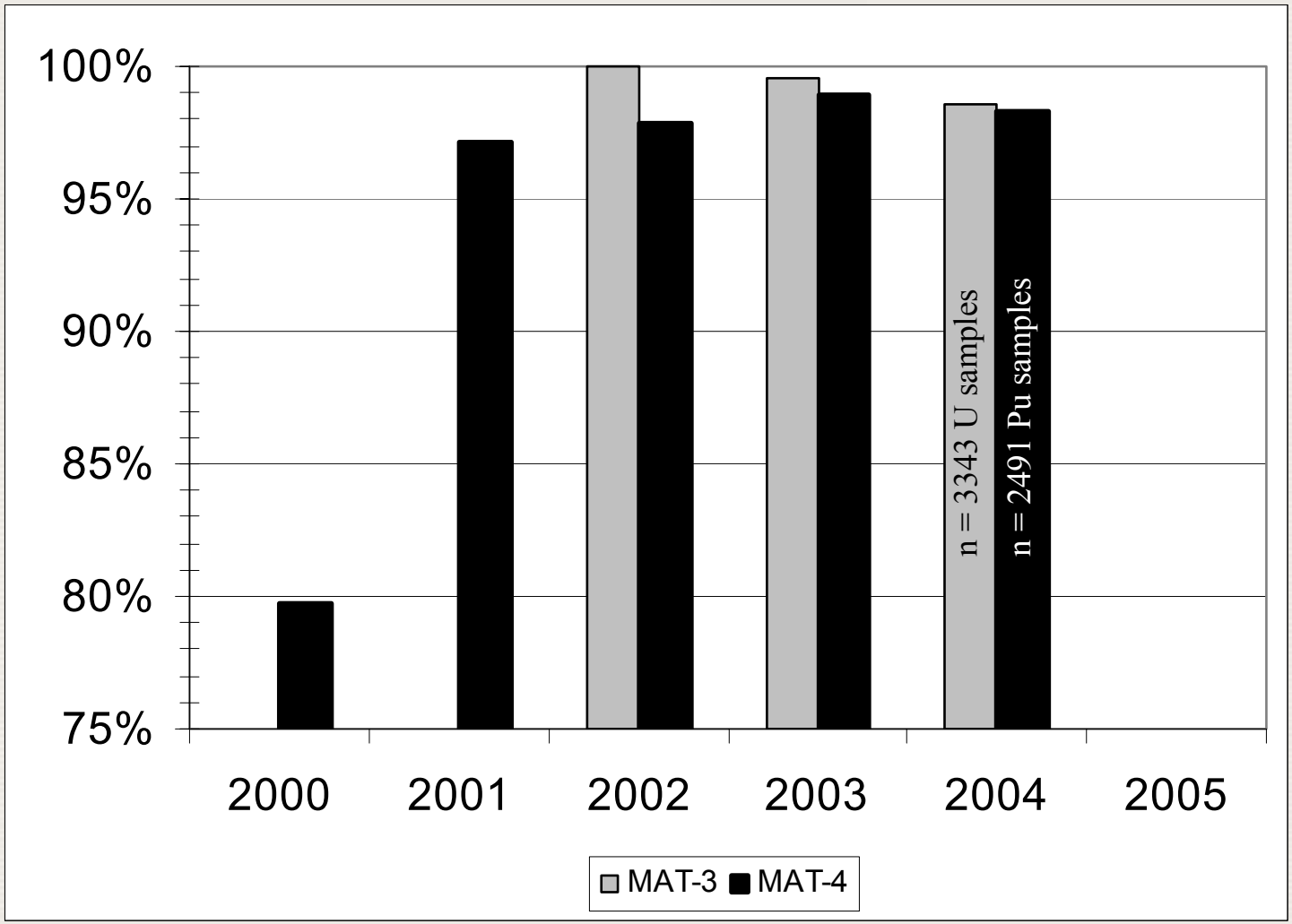
TIMS Success Rate



Nuclear TIMS Lab- BUSY!!

Sample loading

TIMS measurements

Measurement Performance- Assay

Method	Material	Elem.	uncertainty component (CV%)			
			ITV2000		SAL	
			u(r)	u(s)	u(r)	u(s)
GRAV	U-Oxides, UF_6	U	0.05	0.05		
	Pu-Oxide	Pu	0.05	0.05		
TITR	U Oxides, UNH, UF_6	U	0.10	0.10	0.04	0.03
	U-Alloys	U	0.20	0.20	0.04	0.03
	Pu Oxides, PNH	Pu	0.15	0.15	0.06	0.06
	MOX, U/Pu Nitr.Sol.	U	0.10	0.10	0.07	0.07
		Pu	0.20	0.20	0.07	0.07
IDMS Hot Cell	U & Pu Compounds	U	0.20	0.20	0.07	0.09
		Pu	0.20	0.20	0.05	0.08
IDMS Glove Box	U & Pu Compounds	U	0.15	0.10	0.07	0.14
		Pu	0.15	0.10	0.07	0.14
KED	U in Solution	U	0.20	0.15		
	Pu in Solution	Pu	0.20	0.15		
	FBR Mox	Pu	0.30	0.20		
HKED	Spent Fuel Solution, LWR MOX	U	0.20	0.15		
		Pu	0.60	0.30		
COMP	U Compounds	U	0.20	0.15		

Measurement Performance- ^{235}U Abundance (% relative)

Method	Material	uncertainty component (CV%)			
		ITV2000		SAL	
		u(r)	u(s)	u(r)	u(s)
TIMS	DU (<0.3 wt.% ^{235}U)	0.50	0.50	0.18	
	U (0.3% < ^{235}U < 1%)	0.20	0.20	0.09	0.10
	LEU (1% < ^{235}U < 20%)	0.10	0.10	0.06	0.04
	HEU (> 20 wt.% ^{235}U)	0.05	0.05	0.03	0.04

Measurement Performance- Pu Isotopic Analysis (% relative)

Method	Material	Isotope Ratio	Typical Value	uncertainty component (CV%)			
				ITV2000		SAL	
				u(r)	u(s)	u(r)	u(s)
TIMS $^{238}Pu/^{239}Pu$ by alpha spec	High Burnup Pu	$^{238}Pu/^{239}Pu$	0.0170	1.50	1.00	0.21	0.35
		$^{240}Pu/^{239}Pu$	0.4300	0.10	0.05	0.02	0.06
		$^{241}Pu/^{239}Pu$	0.1300	0.20	0.20	0.03	
		$^{242}Pu/^{239}Pu$	0.0800	0.20	0.30	0.04	0.18
	Low Burnup Pu	$^{238}Pu/^{239}Pu$	0.0002	10.00	10.00		
		$^{240}Pu/^{239}Pu$	0.0600	0.15	0.10		
		$^{241}Pu/^{239}Pu$	0.0020	1.00	1.00		
		$^{242}Pu/^{239}Pu$	0.0005	2.00	2.00		
HR Gamma Spec. Measurement time 3 x 1000 sec.; 0.5 g.	High Burnup Pu	$^{238}Pu/^{239}Pu$	0.0170	1.00	1.00	1.00	0.35
		$^{240}Pu/^{239}Pu$	0.4300	0.70	0.70	1.00	1.50
		$^{241}Pu/^{239}Pu$	0.1300	0.70	0.70	0.70	0.53
	Low Burnup Pu	$^{238}Pu/^{239}Pu$	0.0002	5.00	5.00		
		$^{240}Pu/^{239}Pu$	0.0600	1.50	1.50		
		$^{241}Pu/^{239}Pu$	0.0020	1.00	1.00		

Measurement Repeatability

Measurand Description			Comparison with previous evaluations	
		2003	2002	1999-2001
Method	**Detail**	**CV**	**CV**	**CV**
TIMS Plutonium	240:239	0.010	0.011	0.017
	241:239	0.030	0.033	0.023
	242:239	0.033	0.031	0.028
TIMS Uranium 235:238 U By range:	<0.004	0.255	0.212	0.178
	0.004-0.01	0.125	0.113	
	0.01-0.02	0.043	0.049	
	0.02-0.03	0.053	0.071	0.077
	0.03-0.04	0.042	0.057	0.060
	0.04-0.06	0.039	0.034	0.042
	>0.06	0.073	0.028	0.027
IDMS Products	Pu	0.098	0.079	0.100
	U	0.145	0.079	0.100
	U:Pu	0.097	0.057	
IDMS LSD	U & Pu	0.107	0.063	0.068
	U:Pu	0.128	0.044	
D&G U Titration (Manual)	Samples	0.038	0.033	0.045
	Daily Calibration	N.D.	0.005	0.009
D&G U Titration (Automated)	Samples	0.043	0.042	0.040
	Daily Calibration	0.009	N.D.	0.014

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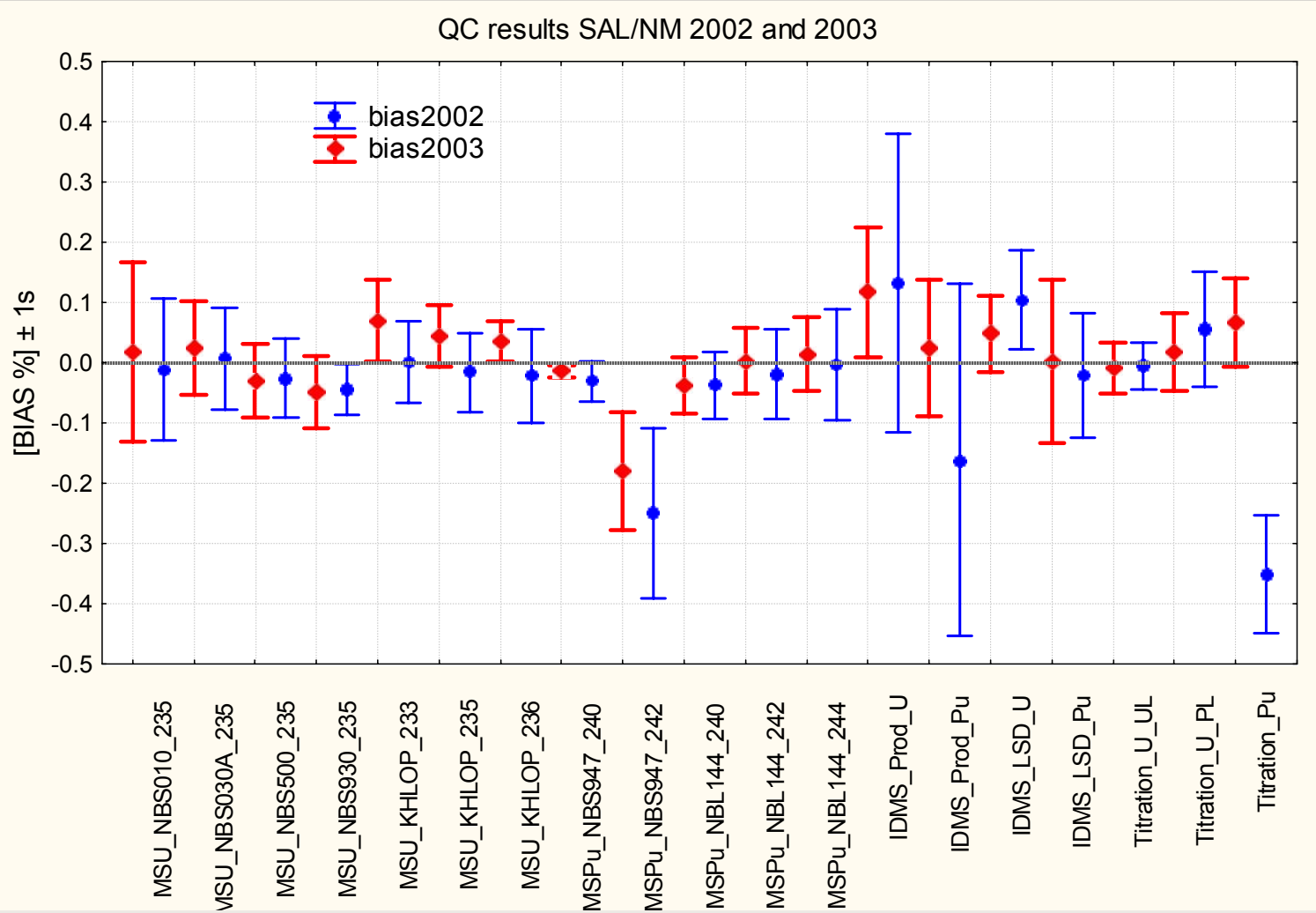
Internal Quality Control



External Quality Control

- SAL currently participates in 2 formal interlaboratory proficiency test programs
- REIMEP (IRMM-EU)
  - Solution based, U & Pu isotopic abundance
  - Annually frequency
- EQRAIN (CEATAC-France)
  - 4 UNH samples/18 months (250g/L)
  - 3 PuNH samples/24 months (5g/L)

2005: Renovations in Nuclear Areas


Hot Environmental Sample Lab

High-resolution ICP-MS Lab

New gloves boxes for Plutonium Lab


First Aid Room

IAEA

SAL 1976-2005

Confidence in Measurements

Steven A. Goldberg

Measurement Evaluation Program Meeting
July 9, 2005
Phoenix, AZ

Defining "Confidence"

- **"The value of chemical measurements depends upon the level of confidence that can be placed in the results."**

  (The Guide to Quality in Analytical Chemistry (CITAC))

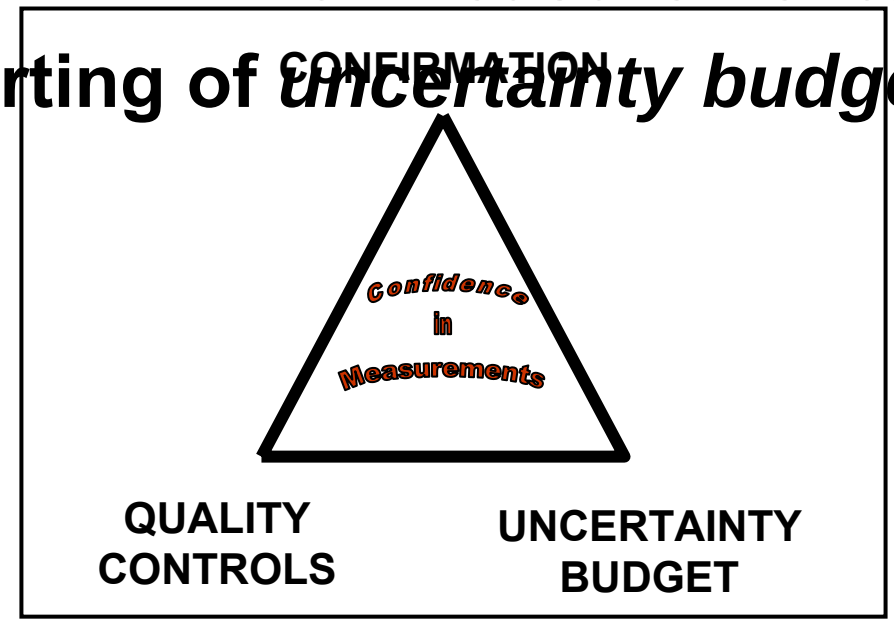
- **Confidence : "*the quality of being certain*"**

  (Mirriam-Webster's Collegiate Dictionary, 10 ed.)

- **Although statisticians define many quantitative measures that incorporate the word "confidence", e.g., "95% confidence interval", there is no standard *quantitative* definition of "confidence" in technical literature.**

Creating Confidence in Measurements

- ***Confidence is derived by integrating several practices:***
  - **Use of *QC practices* and materials, including *traceability* through the use of CRMs**
  - ***Confirmation* of measurements**
  - **Reporting of *uncertainty budgets***



Components of "Confidence"

- **Quality Controls**
  - **Use of CRMs for calibration and traceability**
  - **Follow "best laboratory practices"**
    - **blanks, repeat sampling/measurement, etc.**
  - **Accreditation**
  - **Adopting QA principles (e.g., ISO 17025) may not guarantee the quality of measurement data, but it will increase the likelihood of it being soundly based and fit for its intended purpose.**

Uncertainty is Linked to Traceability & Measurements Must be Traceable - Part I

- **To compare results from different laboratories with confidence, it is necessary to provide traceability by *comparison* to a known reference value.**
- **Traceability is defined as:**

  *The property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken **chain of comparisons** all having stated uncertainties.*

Traceability & Uncertainty – Part II

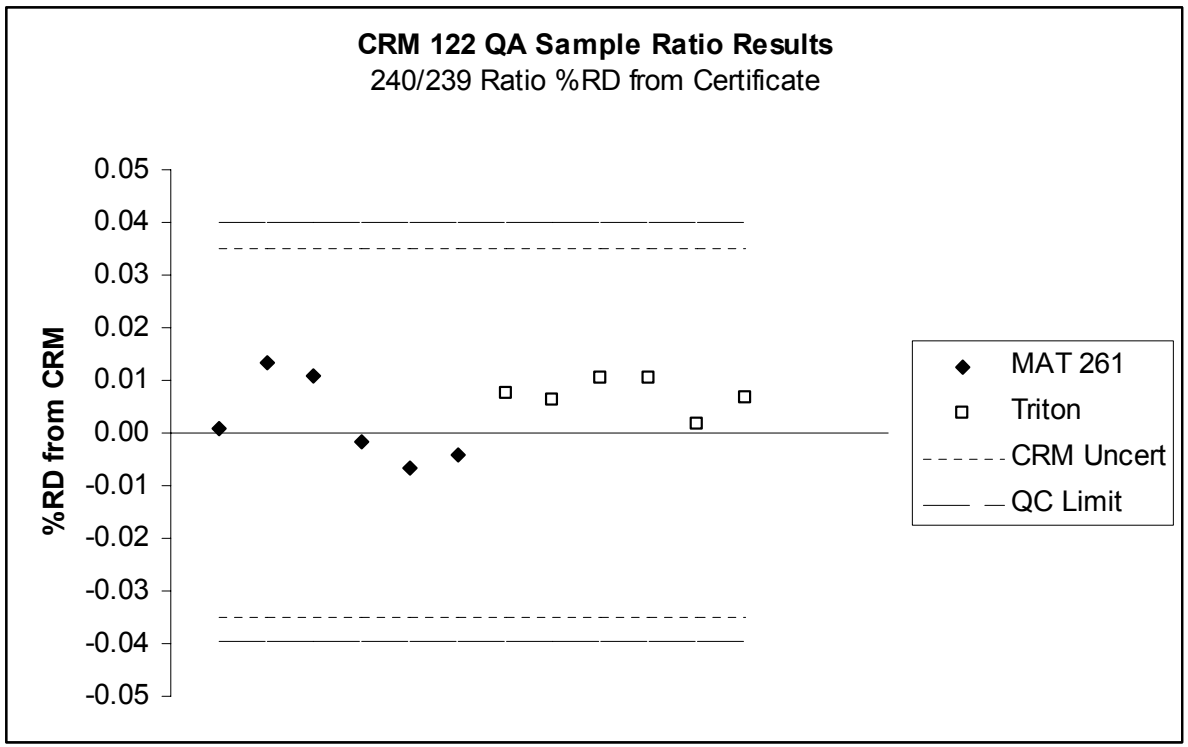
- **Uncertainties in each laboratory's measurement chain influence the agreement between labs and creates the need to use a properly certified reference material or *comparator*.**
- ***Traceability* provides a way to relate all measurements to a consistent measurement scale,**
- ***Uncertainty* characterizes the 'strength' of the links in the chain of comparisons and the agreement to be expected between laboratories making similar measurements.**

Traceability/QA

QA Results CRM 122 $^{240}Pu/^{239}Pu$

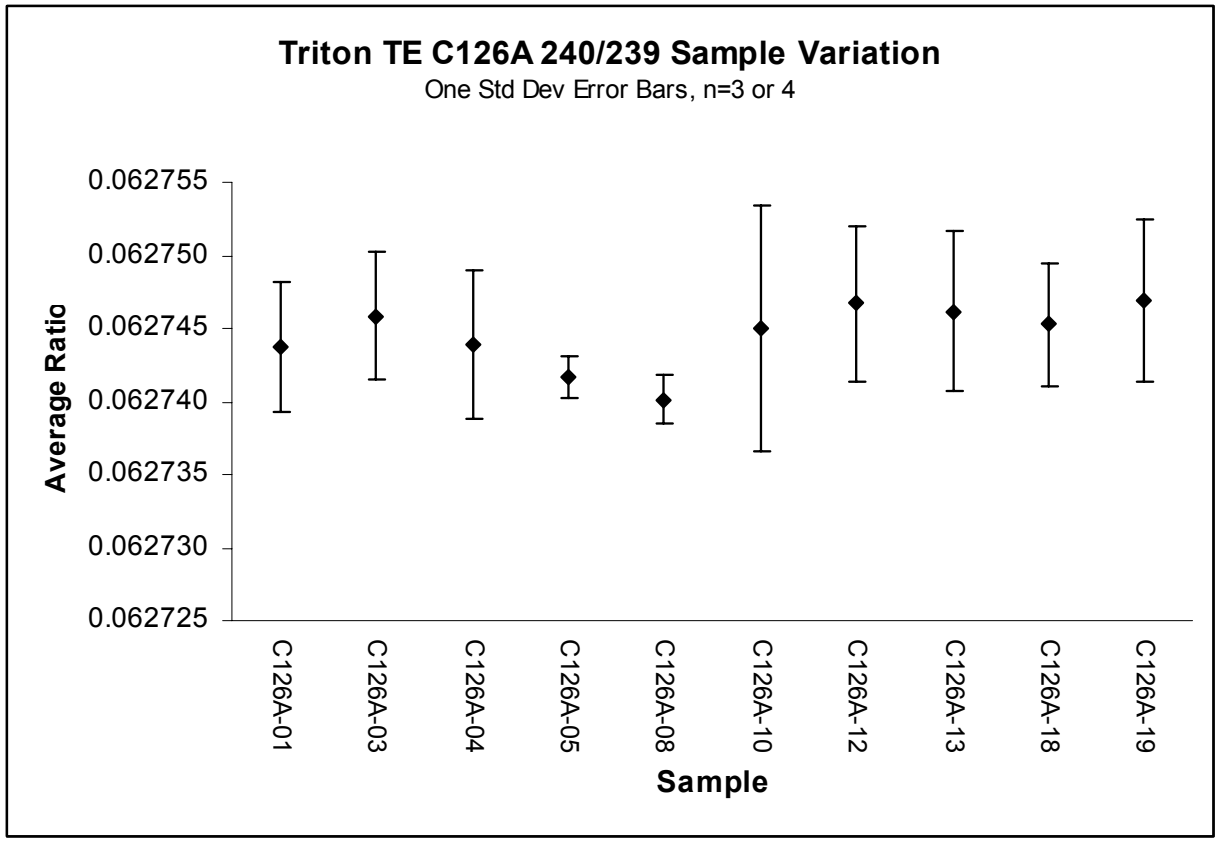
MAT 261: +0.0016%RD; 0.0082% RSD

Triton: +0.0067%RD; 0.0032% RSD



Sample Homogeneity

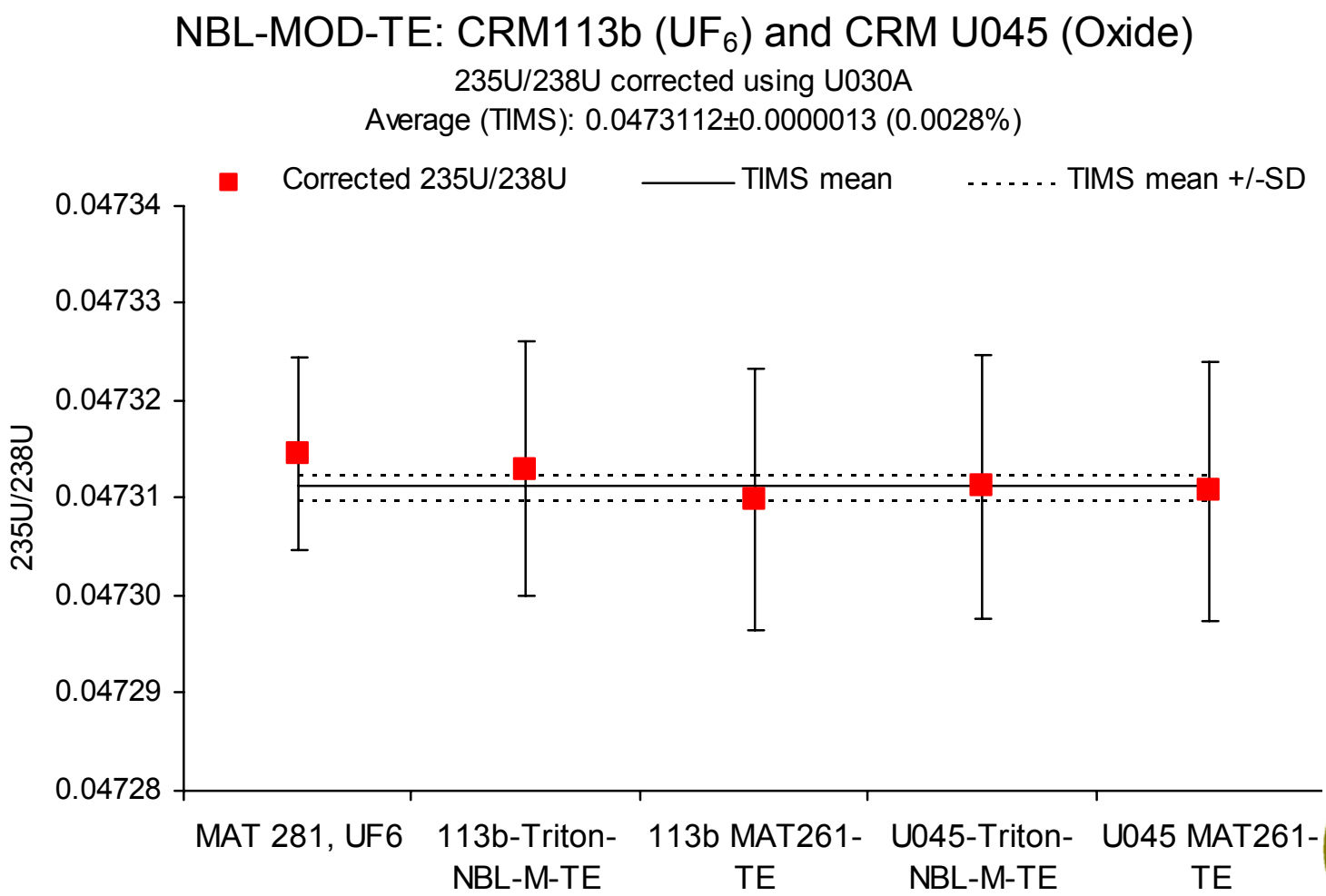
C126-A Sample $^{240}Pu/^{239}Pu$ Homogeneity



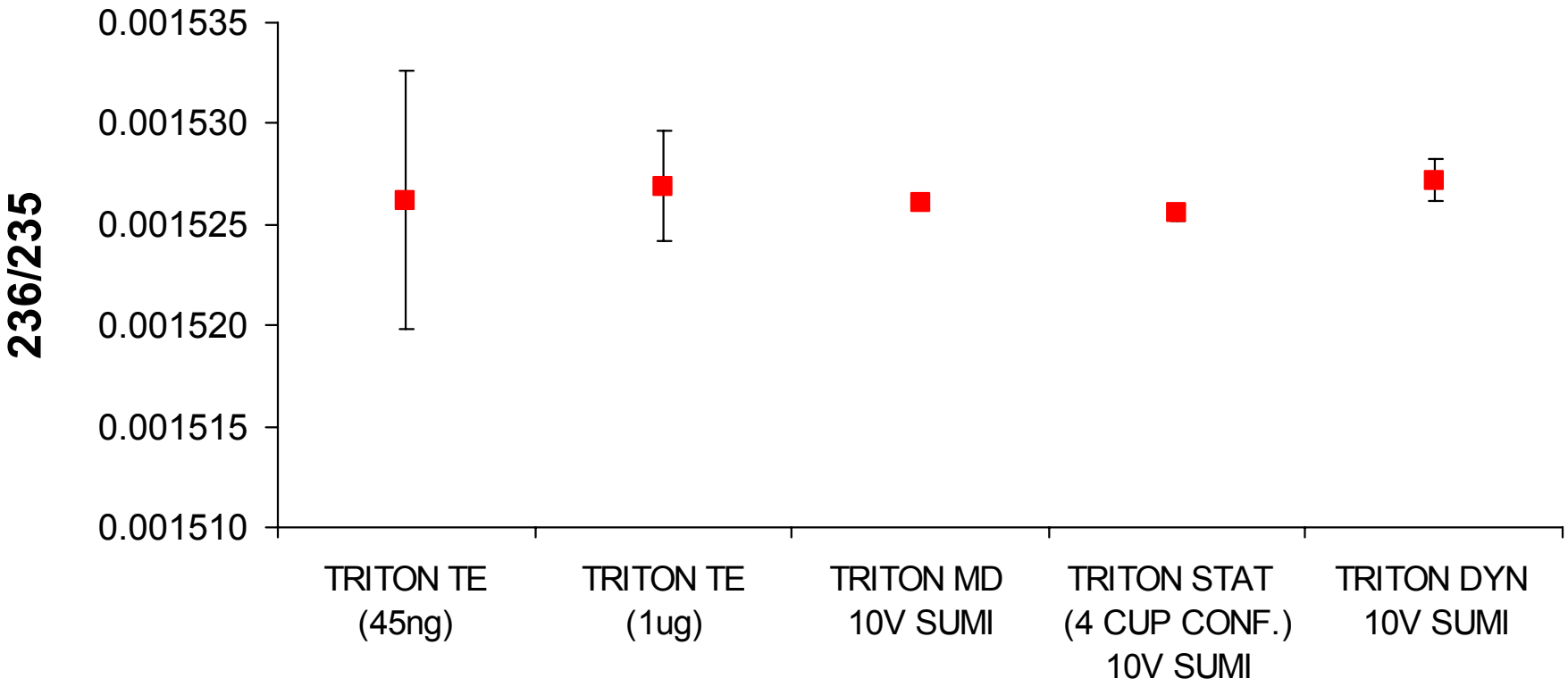
Components of "Confidence"

- Confirmation
  - A means to validate a measurement method – to ensure sound performance characteristics under the conditions to which it is to be applied.
  - Confirmation is sometimes confused with repeatability. Whereas repeatability requires the measurement to be performed several times by one technique, confirmation requires the measurement to be performed by more than one technique.
  - Confirmation increases confidence in the technique under examination and is especially useful where the additional techniques operate on significantly different principles

NBL Modified Total Evaporation

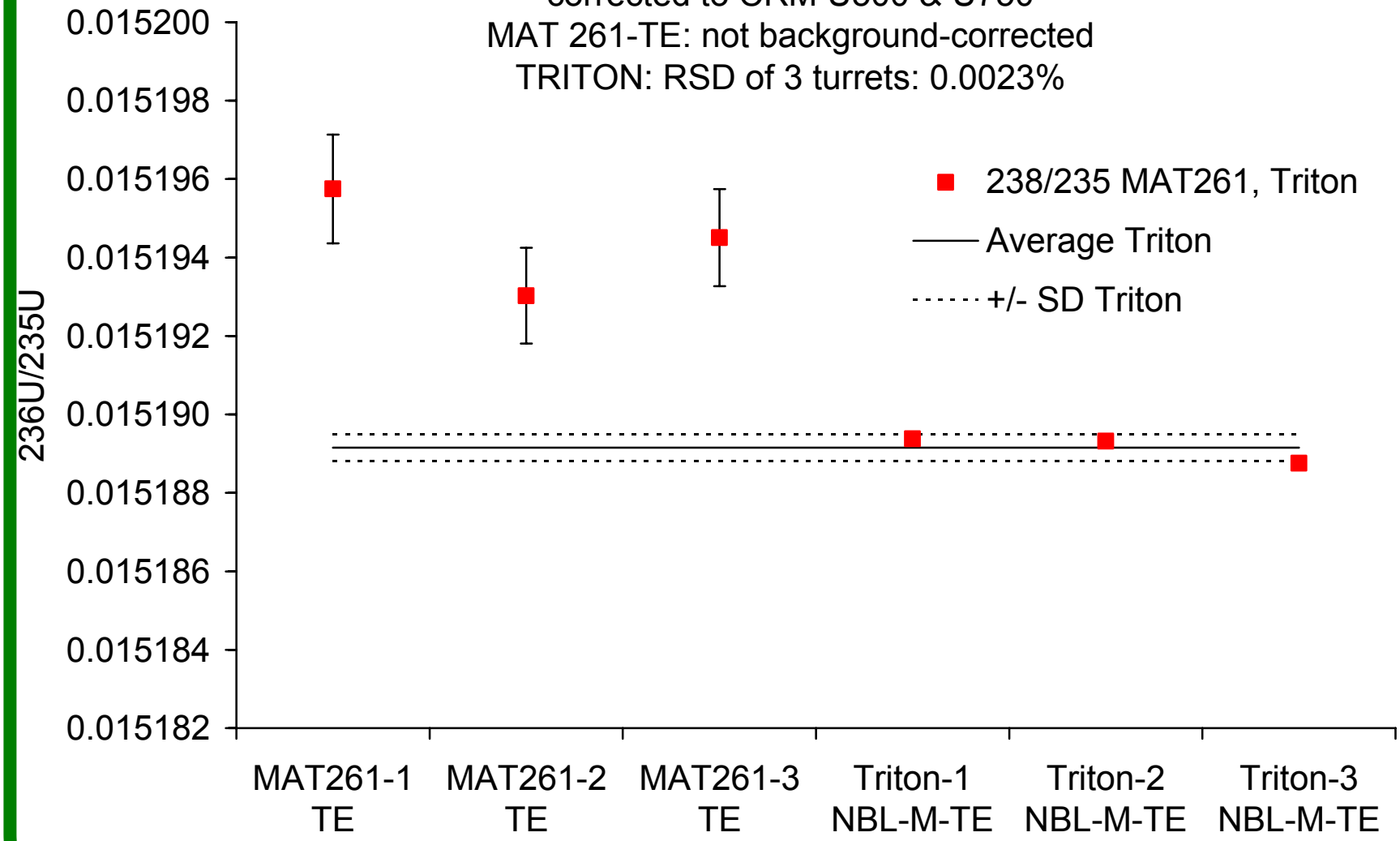


CRM U500 $^{236}U/^{235}U$: Comparison of Techniques



NBL-MOD-TE: CRM U630

corrected to CRM U500 & U750
MAT 261-TE: not background-corrected
TRITON: RSD of 3 turrets: 0.0023%



Components of "Confidence"

- **Uncertainty Budget**
  - **Measurement uncertainty characterizes the range of values within which the true value is asserted to lie, with a specified level of confidence. Every measurement has an uncertainty associated with it, resulting from errors arising in the various stages of sampling and analysis and from imperfect knowledge of factors affecting the result.**
  - **For measurements to be of practical value it is necessary to have some knowledge of their reliability or uncertainty. A statement of the uncertainty associated with a result conveys to the customer the 'quality' of**

Golden Rule

A measurement result is complete only when accompanied by a statement of its uncertainty.

Reasons Why Uncertainties of Measurements are Needed

- **Integral part of any Quality Assurance System for measurement results.**
- **Required by accreditation regulations in all western countries (e.g., ISO 17025 - *General requirements for the competence of testing and calibration laboratories*).**
- **Supports confidence and acceptance of the measurement results.**
- **Provides judgement on the significance of differences in measurements.**

Guide to the Expression of Uncertainty in Measurement (GUM)

- **The GUM defines in detail how a complete result including the uncertainty should be stated.**
- **GUM defines a coherent method to propagate total uncertainties from limited knowledge about measurement components.**
- **GUM defines rules to calculate an analytical result and evaluate its uncertainty in a transparent way.**
- **The law of variance propagation is used.**
- **The calculus is clearly defined and can always be used if 1.) a mathematical model exists for the measurement process and 2.) if the model can be linearized for the input quantities (linear combination of uncertainty components).**

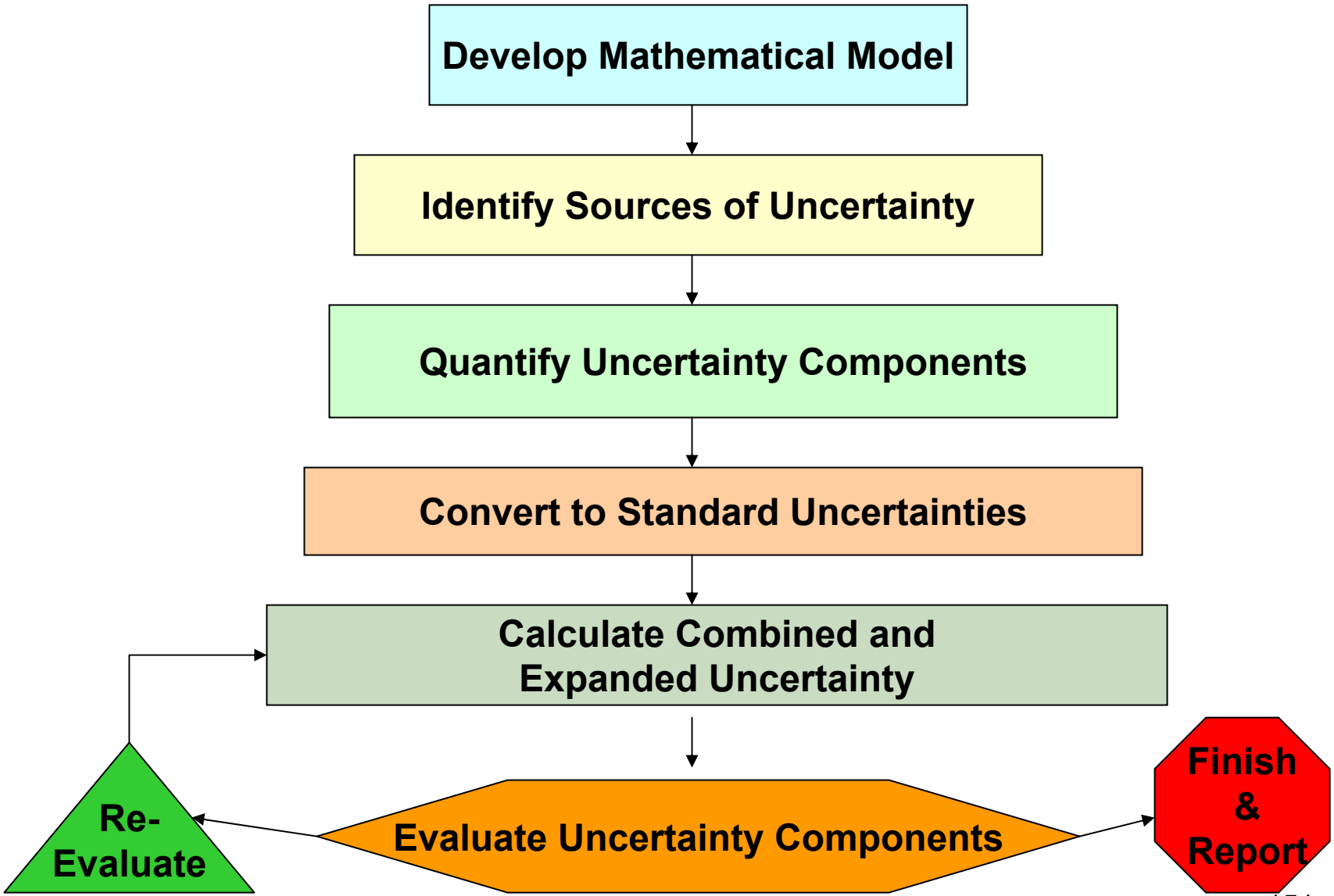
GUM

- Emphasis on evaluating one or more measurements by compiling and adding (propagating) individual uncertainty components.
- This is a change in emphasis, away from evaluating measurement errors by repeated measurements, and towards the concept of evaluating the uncertainty of a measurement through propagation of uncertainty components.
- Thus the traditional concepts of random and systematic errors are not important parts of GUM.

Wide Acceptance of the GUM

- **ANSI - American National Standards Institute**; now an American National Standard (ANSI/NCSL Z540-2-1997, *American National Standard for Expressing Uncertainty--U.S. Guide to the Expression of Uncertainty in Measurement)*.
- **NCSL - The National Conference of Standards Laboratories**
- **NORAMET - North American Collaboration in Measurement Standards**
- **NAVLAP - National Voluntary Laboratory Accreditation Program**
- **A2LA - American Association for Laboratory Accreditation**
- **EUROMET - European Collaboration in Measurement Standards**
- **EUROLAB** - a focus for analytic chemistry in Europe
- **EA - European Cooperation for Accreditation**
- **EU - European Union**; adopted by CEN and published as EN 13005.
- Adopted by **NIST** and national metrology institutes throughout the world: National Research Council (**NRC**) in Canada, National Physical Laboratory (**NPL**) in the United Kingdom, and Physikalisch-Technische Bundesanstalt (**PTB**) in Germany.

Basic Steps to Estimate Uncertainty

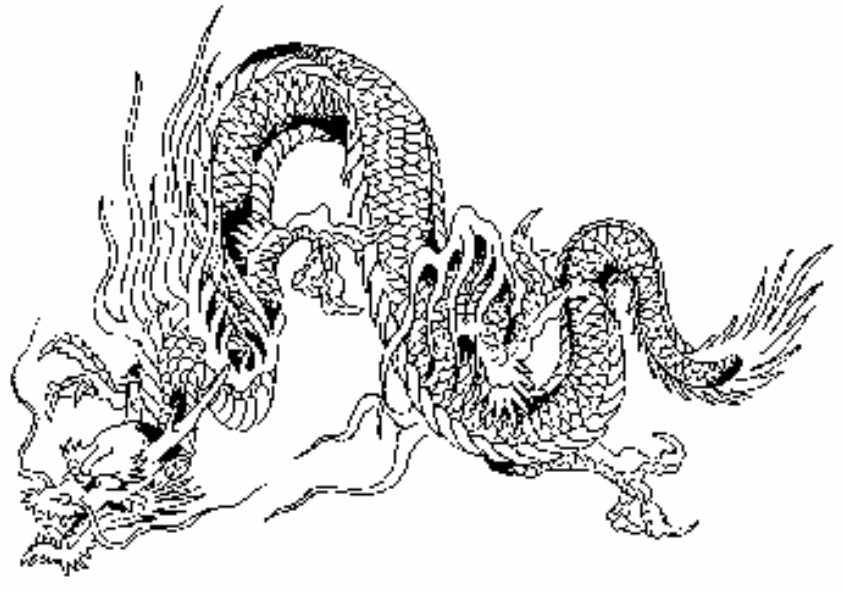


Type A and Type B Evaluations: Overview

- **The uncertainty associated with a measurement generally consists of several components which are grouped into two categories according to the *method used to estimate their numerical values*:**
  - *A. those which are evaluated by statistical methods*
  - *B. those which are evaluated by other means*

Uncertainty Calculations

- **"Here be dragons"**
  ....or more correctly the equivalent Latin phrase *hic sunt dracones* is the chilling warning written by early map-makers at the edges of their known world. Venturing into these regions could have been a terrifying prospect for early explorers as tales of monsters and evil magic fired their imaginations.
- For many analysts, it seems that the estimation of uncertainty is like venturing to the edge of the known world.
- Uncertainty estimation is not that complex and it has its rewards!



Example: Preparation of a U Calibration Solution

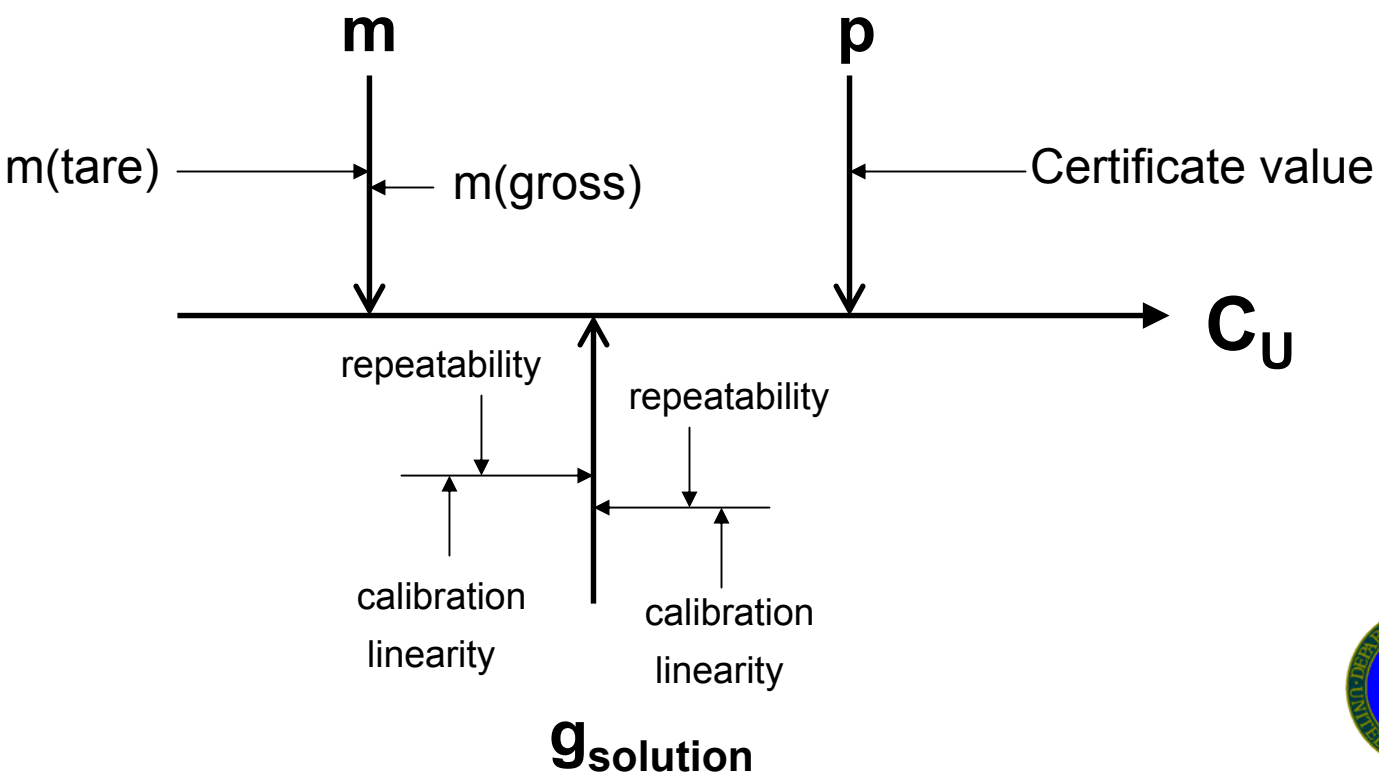
Procedure: Weigh CRM 112-A metal → Dissolve metal → Dilute metal

$$C_U = \frac{m \cdot p}{g_{solution}}$$

- **Where C_U = U concentration of the calibration solution [mg g^{-1}]**
- ***m* = mass of the high purity metal [g]**
- ***P* = purity of the metal given as mass fraction**
- **$g_{solution}$ = grams of solution (HNO_3) used in the digestion and final dilution**

Example: Preparation of a U Calibration Solution

$$C_U = \frac{m \cdot p}{g_{solution}}$$



Example: Preparation of a U Calibration Solution

	Value	u_x Std. Unc.	Type
m	0.1008 g	0.002	A
p	0.9945	0.0012	B
$\mathbf{g_{soln}}$	998.62	0.05	A

Example: Preparation of a U Calibration Solution

- **Measurand value:**

$$C_U = \frac{0.1008 \times 0.9945}{998.62} = 100.38 \mu\text{g U/g of solution}$$

Combined Standard Uncertainty

- **After estimating individual uncertainties or grouping multiple components of uncertainty and expressing them as standard uncertainties, the next step is to calculate the combined standard uncertainty u_c:**

$$u_c(y) = \sqrt{\sum_{i=1}^{N} c_i^2 \cdot u_i^2(x_i)} = \sqrt{\sum_{i=1}^{N} u_i^2(y)}$$

where *y* is a function of several independent parameters $x_1, x_2 \ldots$, c_i is a sensitivity coefficient evaluated as $c_i = \partial y / \partial x_i$, the partial differential of *y* with respect to x_i and $u_i(y)$ denotes the uncertainty component in *y* arising from the uncertainty associated with x_i.

Combined Standard Uncertainty

- **Each variable's contribution u(y) is the square of the associated uncertainty multiplied by the square of the relevant sensitivity coefficient.**
- **The contributions have to be expressed as standard uncertainties, and combined according to the appropriate rules, to give a combined standard uncertainty.**
- **Sensitivity coefficients describe how the value of *y* varies with changes in the parameters x_1, x_2 *etc*.**

Rules for Combining Uncertainties

- **Rule 1: For models involving only a sum or difference of quantities, *e.g.*, $y = (p+q+r+...)$, the combined standard uncertainty $u_c(y)$ is given by:**

$$u_c(y(p,q..)) = \sqrt{u(p)^2 + u(q)^2 + \ldots}$$

- **Rule 2: For models involving only a product or quotient, *e.g.*, $y = (p \times q \times r \times ...)$ or $y = p / (q \times r \times ...)$, the combined standard uncertainty $u_c(y)$ is given by:**

$$u_c(y) = y\sqrt{\left(\frac{u(p)}{p}\right)^2 + \left(\frac{u(q)}{q}\right)^2 + \ldots}$$

  - **where $(u(p)/p)$ *etc*. are the uncertainties in the parameters, expressed as relative standard deviations.**
  - ***NOTE: Subtraction is treated in the same manner as addition, and division in the same way as multiplication.***

Example: Preparation of a U Calibration Solution

	Value	0.9945	0.1008	998.62
	Uncertainty	0.0012	0.002	0.05
p	0.9945	0.9957	0.9945	0.9945
m	0.1008	0.1008	0.1028	0.1008
g_{soln}	998.62	998.62	998.62	998.67
C_U	1.00384E-04	1.00505E-04	1.02376E-04	1.00379E-04
u(y,xi)		1.21127E-07	1.99175E-06	-5.02589E-09
$u(y)^2$,$u(y,x_i)^2$	3.9818E-12	1.4672E-14	3.9671E-12	2.5260E-17
$u(C_U)$	1.99543E-06			
u(y,xi) relative		0.057	0.940	0.002

Reporting of Results

A reported result should include:

- **A clear identification of the measurement.**
- **A clear definition of the measurand (including the unit).**
- **The result and the expanded uncertainty $Y = y \pm U$ with the unit for y and U.**
- **The coverage factor k, which was used to calculate U and the assumed level of confidence.**
- **A reference to a detailed evaluation report that includes a full uncertainty budget.**

Reporting an Uncertainty Budget

- The uncertainty analysis for a measurement, sometimes called the uncertainty budget, should include a list of all sources of uncertainty together with associated standard uncertainties, degrees of freedom, and the methods of evaluating them.
- For repeated measurements the number of observations, n, has to be stated.
- For clarity, present the data in a table.
- In the table, reference all components by a physical symbol X_i or short identifier. Provide for each the estimate x_i, the associated standard uncertainty $u(x_i)$, the sensitivity coefficient c_i and the different uncertainty contributions $u_i(y)$.
- Err on the side of providing too much information rather than too little

Uncertainty Budget

Quantity	Estimate	Type	Standard Uncertainty	Sensitivty Coefficient	Contribution to Standard Uncertainty
X_1	x_1	A	$u(x_1)$	c_1	$u_1(y)$
X_2	x_2	B	$u(x_2)$	c_2	$u_2(y)$
X_3	x_3	A	$u(x_3)$	c_3	$u_3(y)$
⋮	⋮		⋮	⋮	⋮
X_N	x_N	A	$u(x_N)$	c_N	$u_N(y)$
Y	y				u(y)

- Also consider adding a column for Relative Standard Uncertainty

References to Information Presented in this Talk

- ISO, *Guide to the Expression of Uncertainty in Measurement*, International Organization for Standardization, 1995.
- Taylor, B.N., and Kuyatt, C.E., *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note 1297, 1993.
- European Co-Operation for Accreditation, *Expression of the Uncertainty of Measurement in Calibration*, Publication EA-4/02.
- *Guide to the Expression of Uncertainty in Measurement*, *Supplement 1, Numerical Methods for the Propagation of Distributions*, 2004, draft.
- Eurachem/CITAC Guide: *Quantifying Uncertainty in Analytical Measurement,* 2000.
- ISO, International Vocabulary of Basic and General Terms in Metrology, 1993.
- *ISO/IEC 17025:1999. General Requirements for the Competence of Calibration and Testing Laboratories. ISO, Geneva, 1999.*
- Expression of the Uncertainty of Measurement in Calibration, European Cooperation for Accreditation EA 4/02, 1999.

Software

- *Uncertainty Analyzer:* Integrated Sciences Group; http://www.isgmax.com
- *Gum Workbench*: Metrodata GmbH in Germany; distributed by Quametec; http://www.metrodata.de/
- Uncertainty Calculator
- UnCalc
- Predictor
- Expression Buddy
- Evaluator
- Variation

FY 2004 NBL CALEX Program Phoenix, Arizona

July 9, 2005

B. (Chino) Srinivasan

CALEX Program History

Prior to 1979

Program operated by Rocky Flats National Laboratory

Part of the Plutonium metal Exchange Program

1979- mid 1990s

- Operated by Mound Laboratories
- CALEX 1 standard introduced in 1979

1995 – present

- Operated by NBL
- CALEX II made in 1995

CALEX I and II Standards: Pu mass

	Calex I 05/29/1979	Calex II 07/24/1995
No. of units	6	10
PuO_2 mass	454.60 g	2000 g
Pu concentration	87.82 wt %	87.41 wt %
Pu mass	399.23 g	1748.20 g

CALEX I and II Standards (continued)

Parameter	Calex I 05/29/1979	Calex II 07/24/1995
^{238}Pu	0.0102 wt %	0.0801 wt %
^{239}Pu	93.7336 wt %	86.5324 wt %
^{240}Pu	5.8560 wt %	12.1705 wt %
^{241}Pu	0.3712 wt %	1.0096 wt %
^{242}Pu	0.0290 wt %	0.2074 wt %
^{241}Am	0.0061 wt %	0.4791 wt %
Peff	2.3012 mW/g	3.5682 mW/g
Power	918.71 mW	6237.93 mW

Nuclides Half Lives and Specific Power

Parameter	Half-life (year)	Specific power (mW/g)
^{238}Pu	87.70	567.57
^{239}Pu	24119	1.9300
^{240}Pu	6564	7.0800
^{241}Pu	14.290	3.410
^{242}Pu	373000	0.1200
^{241}Am	433.0	114.2

FY 2004 Program

Participants

- Hanford (Calex 1)
- LLNL (Calex I and II)
- SRS (Calex I)

Experimental Measurements

Experimental measurements by participants

- Power by calorimetry
- Pu isotopes and ^{241}Am abundance by high resolution gamma spectrometry
- Calculate P_{eff} from gamma isotope abundance measurement and specific power
- Calculate Pu mass from measured power and calculated P_{eff}

Reference Material Values

Correct for radioactive decay to date of experiment

- Isotope abundance
- Mass of Pu
- P_{eff}
- Power

Statistical Evaluation of Experimental Results

Evaluated quantities

- Mass
- Power
- Peff
- Isotope abundance

Evaluation basis

- Experimental value/Reference value
- % RD

Results Presentation

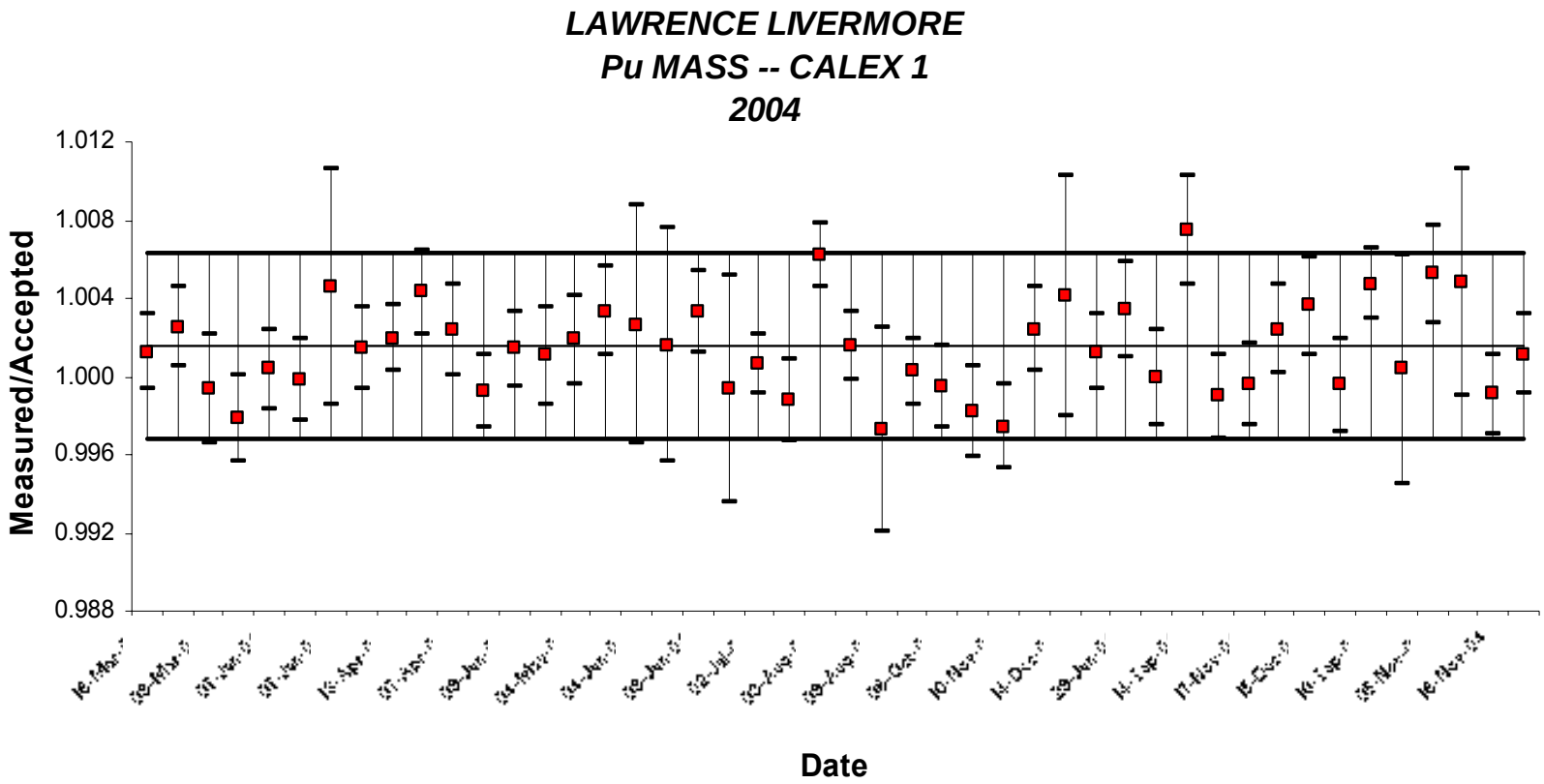
Tables

- Quarterly summary
- Annual summary

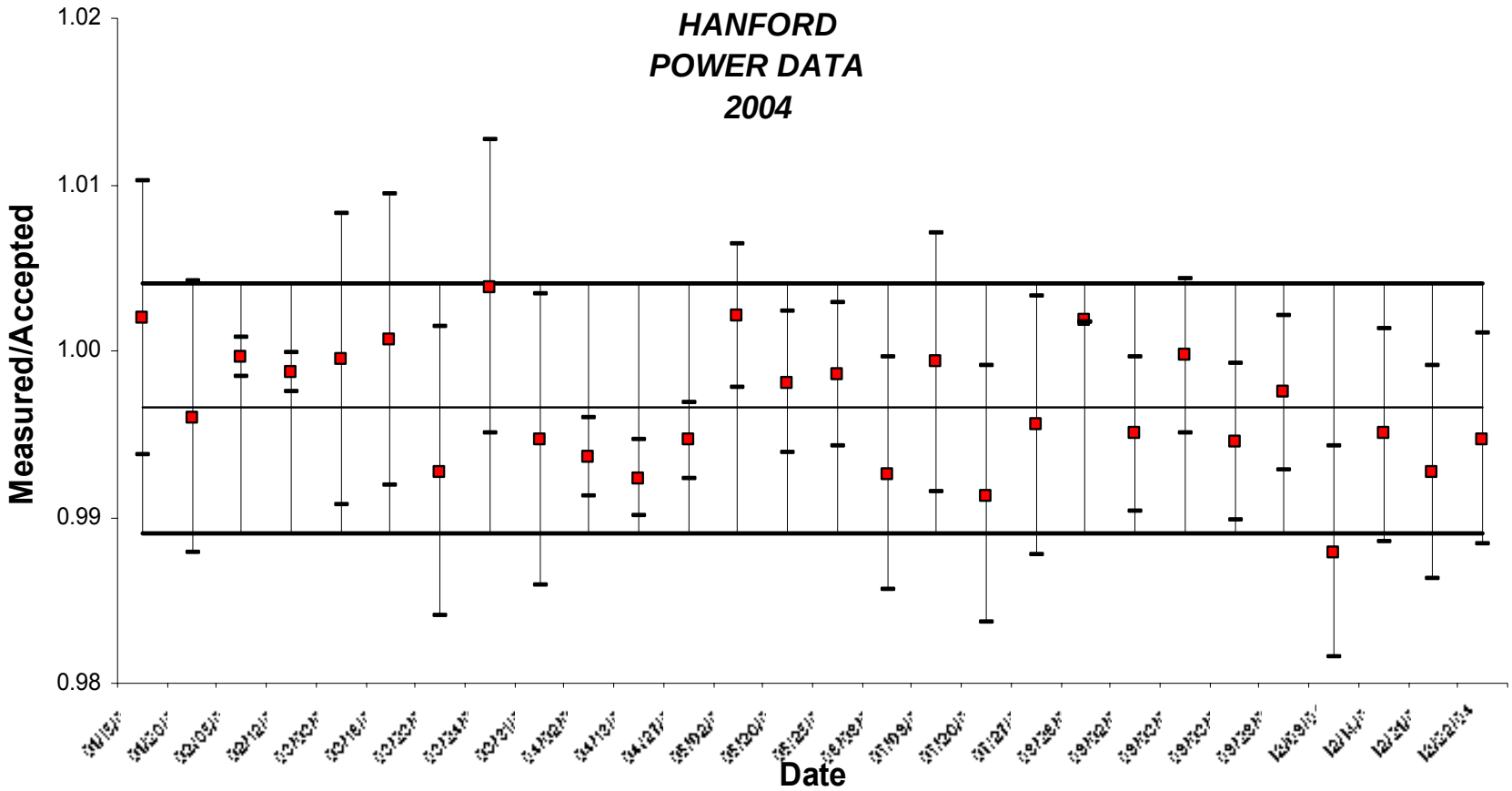
Graphs

- Quarterly summary
- Annual summary

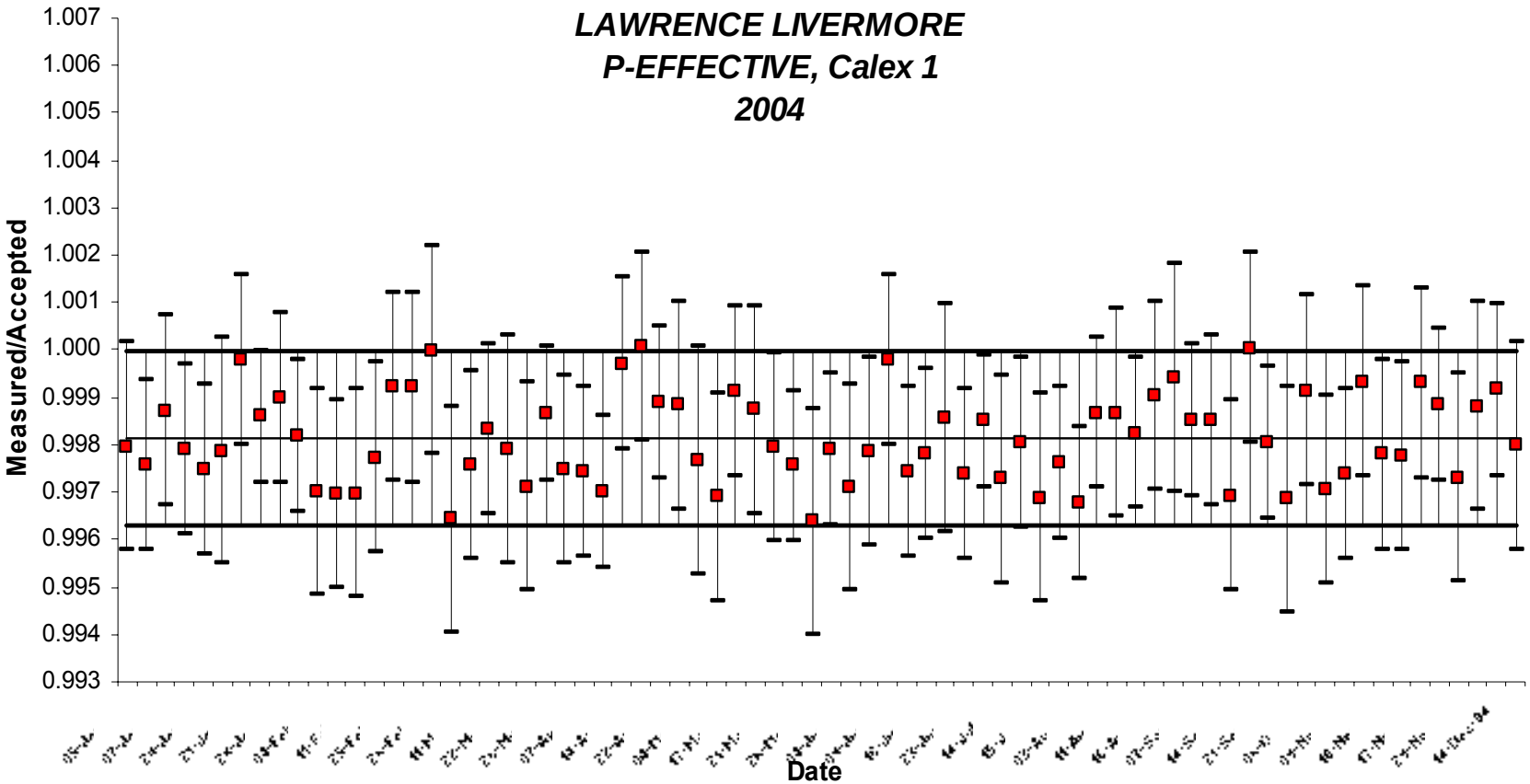
Example of Pu Mass Evaluation



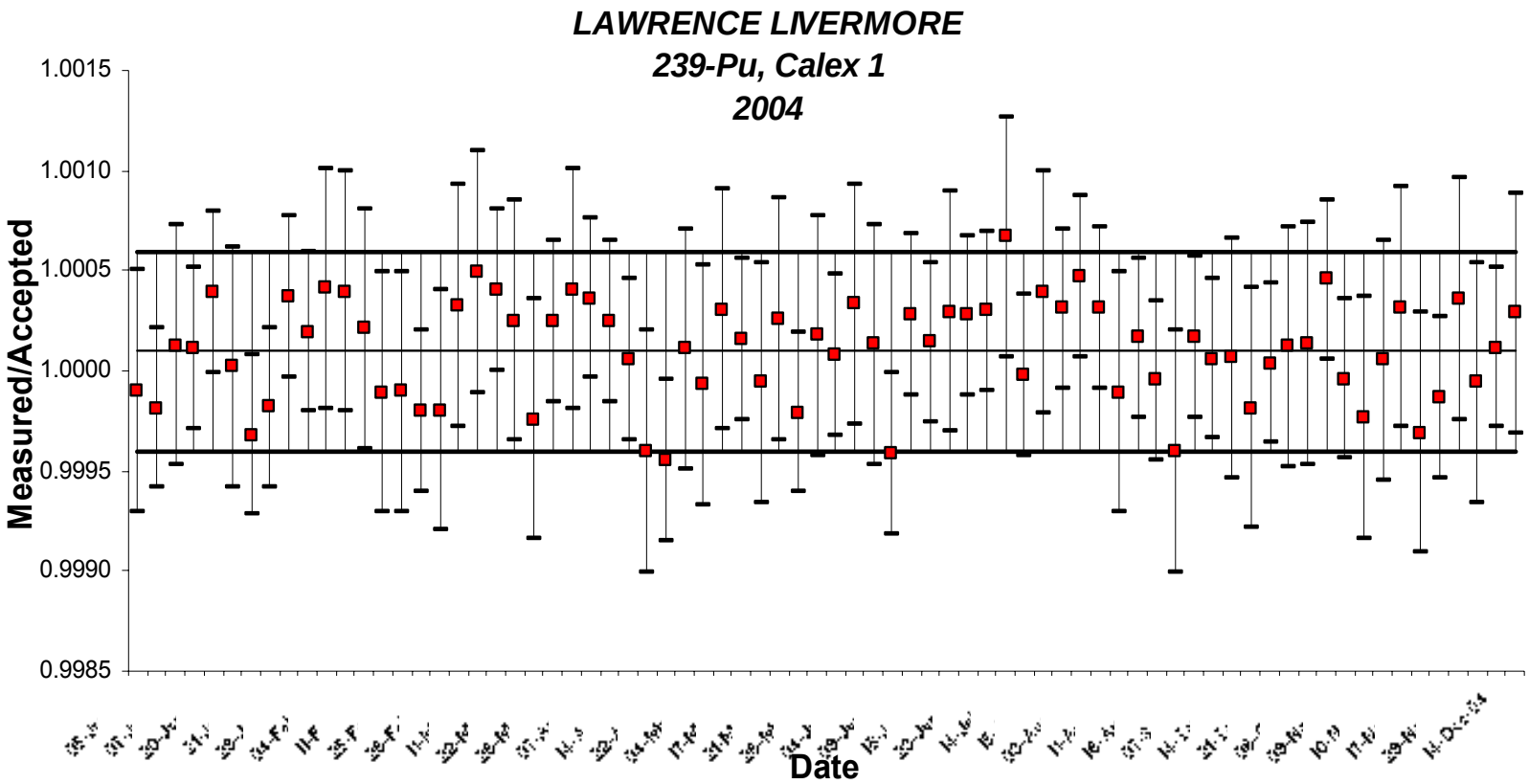
Example of Calorimetric Power evaluation



Example of P_{eff} Evaluation



Example of ^{239}Pu abundance evaluation



CALEX I: Conclusions

- **Pu mass determination uncertainties within 0.3%**
- **Power measurement uncertainties are within 0.3%**
- **P_{eff} uncertainties are within 0.2%**
- **Isotope measurement uncertainties depend upon abundance**

FY 2004 Program: Calex II measurements

LLNL measured Calex II for isotopic abundance only

CALEX II: Certification Work

	LANL	NBL
Sampling	Five 5-g samples	Five 5-g samples
Moisture	Heating to 950°C	Heating to 950°C
Pu assay	Controlled potential coulometry	Controlled potential coulometry
Pu isotopes	TIMS	TIMS
^{241}Am	Gamma spectrometry	Gamma spectrometry

CALEX II: Moisture and Pu Assay

	NBL	LANL	Remarks
Moisture	0.025	0.026	Agrees
Pu (wt %)	87.332	87.550	Does not agree; 0.25% deviation

CALEX II: Plutonium Isotopes

	NBL	LANL	Remarks
^{238}Pu (wt %)	0.078	0.083	6% deviation
^{239}Pu (wt %)	86.7528	86.7507	Agrees
^{240}Pu (wt %)	12.1466	12.1452	Agrees
^{241}Pu (wt %)	0.8173	0.8164	Agrees
^{242}Pu (wt %)	0.2054	0.2047	Agrees
^{241}Am (µg/g)	5853	5811	Agrees

CALEX II: Calculated P_{eff} from Analytical Data

Assay	Isotopics	P_{eff} (mW/g)
NBL	NBL	3.2074
LANL	NBL	3.2154
NBL	LANL	3.2280
LANL	LANL	3.2360

CALEX II: Conclusions

- ^{238}Pu discrepancy is resolved; lower abundance is correct.
- Pu concentration discrepancy is yet to be resolved
  - Study and understand past experimental work
  - Determine need for additional experiments
  - Draw up certification analyses plan
  - Conduct certification experiments

CALEX II: Recertification

- Sampling at SRS and LANL
  - SRS sampling done
  - Need to discuss sampling at LANL
- Samples Analyses at NBL and LANL
  - Moisture
  - Pu assay
  - Pu isotopes for verification only
  - ^{241}Am for verification only

Calorimetric Assay:Update

Clifford Rudy

LA-UR-05-4935

New Brunswick Laboratory
Measurement Evaluation Meeting

July 9, 2005

Phoenix, Arizona

Los Alamos

LANL Calorimetry Team

David Bracken
Lou Carrillo
John Determan
Clifford Rudy
Pete Santi
Morag Smith

Los Alamos

Overview

- This talk concentrates on calorimetry advances at LANL over the past five years
- Advances made possible through the funding support of USDOE 20.3
- Other topics:
  - Facility experience with calorimetry
  - International interactions

Topics

- MultiCal
- Large Volume Calorimeter
- Small Sample Calorimeters
- New Applications
- International
- Facility Experience

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Heat Standards Calorimeters

- 2 calorimeters operating in TA-55
- To be replaced by 2 newer systems operated by a heat standards version of Multical 4.0
- Heat standards calibration period extended to a total of 10 years for items with good historical data

MultiCal: Calorimeter Data Acquisition Software

- Developed at LANL by
  - Connie Schneider
  - Rod Biddle
  - Tom Kelley
  - Morag Smith
  - John Determan
- Used routinely at LANL and other sites
- Development supported by SO 20.3

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MultiCal Advances

- Graphics
- Ease of Use
- Flexibility
- Latest Version: MultiCal 4.0

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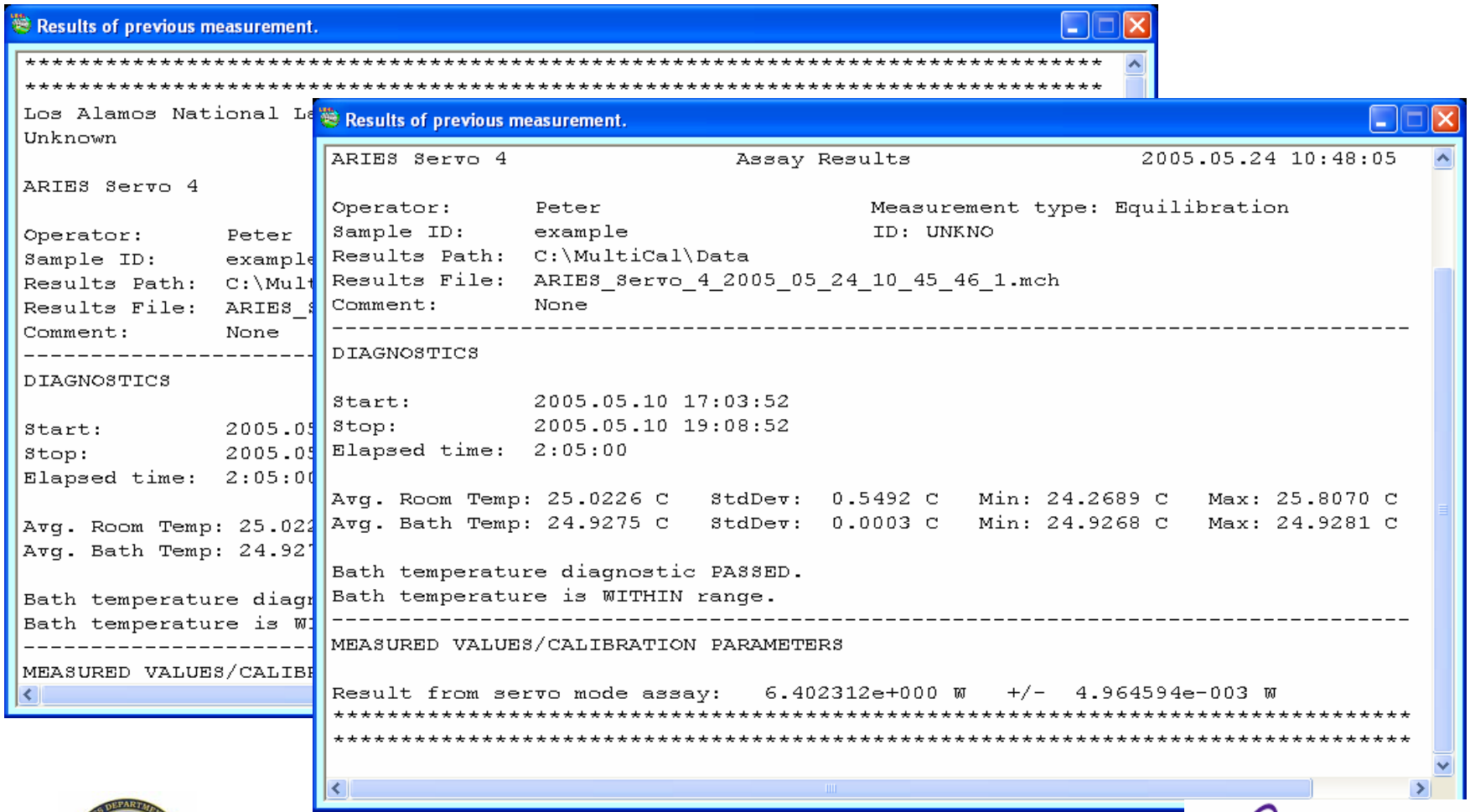
Assay Measurement Results



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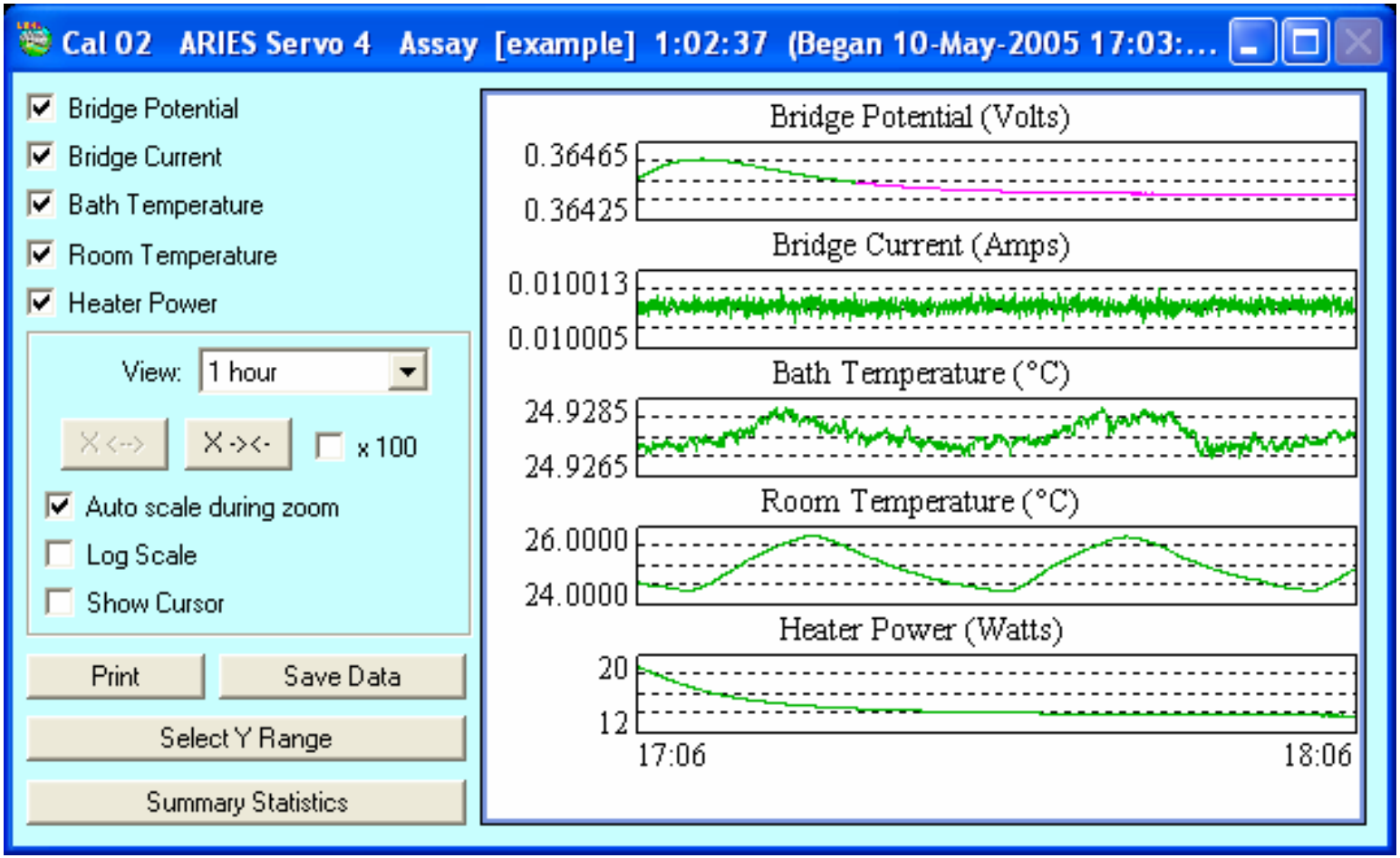
Graphical Display



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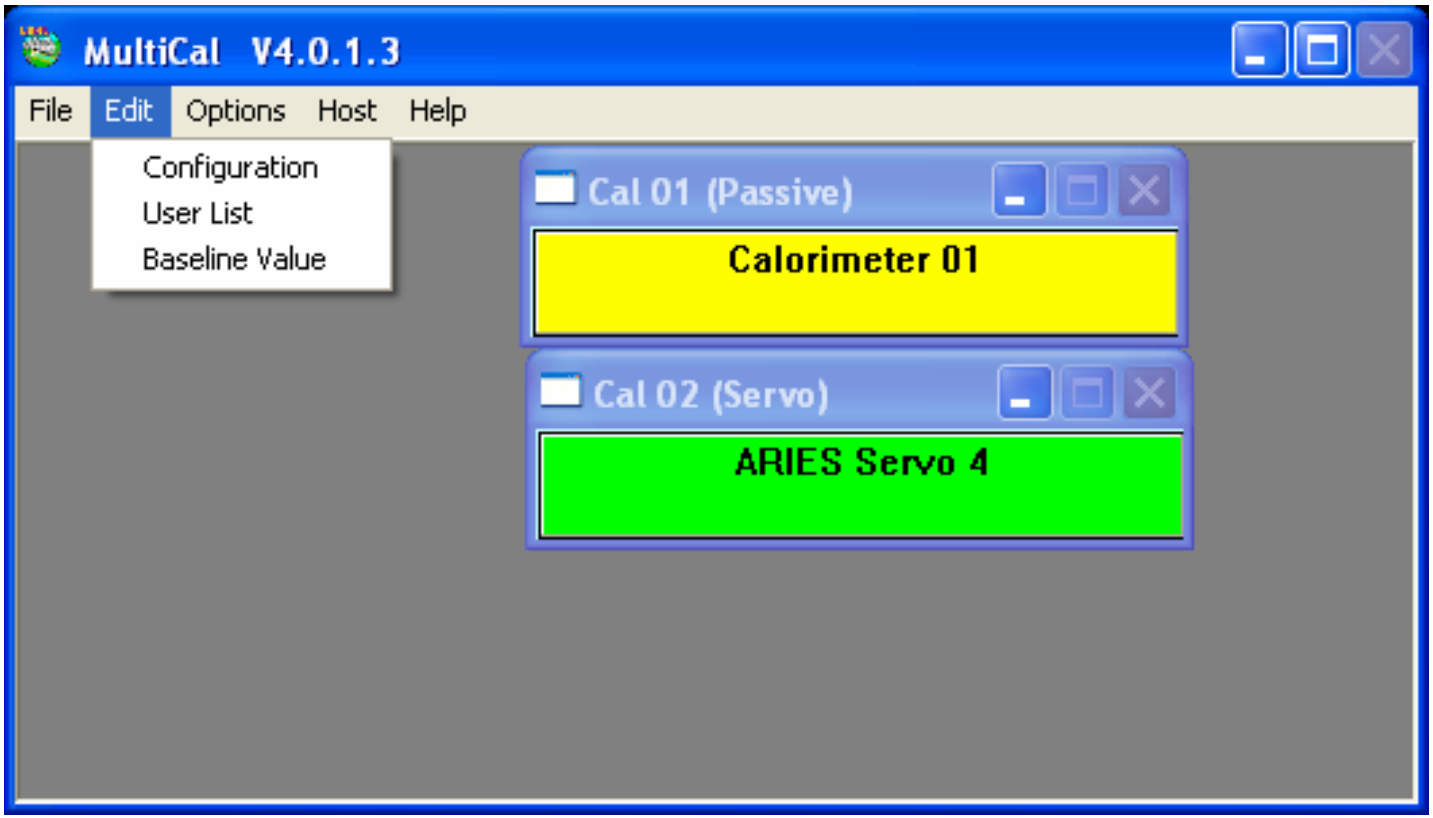
Configuration



Configure an existing calorimeter or add a new calorimeter.
A password is required to access the Configure option

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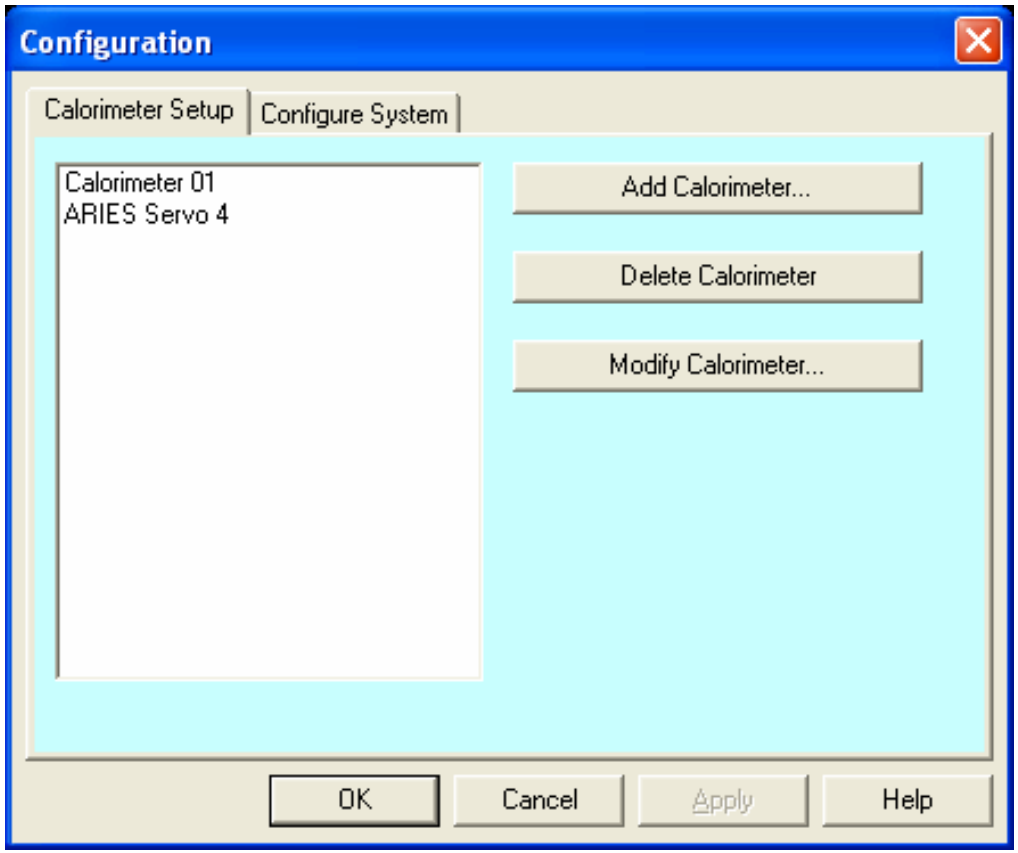
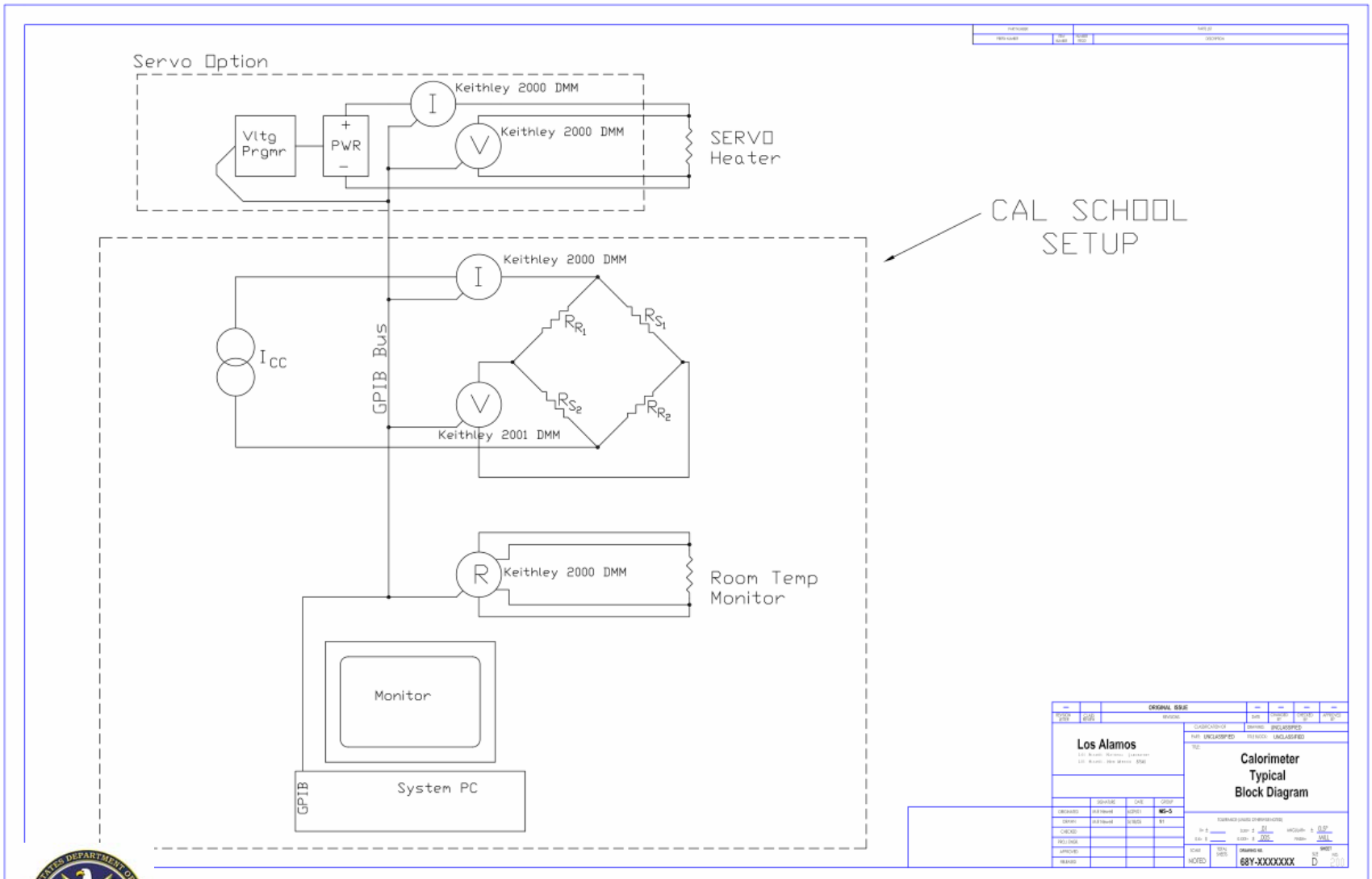
Configure Calorimeter

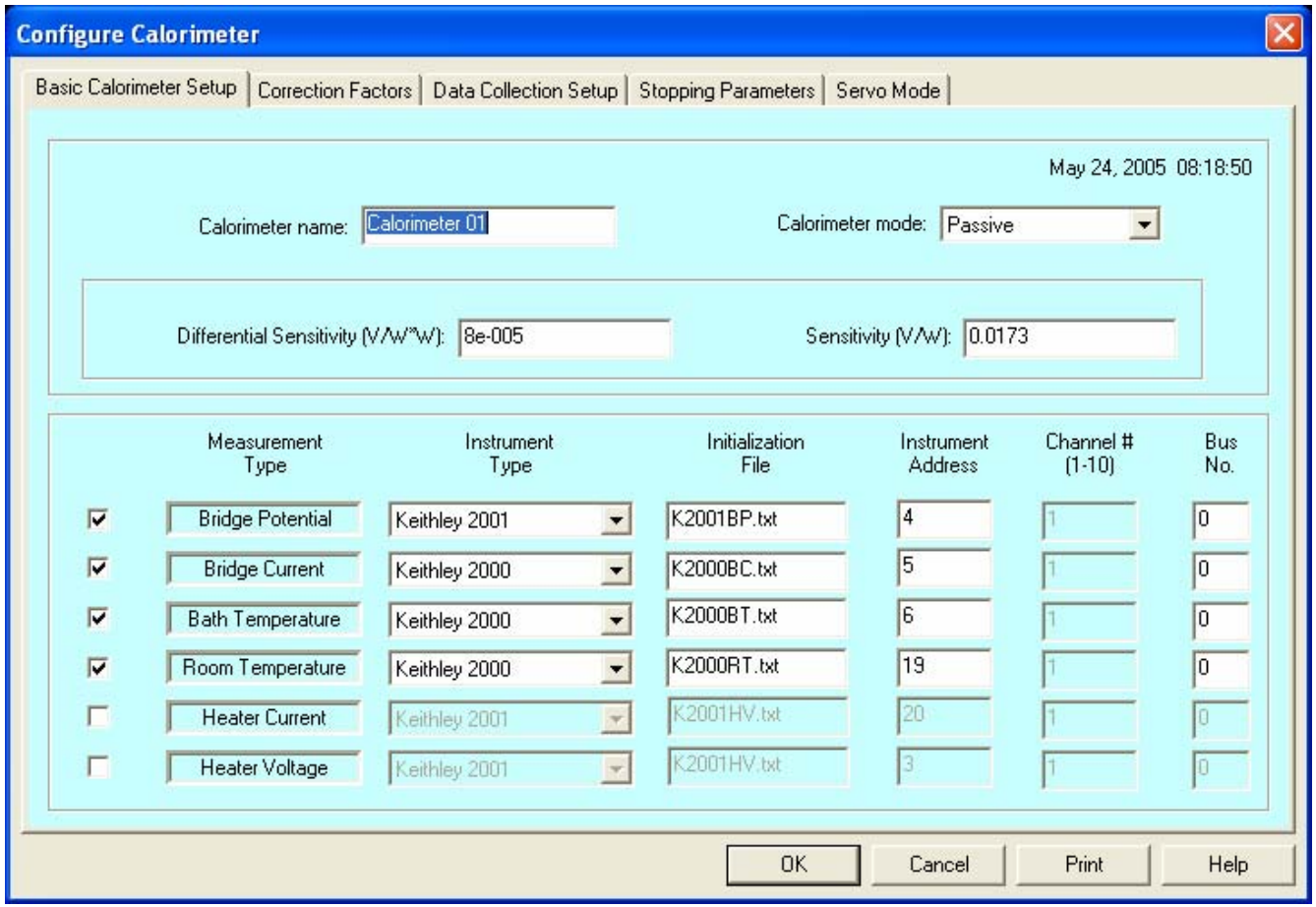


Select a calorimeter then click on Modify Calorimeter to view or change settings for a calorimeter

Calorimeter Setup Using MultiCal



Calorimeter Setup



Defines calorimeter hardware interfaces, mode of operating and corrections.

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MultiCal Options

- Passive/Servo Operation
- Endpoint detection/prediction
- Easily adaptable to thermo-electric calorimeter operation
- Run up to 8 Calorimeters

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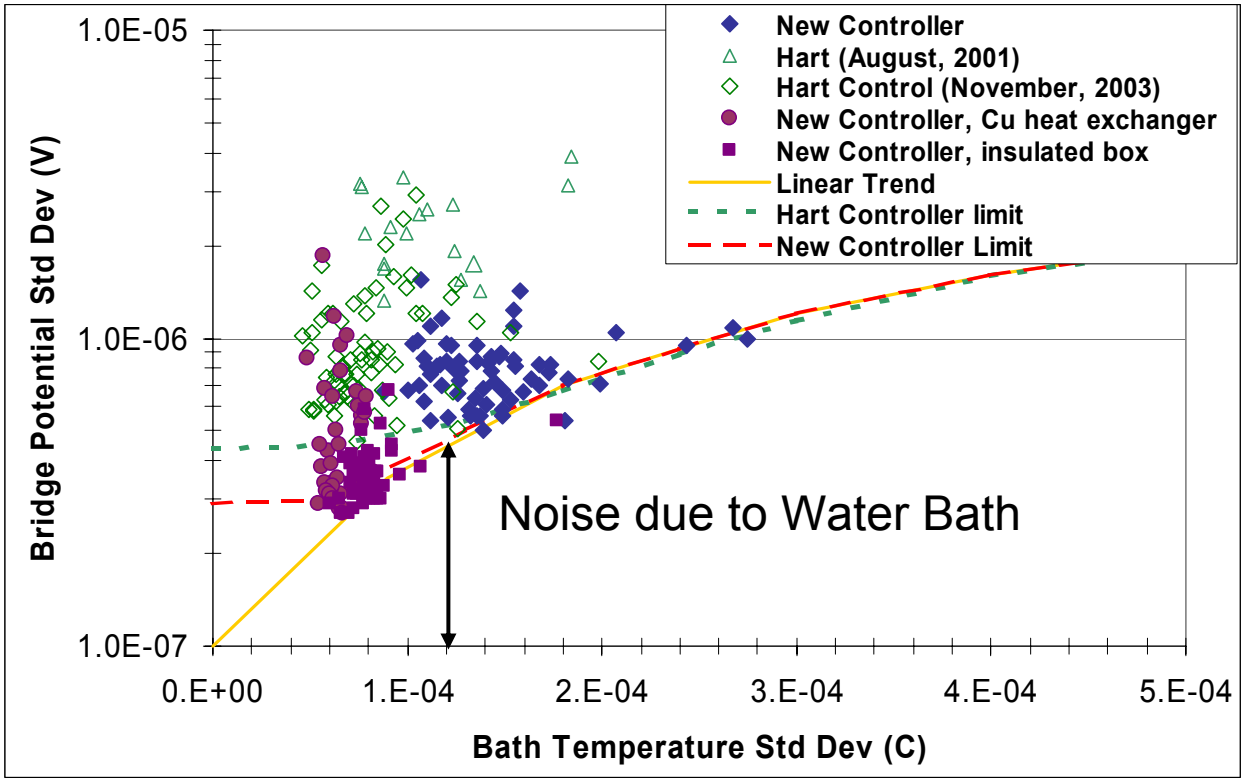
Improved Water Bath Control



4 hour sampling time

- ~30% improvement in water bath control over Hart Controller
- ~35% improvement in baseline Bridge Potential standard deviation

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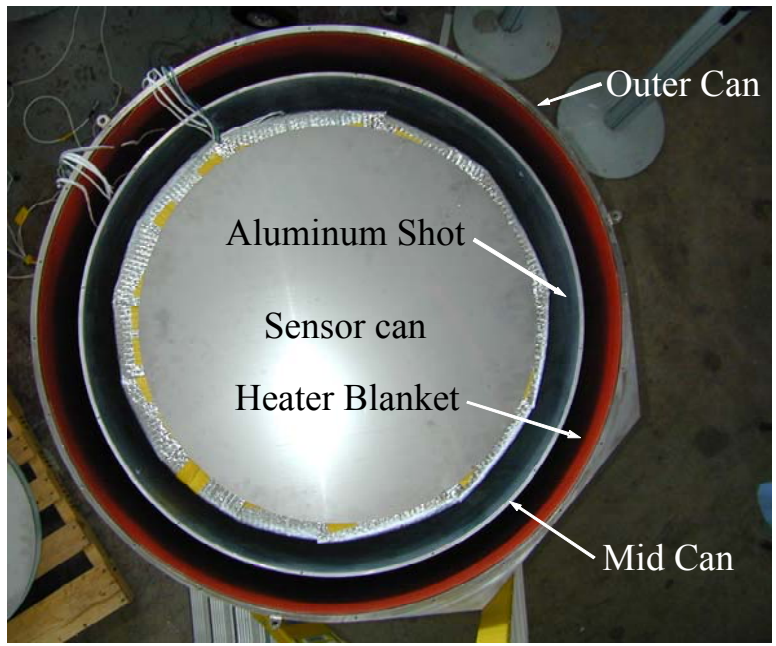
Large Volume Calorimeter

- Measurement Chamber
  - Measurement Chamber
    - 0. 66 m(26”) diameter, 1 m(39.3”) height
    - Can measure 55 gal drum with retaining ring + bolt
  - 1 m^2 thermoelectric sensors
  - Temperature control using electric heaters:
    - No water

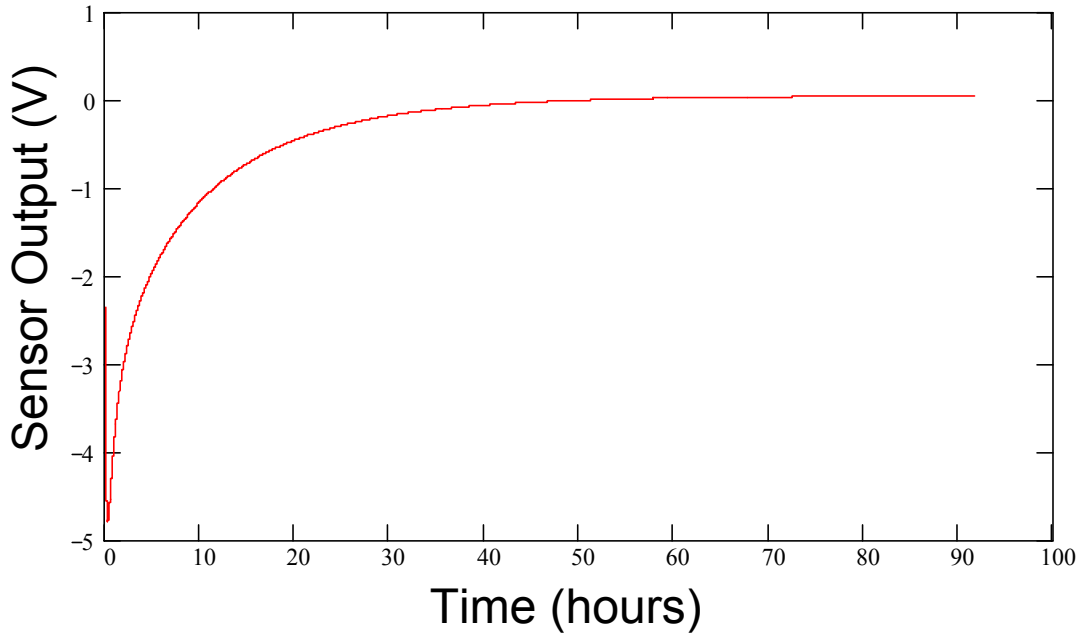
LVC: Inserting Sensor Array

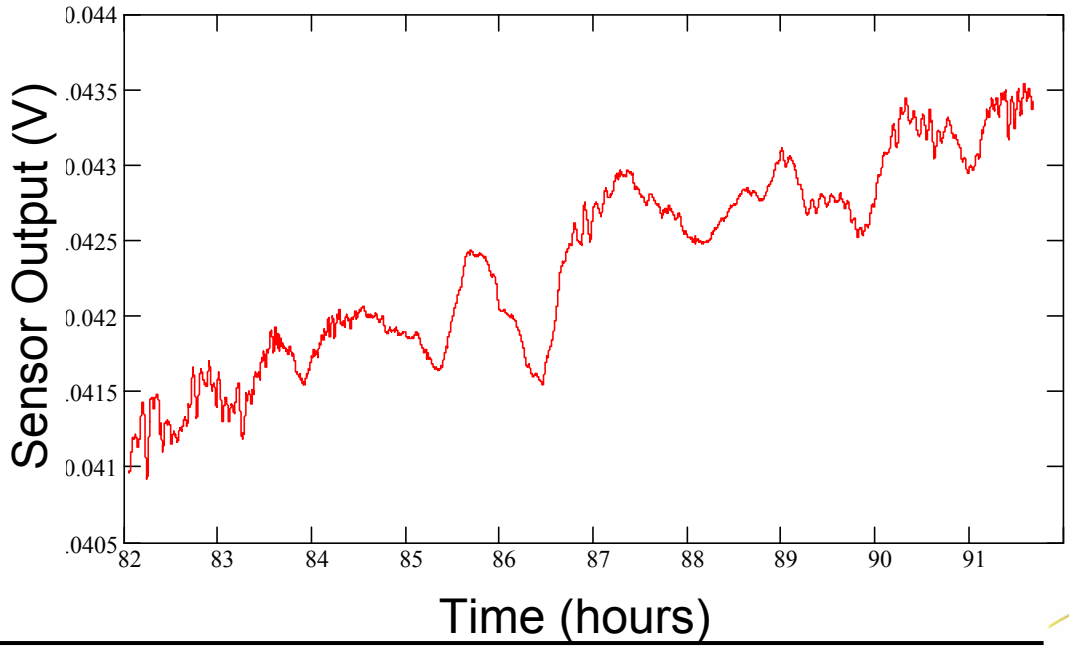
Large Volume Calorimeter in Operation

LVC design features



LVC run





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LVC can Fit in Transportable Calorimetry Laboratory

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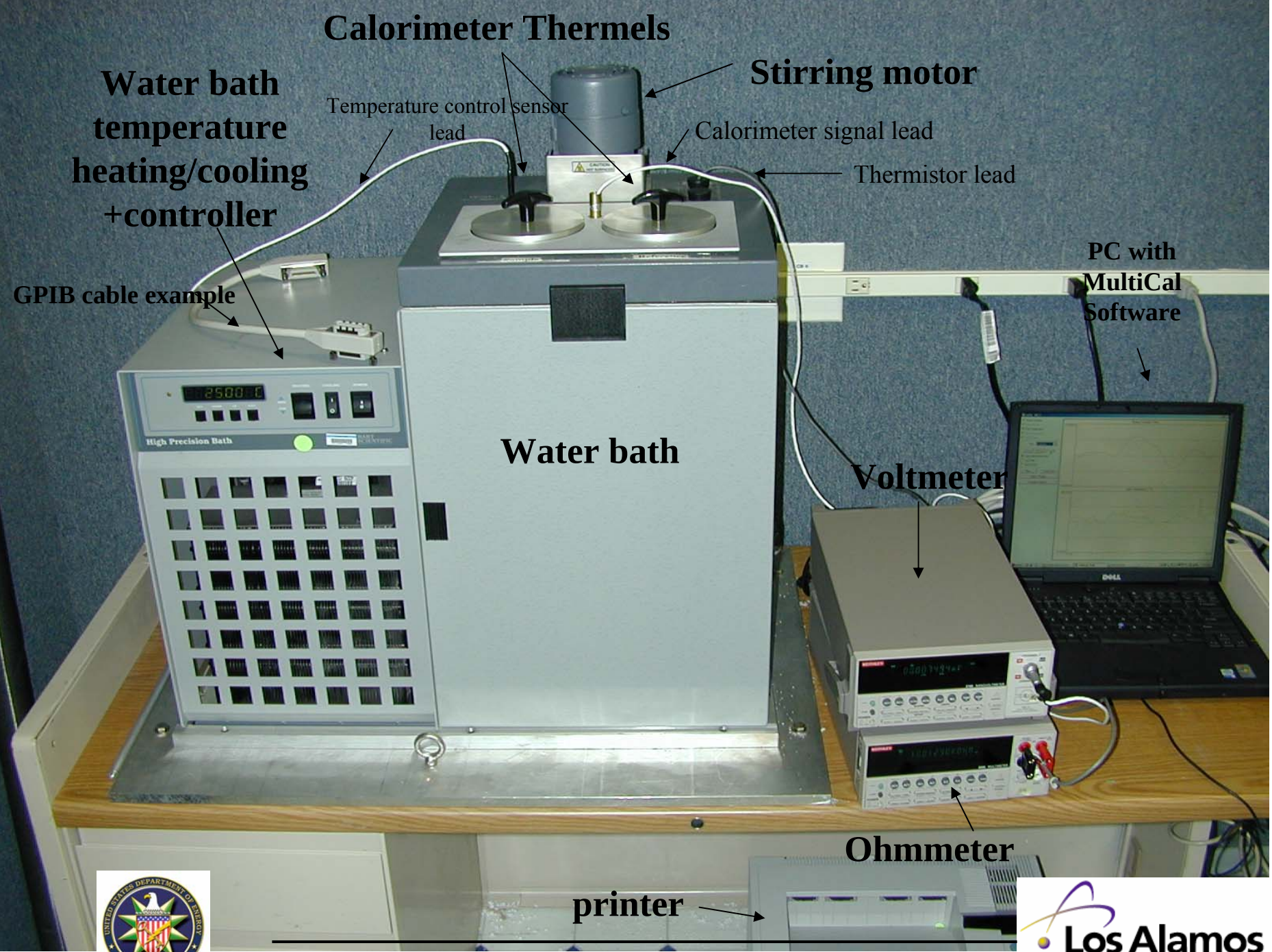
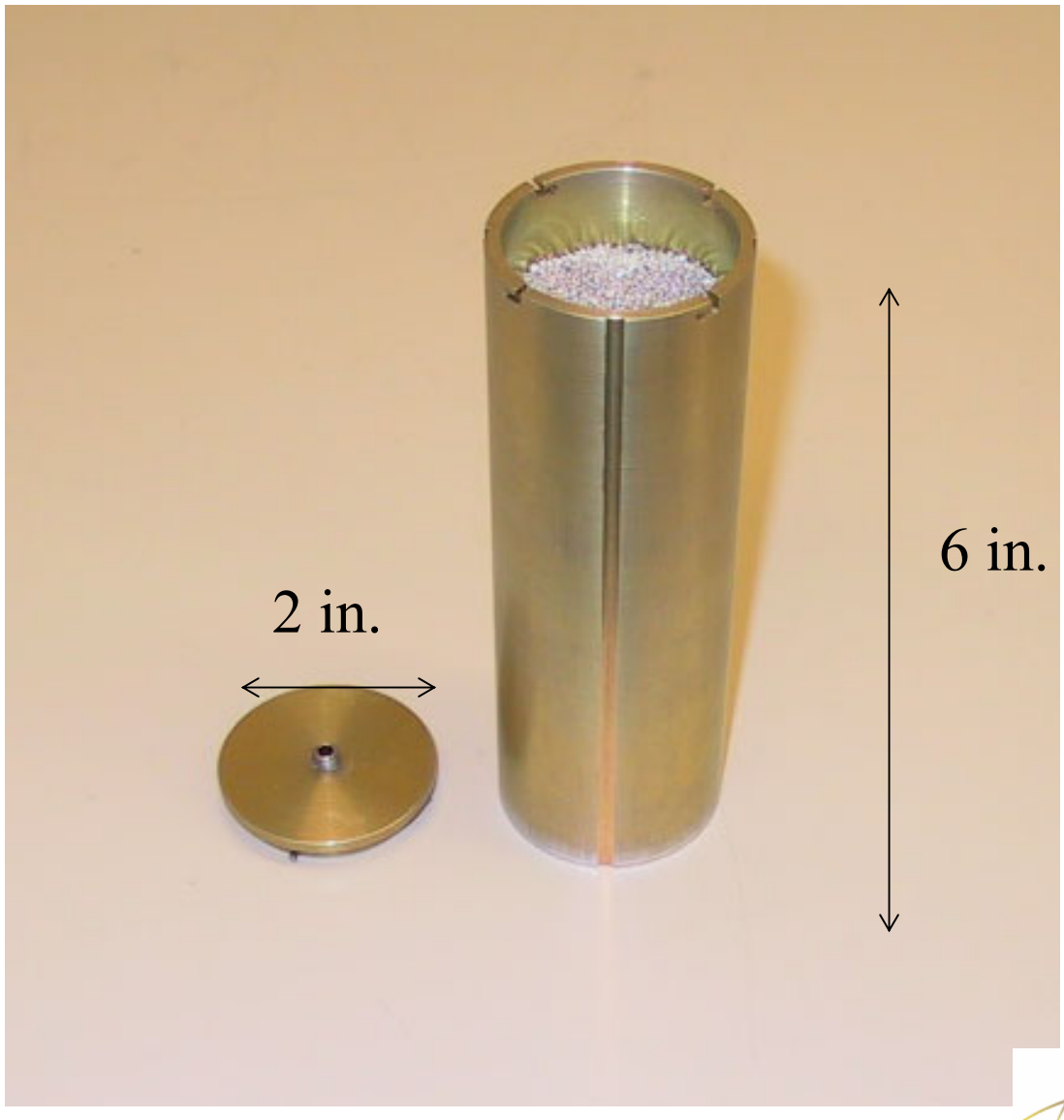
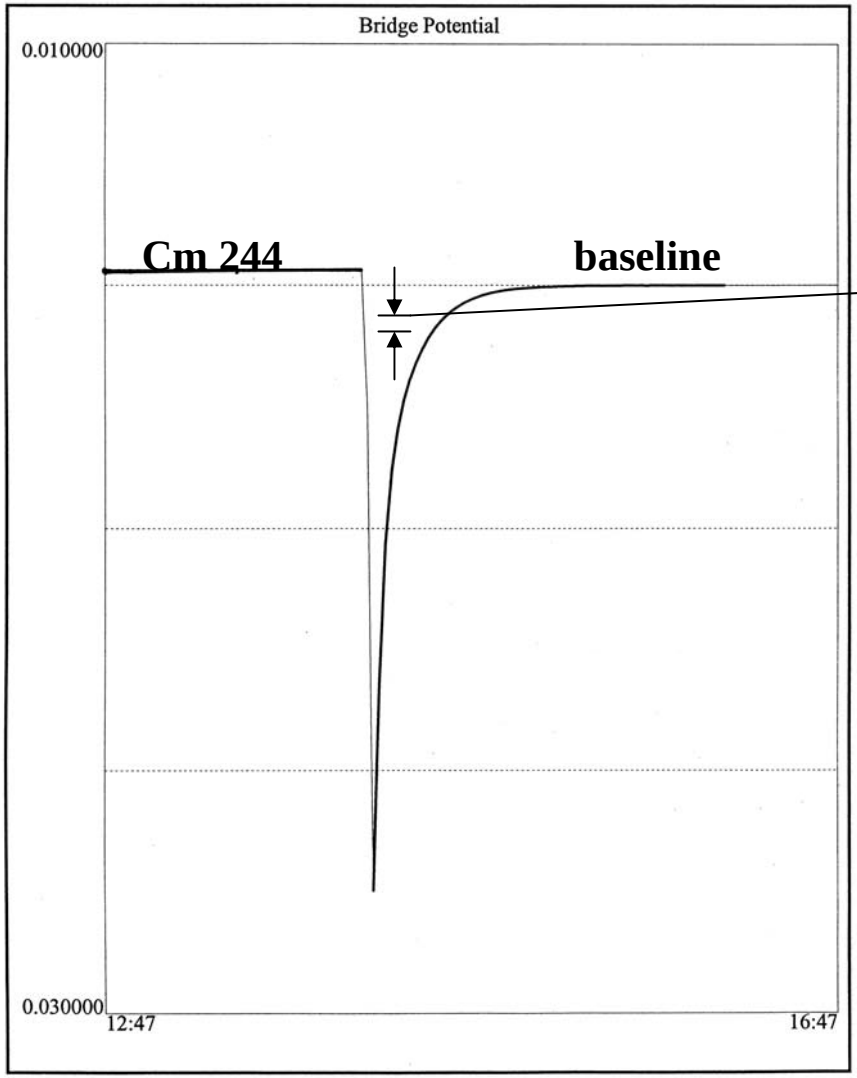

Calorimeter Thermels
Stirring motor
Water bath temperature heating/cooling +controller
Temperature control sensor lead
Calorimeter signal lead
Thermistor lead
PC with MultiCal Software
GPIB cable example
Water bath
Voltmeter
Ohmmeter
printer

SSC2 Cal can



Small Sample Calorimeter 2
Measurement of 0.0019 g Cm-244 sample



Replicate Measurement Results

625 μV

623 μV

627 μV

625 μV

627 μV

626 μV

Precision=0.2% RSD

Power:Book - cal average => 0.8%

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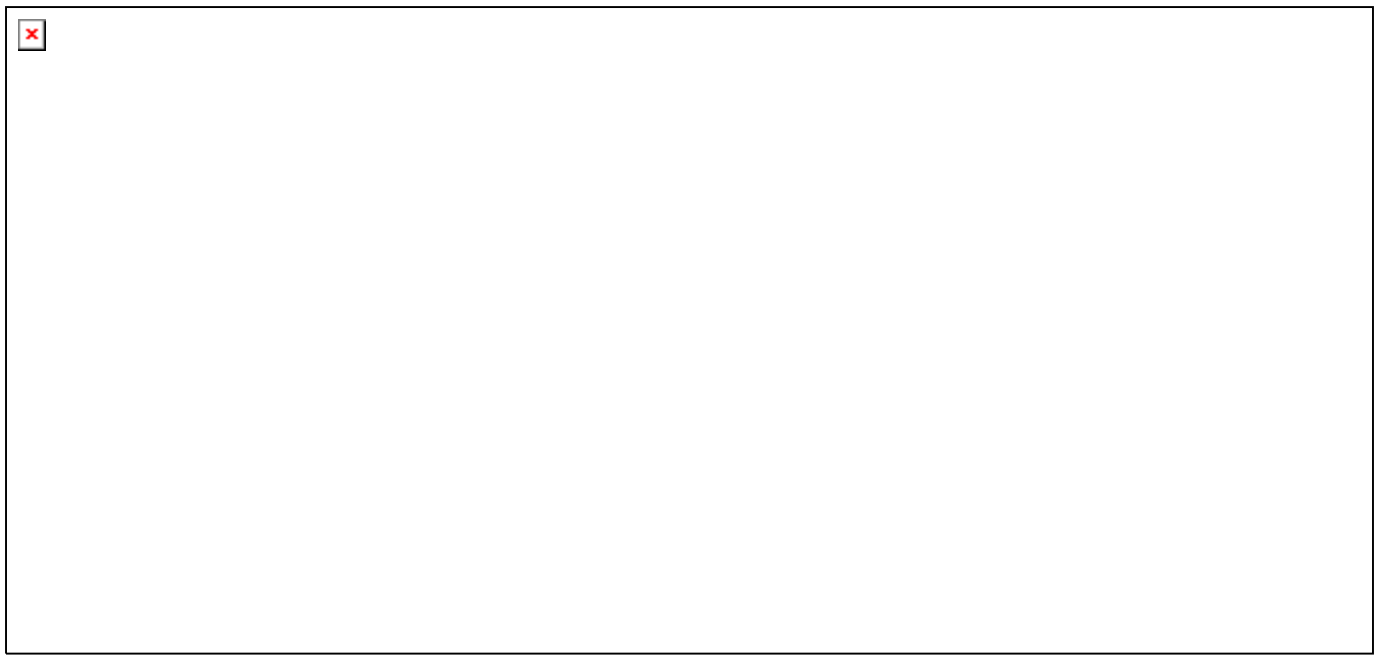
Calorimetry vs Mass Pu Metal Foils: SSC2



New Calorimetry Applications

- U-235 assay using calorimetry and gamma-ray spectroscopy
- Pu-242 assay using calorimetry, gamma-ray spectrometry and neutron counting.
- U-233 assay using calorimetry and gamma-ray spectroscopy
- Direct alpha activity(Ci) assay of Pu using calorimetry alone

HEU calorimetric assay

- Gamma-ray analysis programs(e.g. FRAM) now can yield the U-234, U-235 and U-238 mass fractions, thus allowing a $P_{\mathbf{eff}}$ calculation for HEU
- 2 calorimeters for HEU assay set up at 2 sites: No measurements yet

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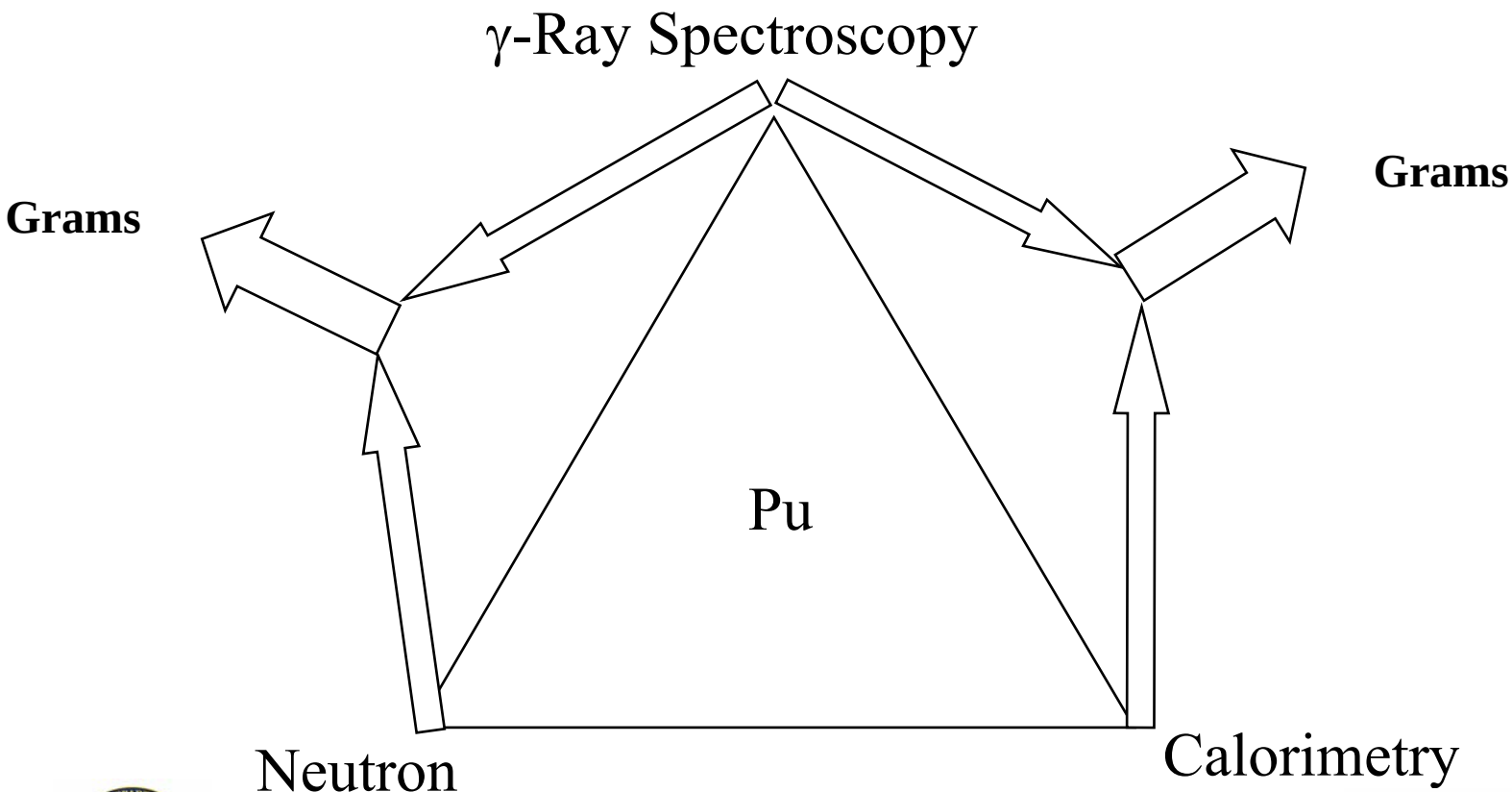
NDA Techniques Are Combined to Determine Mass of Plutonium



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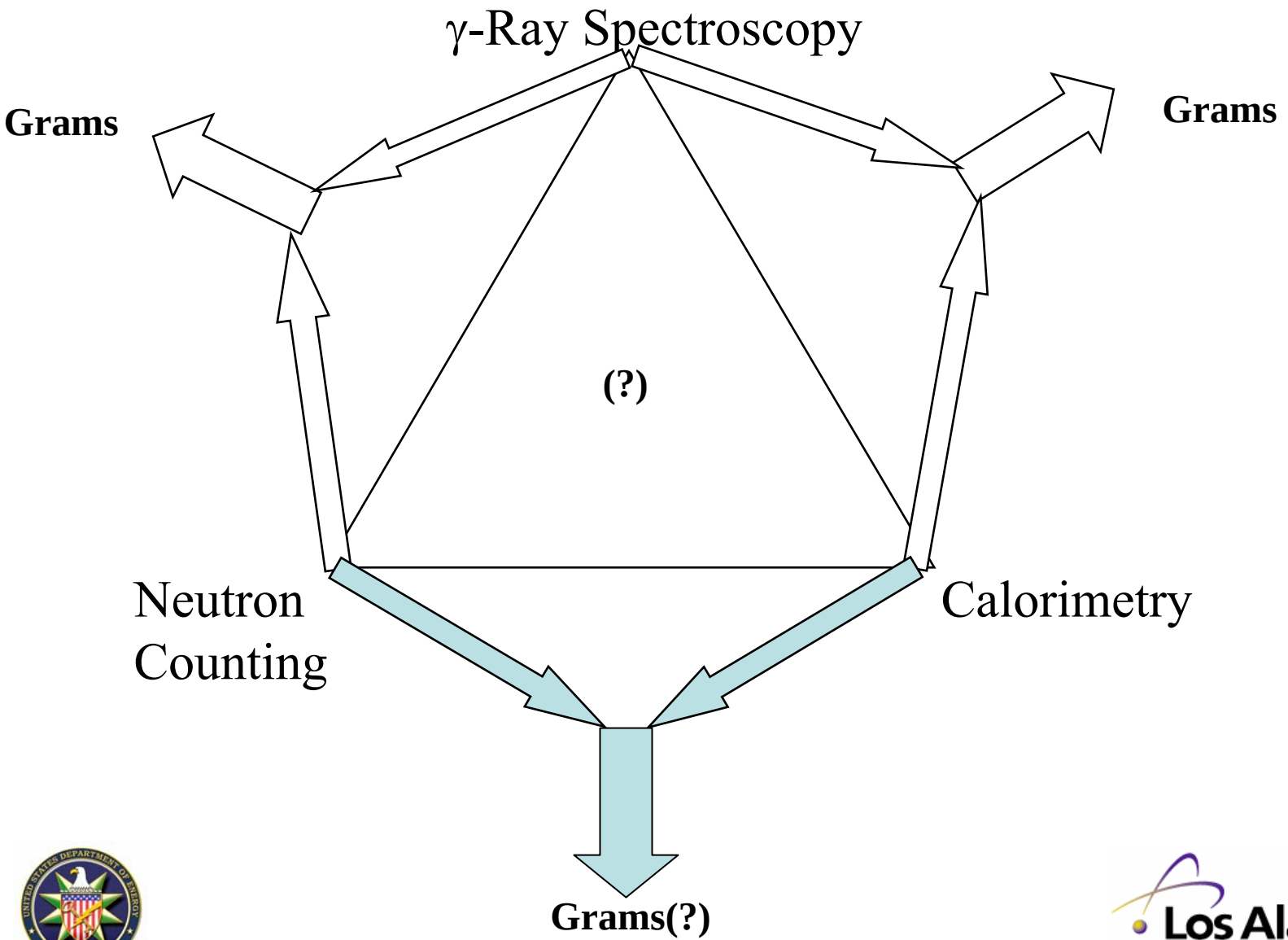
Could a combination of Neutron Counting & Calorimetry be used for Assay ?



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Cal/neutron/γ measurement of plutonium enriched in Pu-242

$$R_{242} = \frac{g_{242}}{g_{tot}} = \frac{1}{1 + \dfrac{n_{242} - kP_{242}}{\sum_{i=238,238,240,241,Am} (kP_i - n_i) R_i'}}$$

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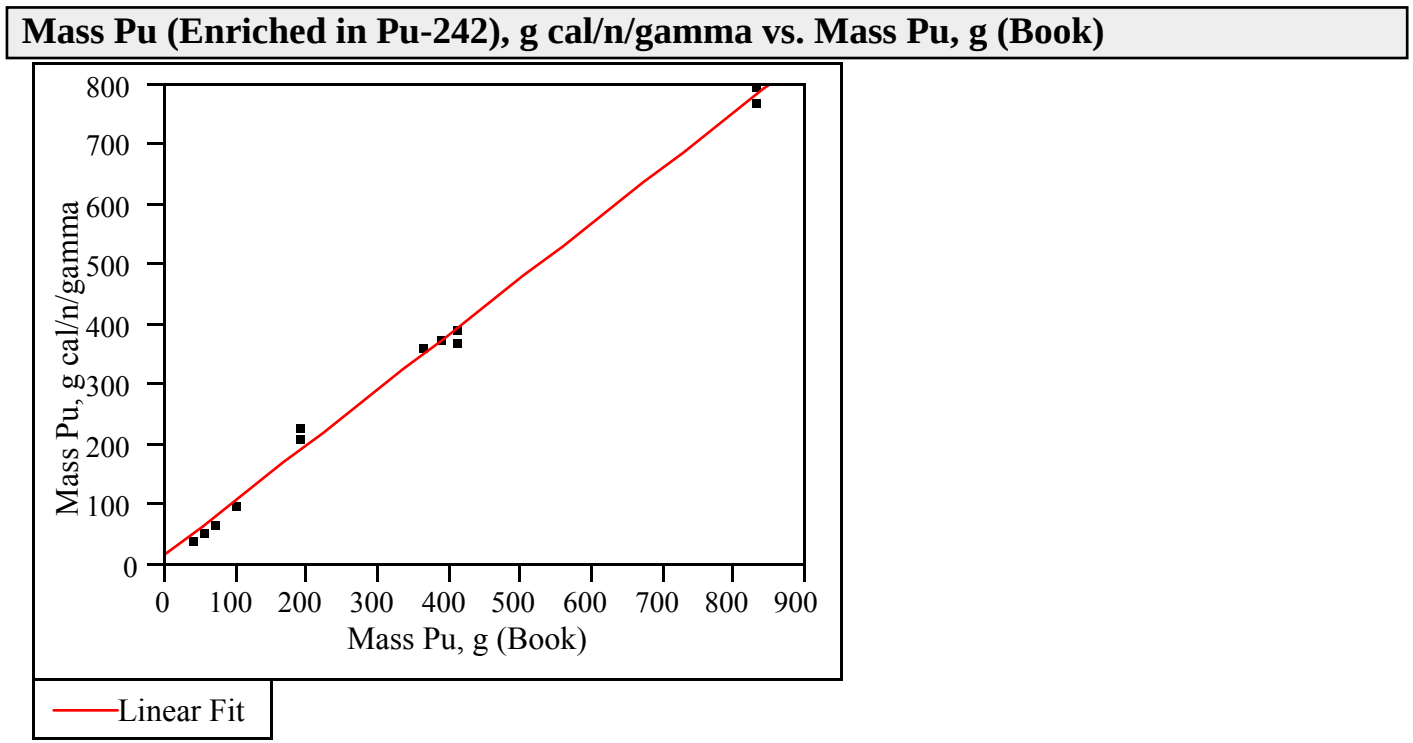
Cal/neutron/γ measurement results



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U-233 Calorimetric Assay

- Apply same technique as used for Pu cal assay to U-233 assay
- Specific power of U-233 is 7X less than Pu-239

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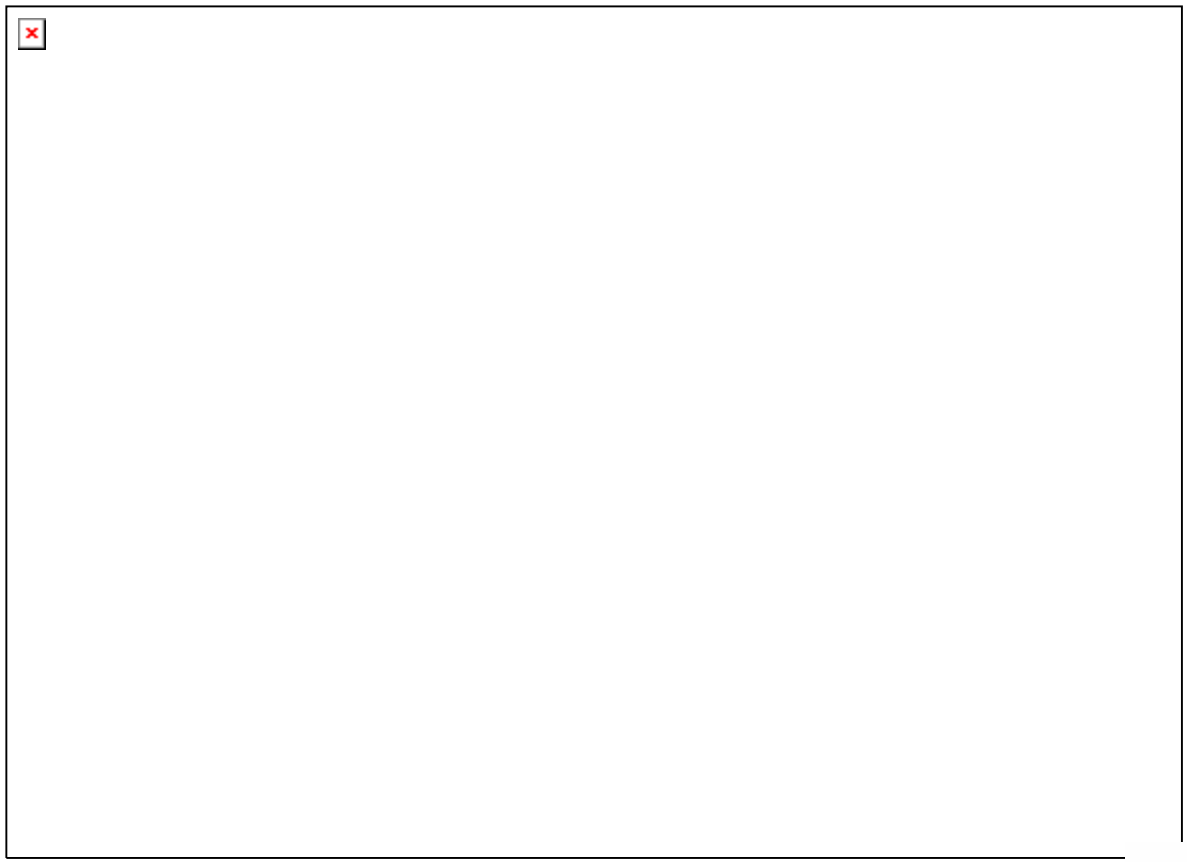
U-233 Gamma-Ray Measurements



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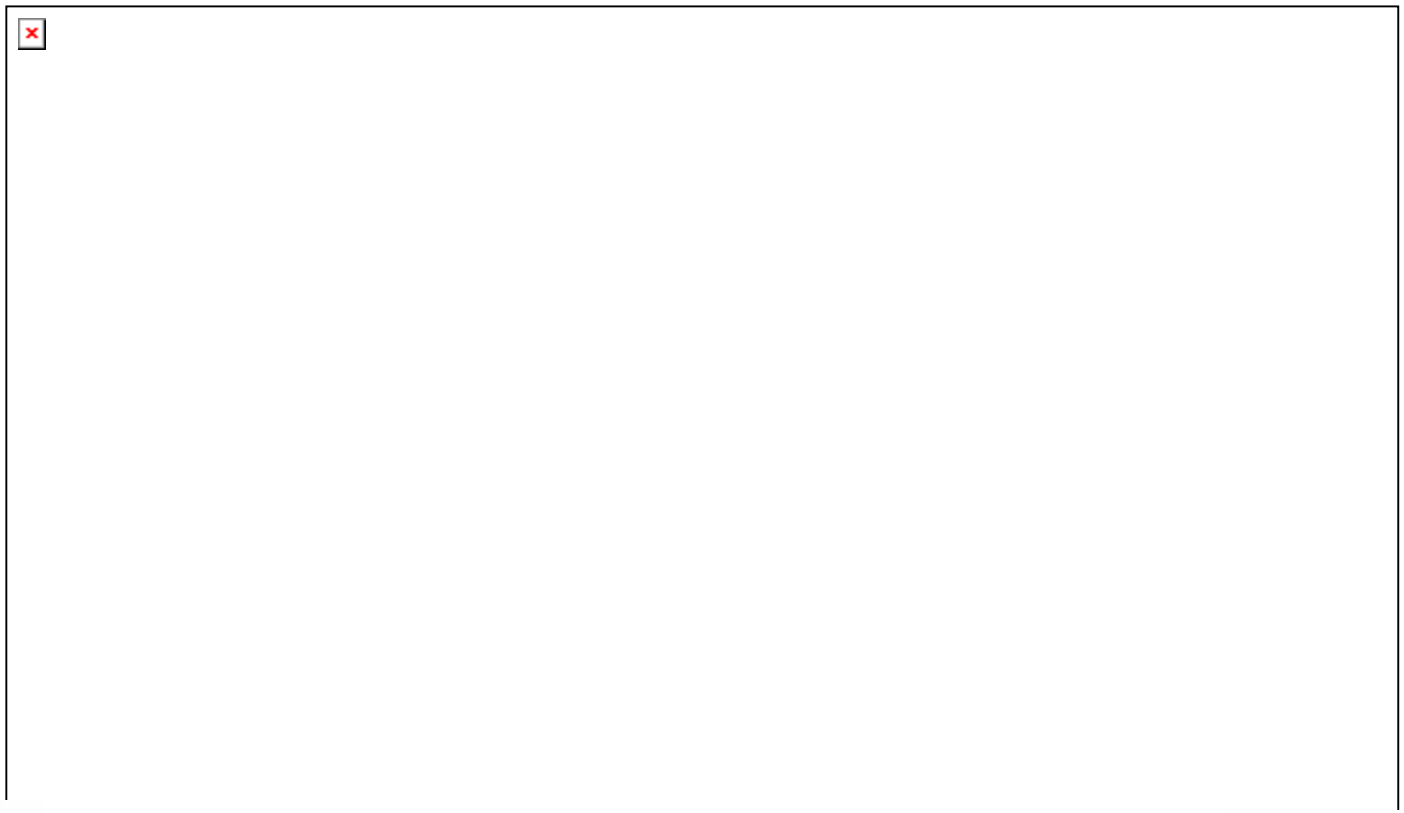
High Energy Gamma-Ray Measurements used for U-233 Known-Age determination



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Calorimetric Assay of U-233

- Majority of thermal power is from isotopes U-232 and U-233. U-234 may be present up to a few percent: not assayed
- Sufficient gamma-ray information available to determine U-232 and U-233
- Note: if age of U-233 known can relate U-233 content to Th-229 daughter gamma-ray activity
- Measured 17 items at LANL. Total book value U-233 mass 2.22 kg, total cal/iso, 2.17 kg

Use Calorimetry as Direct Measure of Alpha Activity(Curies) in SNM

- Activity$_i$ (dis/sec)= $\lambda_i N_i$
  - λ_i = specific activity= $\ln(2)/t_{1/2,i}$ (sec)
  - N_i= Number of atoms of isotope i

Power$_i$ (MeV/sec)= $\lambda_i N_i Q_i$

Q_i= Q value for isotope i decay

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Pu and ^{241}Am Decay Modes

Isotope	Primary Decay Mode
^{238}Pu	alpha
^{239}Pu	alpha
^{240}Pu	alpha
^{241}Pu	beta
^{242}Pu	alpha
^{241}Am	alpha

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^{241}Pu Contribution to Total Thermal Power Emitted by Pu + ^{241}Am With 6% ^{240}Pu is Small

Isotope	Wt. Fraction	Specific Power mW/g	Isotope Power mW	% Total Power
^{238}Pu	0.00012	567.57	0.0681	2.87
^{239}Pu	0.9382	1.9288	1.810	76.17
^{240}Pu	0.059	7.824	0.418	17.59
^{241}Pu	0.0024	3.412	0.0082	0.34 ←
^{242}Pu	0.0002	0.01159	$2x10^{-5}$	0.0
^{241}Am	0.00063	114.2	0.072	3.03

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Use Calorimetry as Direct Measure of Alpha Activity(Curies) in SNM(continued)

- MeV/sec => Joules/Sec => Watts
- For Pu item: Power (Watts)= $\Sigma_i \lambda_i N_i Q_i$ where i = Pu isotopes and Am-241

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The Q value for Alpha Decay Varies $Q_{av} \pm 6.6\%$

Isotope	Q_{alpha} (Mev)
^{238}Pu	5.59320
^{239}Pu	5.24450
^{240}Pu	5.25578
^{241}Pu	5.14010
^{242}Pu	4.98270
^{241}Am	5.63781

Use Calorimetry as Direct Measure of Alpha Activity(Curies) in SNM(continued)

- MeV/sec => Joules/Sec => Watts
- For Pu item: Power (Watts)= $\Sigma_i \lambda_i N_i Q_i$ where i = Pu isotopes and Am-241

For Pu: Power = $Q_{av}(\Sigma_i \lambda_i N_i)$

Power/Q_{av}= $\Sigma_i \lambda_i N_i$= total alpha activity (dis/sec:Curies)

Use for determination of alpha source term activity

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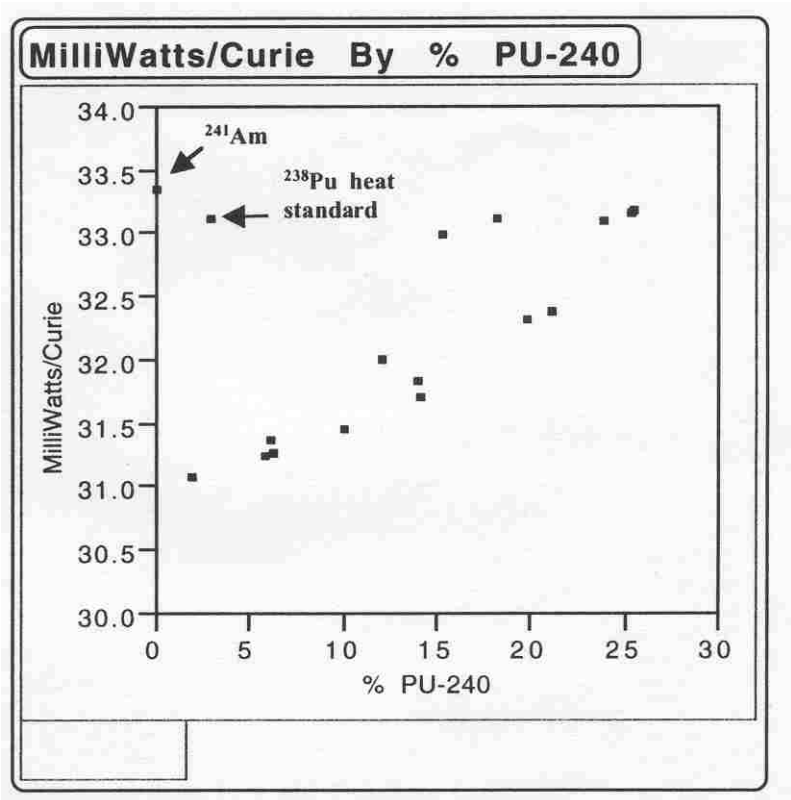
The Overall Range of Watts/Activity is About 6.6% for a Range of Pu Burnup Between 2 – 25% ^{240}Pu



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LANL:International Calorimetry Collaborations

- Russia: Calorimeter/NMC/Gamma-Ray instruments set up at VNIIM(Bochvar) in Moscow. Status:operational
- Germany (Karlsruhe): Small sample calorimeter (SSC1) used for research
- China: 5” Gradient calorimeter system to be sent

RF Cal Assay Instrument Summary

- 15 Servo Controlled Calorimeters
- 4 Pre-Heaters
- 8 Water Bath Calorimeters
- 3 Isotopic Systems

High-Throughput Calorimetry Observations

- Requires Backlog of Samples
- Coordination with production critical
- Measurement sensitive to Room Temp
  - Room must be constant within 3 degrees

Importance of ^{241}Am Determination in the Characterization of PuO_2 Standards for Calorimetric Assay

Thomas E. Sampson

Safeguards Science and Technology, N-1
Los Alamos National Laboratory
Los Alamos, NM 87545
USA

LA-UR-05-4546

Calorimetric Assay

- Measure total *Sample Power* in a calorimeter

Watts

- Measure isotopic composition of sample, including ^{241}Am, and compute *Effective Specific Power, P_{eff}*

$$P_{eff}(\text{Watts/g Pu}) = \sum P_i * f_i$$

P_i = Watts/g isotope

f_i = Isotopic fraction in sample, relative to plutonium

i = ^{238}Pu, ^{239}Pu, . . . , ^{242}Pu, ^{241}Am

- Compute total Pu mass

$$\text{grams Pu} = \frac{\text{Sample Power (Watts)}}{P_{eff}\ (\text{Watts/g Pu})}$$

Calorimeter Calibration

- ^{238}Pu heat standards
  - Power calibrated against NIST-traceable electrical standards
  - Errors < 0.1%
- PuO_2 standards
  - Known Pu mass from analytical chemistry
  - Known Pu isotopic composition from analytical measurements (mass spec and various methods for $^{241}Am/Pu$)

    Gives P_{eff}
  - P_{eff} combined with Pu mass gives Watts

PuO_2 Standards for Calibration and NDA Measurement Control

- Gamma-Ray Isotopic Analysis
  - Control and verify accuracy
    - Pu isotopic fractions
    - ^{241}Am isotopic fraction
    - P_{eff}
- Calorimetry
  - Control
    - Power measurement (Watts)
  - Calibrate
    - Power (Watts)
- All of the above require highly accurate and precise analytical characterization of the Pu in the standard.

Characterization Errors Affect Standard's Usefulness

- Errors occur in
  - Pu concentration
  - Weighing (usually negligible)
  - Pu isotopic fractions
  - ^{241}Am/Pu ratio

- This paper examines the effect of errors in ^{241}Am/Pu on P_{eff}

Error Propagation for P_{eff}

$$P_{eff} = \sum_i P_i * f_i$$

P_i = Watts/g isotope

f_i = Isotopic fraction in sample, relative to plutonium

i = ^{238}Pu, ^{239}Pu, . . . , ^{242}Pu, ^{241}Am

Assumptions

P_i without error

Neglect correlations in f_i

Variance of P_{eff}

$$\left(\Delta P_{eff}\right)^2 = \sum_i P_i^{\,2} * \left(\Delta f_i\right)^2$$

P_i = Watts/g isotope

f_i = Isotopic fraction in sample, relative to plutonium

i = ^{238}Pu, ^{239}Pu, . . . , ^{242}Pu, ^{241}Am

Specific Power Values P_i for the Isotopes of Plutonium

Isotope	Half Life (yrs)	Specific Power,P_i (mW/g isotope)	Uncertainty in P_i (% RSD)
Pu-238	87.74	567.57	0.046
Pu-239	24119.	1.9288	0.016
Pu-240	6564.	7.0824	0.028
Pu-241	14.348	3.412	0.064
Pu-242	376300.	0.1159	0.26
Am-241	433.6	114.2	0.37

Uncertainties in P_i do not contribute to random error.

Test Case 1
Typical Weapons Plutonium for Disposition

- Characterized by "routine" mass spec. with repeated measurements
- Gamma Counting for ^{241}Am/Pu
- a'priori "routine" mass spec errors (95% confidence)
  - < [0.1% relative or 10^{-5} absolute] whichever is larger
- a'priori "routine" gamma counting errors for ^{241}Am/Pu
  - $\pm$ 5% (1 RSD)
- ^{241}Am contributes 13% of the total power

Test Case I. Weapons Disposition Pu Isotopic Errors: Larger of-- a'priori or Observed from Repeats

Isotope	Mass % (wrt Pu)	Relative Error (% RSD)	$(P_i)^2\ (\Delta f_i)^2$
Pu-238	0.010	2.7	2.35 E-6
Pu-239	94.05	0.05	8.23 E-7
Pu-240	5.800	0.08	1.08 E-7
Pu-241	0.100	1.4	2.28 E-9
Pu-242	0.040	1.1	2.60 E-13
Am-241	0.300	7.1	5.92 E-4
P_{eff} (mW/gPu)	2.6276	Variance of P_{eff}	5.95 E-4
		Std. Dev of P_{eff}	2.44 E-2
		% RSD, P_{eff}	0.93

Test Case I. Weapons Disposition Pu Isotopic Errors: "Routine" Analytical Results

- Over 99% of the variance in P_{eff} comes from ^{241}Am
- % RSD in P_{eff} (from routine analytical characterization) is significantly greater than that from an NDA gamma isotopic measurement. [see next slide]
- This characterization would not be suitable for use as a standard for Calorimetric Assay.

Variance Components for a Typical FRAM Measurement of 3.5 kg of Weapons Disposition Plutonium

Isotope	Mass % (wrt Pu)	Relative Error (% RSD)	$(P_i)^2 (\Delta f_i)^2$
Pu-238	0.010	7.0	1.58 E-5
Pu-239	94.05	0.15	7.40 E-6
Pu-240	5.800	2.0	6.75 E-5
Pu-241	0.100	0.30	1.05 E-10
Pu-242	0.040	10.0	2.15 E-11
Am-241	0.300	1.0	1.17 E-5
P_{eff} (mW/gPu)	2.6276	Variance of P_{eff}	1.02 E-4
		Std. Dev of P_{eff}	1.01 E-2
		% RSD, P_{eff}	0.39

Variance Components for a Typical FRAM Measurement of 3.5 kg of Weapons Disposition Plutonium

- The typical uncertainty in P_{eff} for a NDA gamma ray isotopic measurement is <0.5% (RSD).
- Standards must have a significantly smaller uncertainty to be useful.

Test Case 2 The CALEXII Standard Medium Burnup Reactor Grade Plutonium

- Characterized by "standards grade" mass spec. with repeated measurements
- Gamma Counting for ^{241}Am/Pu
- Errors: Observed from repeated measurements
- ^{241}Am contributes 18% of the total power

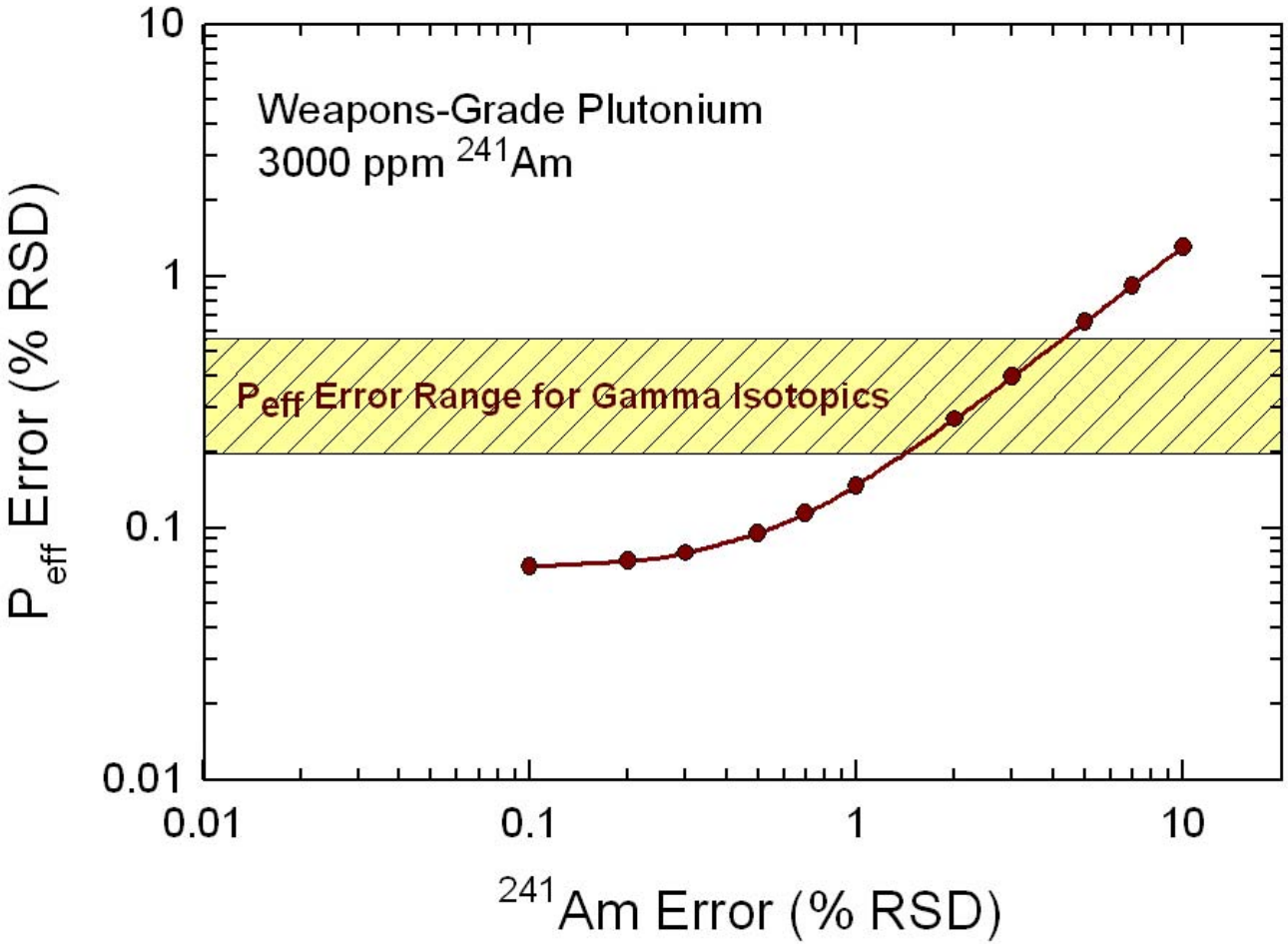
Test Case 2. The CALEXII Standard Medium Burnup Reactor Grade Plutonium

Isotope	Mass % (wrt Pu)	Relative Error (% RSD)	$(P_i)^2 (\Delta f_i)^2$
Pu-238	0.078	0.26	1.27 E-6
Pu-239	86.701	0.004	4.47 E-9
Pu-240	12.190	0.033	8.12 E-8
Pu-241	0.824	0.22	3.82 E-9
Pu-242	0.208	0.34	6.71 E-13
Am-241	0.585	2.1	1.97 E-4
P_{eff} (mW/gPu)	3.67282	Variance of P_{eff}	1.98 E-4
		Std. Dev of P_{eff}	1.41 E-2
		% RSD, P_{eff}	0.38

Test Case 2. The CALEXII Standard Medium Burnup Reactor Grade Plutonium

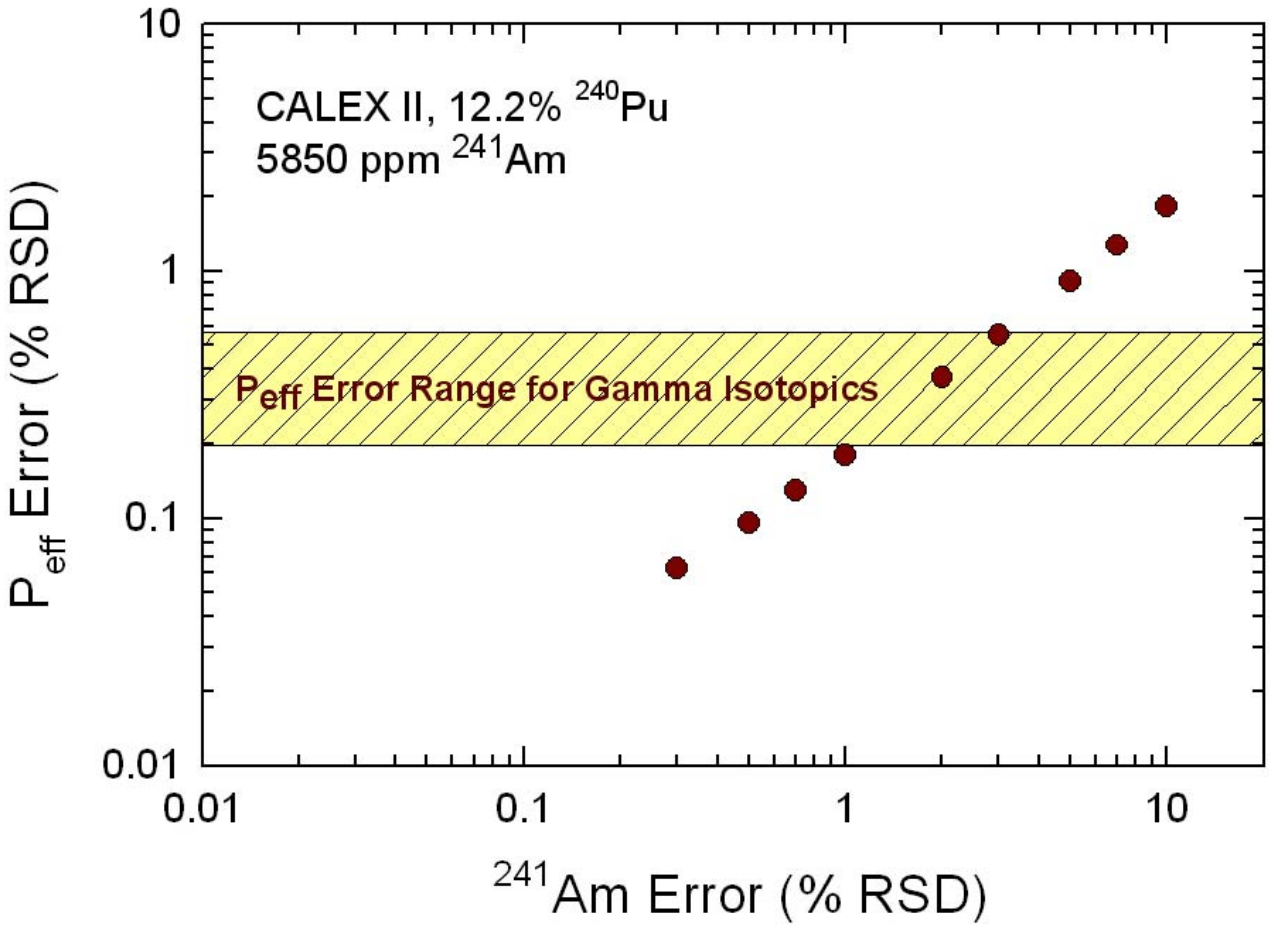
- Analytical characterization with "standards grade" effort.
- All analytical errors are smaller than previous example.
- ^{241}Am/Pu by gamma counting.
- Still, ^{241}Am errors dominate.
  - Over 99% of P_{eff} variance from ^{241}Am
- Total P_{eff} uncertainty (analytical) ~ NDA gamma isotopic uncertainty. Still not good enough to be a standard.

What ^{241}Am Error Yields a Good Standard for Calorimetric Assay?



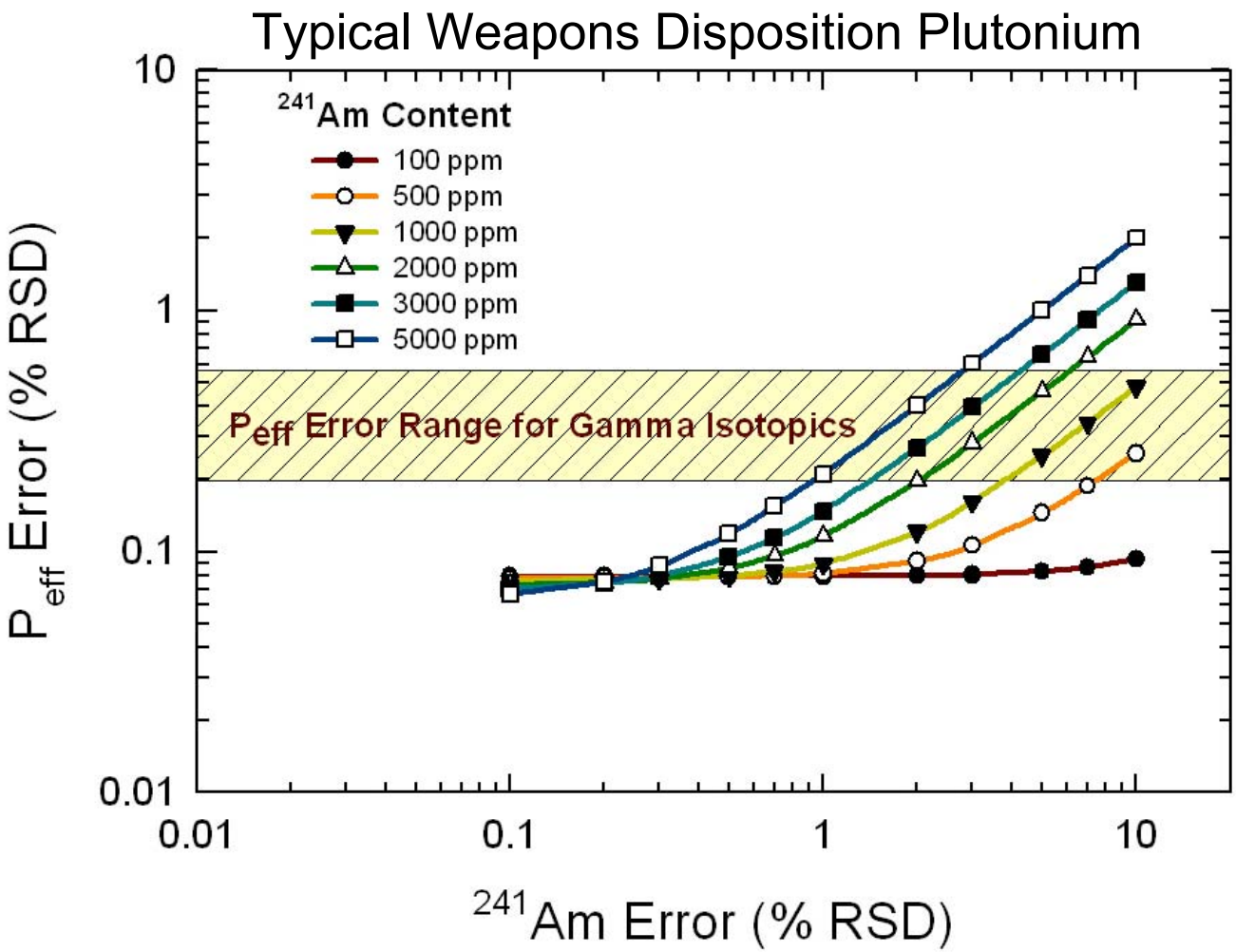
^{241}Am error of ~ 0.5% produces a P_{eff} uncertainty 2-4 times smaller than typical FRAM gamma isotopic results.

What ^{241}Am Error Yields a Good Standard for Calorimetric Assay?



Result is similar for the CALEX II standard. An error of ~ 0.5% (RSD) should produce a standard adequate for Calorimetric Assay.

^{241}Am Concentration Dependence of Errors



Larger ^{241}Am values require smaller errors to keep P_{eff} error in the 0.1 – 0.15% range.

Conclusions

- Routine and even Standards quality analytical measurements of ^{241}Am/Pu using gamma counting are not adequate for standards for calorimetric assay.
  - Need ^{241}Am/Pu errors that are 2—10 times smaller than current gamma counting practice.
- Analytical laboratories should bring more accurate techniques (such as IDMS) into routine use.
- CRM standards for ^{241}Am in plutonium need to be developed for both the analytical and NDA community.

Status of Multiplicity Counting

Peter A. Santi and William H. Geist

Los Alamos National Laboratory

Safeguards Science and Technology Group (N-1)

July 9, 2005

Sponsored by the DOE Office of Security, Office of Materials Inventory and Technology Department (SO-20.3)

LA-UR-05-4941

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Standard Point Model

Point Model Multiplicity Equations:

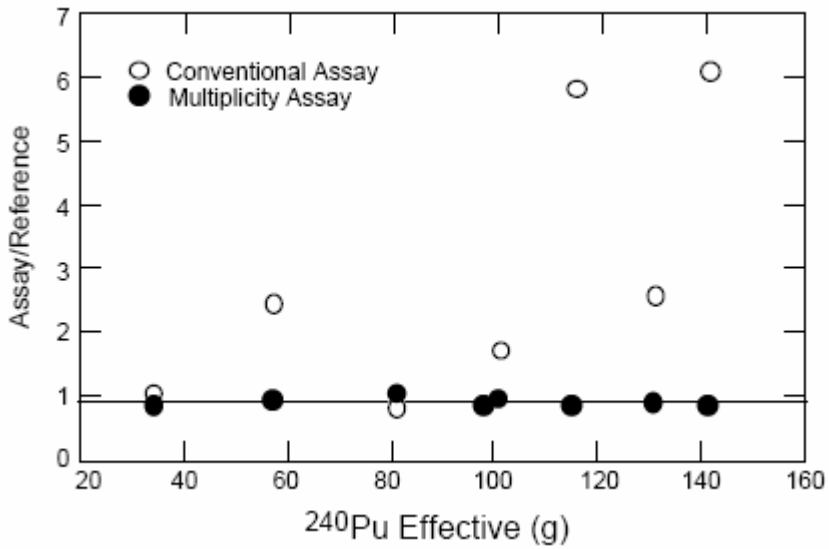
$$S = F\varepsilon\nu_{s1}(1+\alpha)$$

$$D = \frac{1}{2}F\varepsilon^2 f_d M^2\left\{\nu_{s2} + \left(\frac{M-1}{\nu_{i1}-1}\right)\nu_{s1}(1+\alpha)\nu_{i2}\right\}$$

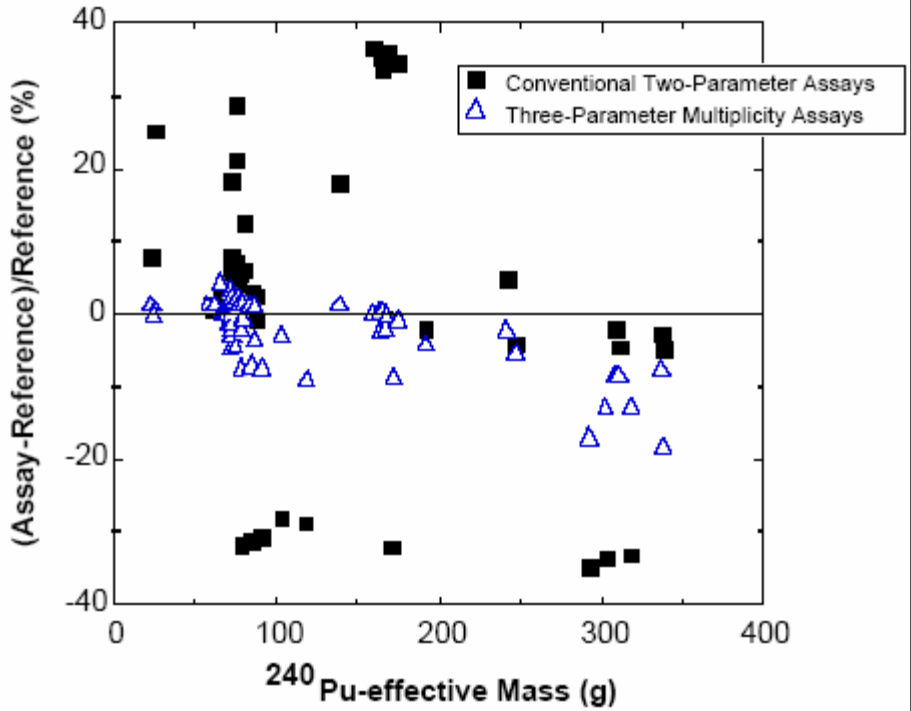
$$T = \frac{1}{6}F\varepsilon^3 f_t M^3\left\{\nu_{s3} + \left(\frac{M-1}{\nu_{i1}-1}\right)[3\nu_{s2}\nu_{i2} + \nu_{s1}(1+\alpha)\nu_{i3}] + 3\left(\frac{M-1}{\nu_{i1}-1}\right)^2 \nu_{s1}(1+\alpha)\nu_{i2}^2\right\}$$

Converts S, D, T counting rates into item properties: spontaneous fission rate (F) (proportional to Pu mass), ratio of (α,n) to spontaneous fission neutrons (α), multiplication (M)

Improvement over Coincidence Counting



Five Ring Multiplicity Counter results for 8 Pu metal samples



Metal and Oxide results using In-Plant Pyrochemical Multiplicity Counter

N. Ensslin, et al., "Application Guide to Neutron Multiplicity Counting", LA-13422-M (1998)

Applicability of Multiplicity Counting

Table 7.1. Summary of past or expected multiplicity counter performance on various nuclear material categories. A well-designed multiplicity counter with roughly 50% to 55% detection efficiency is used, unless otherwise specified in the text.

Nuclear Material Category	SNM Mass (g)	(α,n)/sf rate α	Counting Time (s)	Assay Precision (% RSD)	Assay Bias (%)	References
Plutonium Metal	2000 g	0 to 0.2	1000 s	7.1%	-10.6%[a]	Langner 91b
	2000 g	0 to 0.2	3000 s	5.1%	-4.7%[a]	Krick 92b
	4000 g	0 to 0.2	1800 s	2.0%	0.0%	Langner 93b
	200-4000 g	0 to 1.3	3600 s	3.3%	-1.8%	Ensslin 98
Plutonium Oxide	2000 g	1	5000 s	0.7%	0.6%	Langner 91b
	1000 g	1	3000 s	0.8%	-2.7%	Krick 92b
	1000 g	1	1800 s	2.2%	-0.1%	Langner 93b
	4000 g	1-4	1800 s	3.0%	2.4%	Stewart 95
	1000 g	1-4	600 s	1-3%	0.9%	Stewart 98
Plutonium Scrap	100 g	5	1000 s	12%	2-5%	Langner 92
	100-1200 g	1-6	3600 s	4.5%	1.5%	Ensslin 98
Plutonium Residues	120 g	13-29	3000 s	20%	2-10%	Krick 92b
	300 g	7-34	3600 s	18.9%	-4.0%	Ensslin 98
	20-100 g	8-30	3600 s	7%	7%	Langner 98
	100 g	5-9	3600 s	8.7%	3.2%	Langner P.C.
Plutonium Waste (estimated)	1 g	1	1000 s	2%	1-2%	Ensslin 95
	1 g	5	1000 s	10%	2-5%	Ensslin 95
	1 g	20	1000 s	50%	5-10%	Ensslin 95
Plutonium Oxide in Excess Weapons Materials	1000 g	1 - 10	1500 s	6.0%	0.02%	Stewart 96
	1000 g	1 - 8	1000 s	5.0%	1.0%	Stewart 97(PC)
	4000 g	1 - 6	1800 s	4.2%[b]	0.8%	Langner 96b
	4000 g	1 - 6	1800 s	5.8%[c]	-1.0%	Langner 97b
Mixed Uranium/ Plutonium Oxide	300 g	1 - 2	1000 s	1-2%	1-3%	Menlove 93
Large Drum Inventory Verification	1 - 4000 g	1 - 6	6 - 12 h	10.2%	-0.5%	Rinard 97
	1 - 4000 g	7 - 50	6 - 12 h	N/A	N/A	Rinard 97

[a] Assay bias quoted without multiplication correction curve for metal.
[b] Assay precision based on counting statistics, gamma-ray isotopics, and scatter relative to calorimetry.
[c] Assay precision based on counting statistics and scatter relative to destructive analysis.

N. Ensslin, et al., "Application Guide to Neutron Multiplicity Counting", LA-13422-M (1998)

Los Alamos

Point Model Assumptions

All induced fission neutrons are emitted simultaneously with original spontaneous fission or (α,n) reaction. (superfission concept) (neutrons reflected back into sample)

Uniform detection efficiency and probability of fission over sample volume. (point model) (dense or thick materials have variable probability of fission over sample volume.)

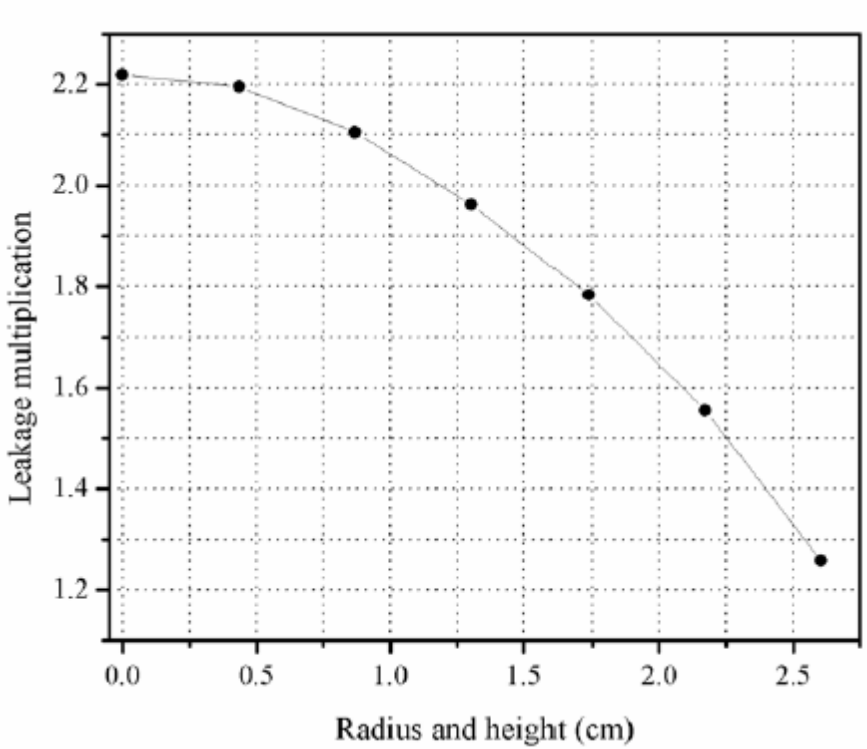
Neutrons from (α,n) reactions in sample have same energy spectrum as spontaneous fission neutrons. (Strictly true only for pure plutonium oxide)

Neutron capture without multiplication is negligible. (Presence of poly or water in item).

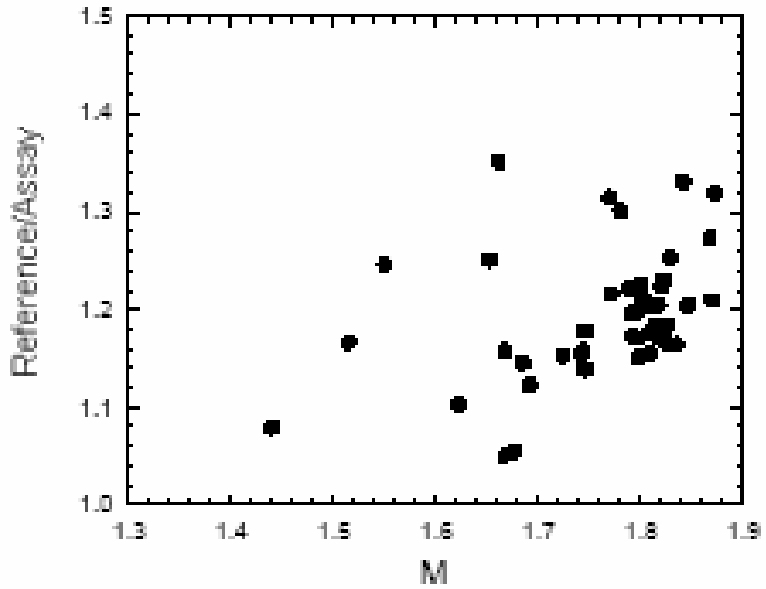
No correlation between neutron multiplicity and neutron energy emitted in each fission.

High Multiplication Pu Samples

MCNPX
2 kg Pu metal cylinder (dia=height)



Savannah River Site (SRS)
FB Line NMC
(uncorrected)



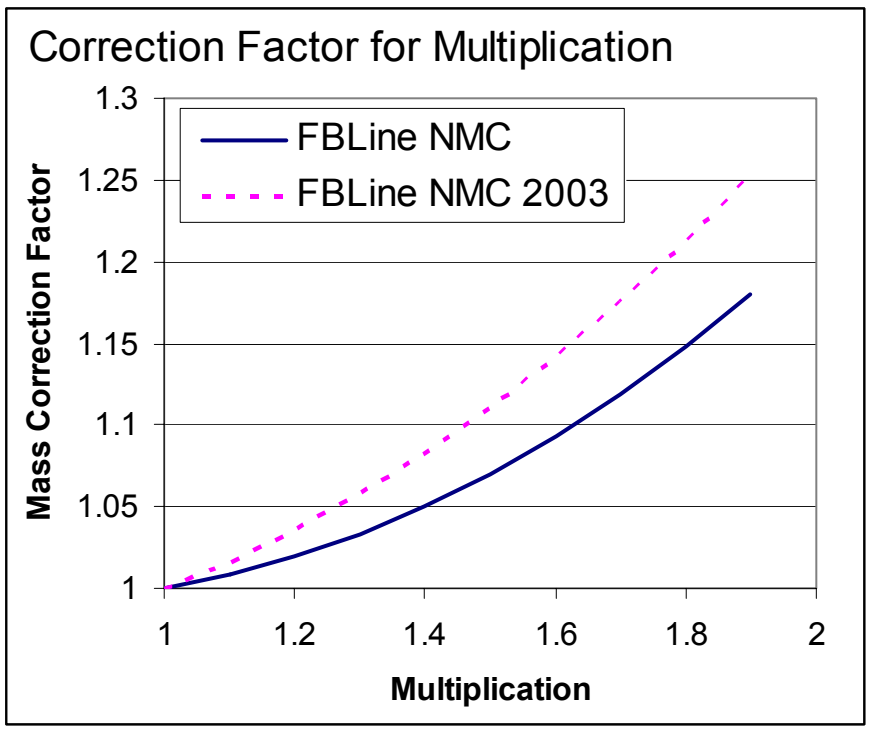
W.H Geist, et al.
"Analysis of FB-Line Neutron Multiplicity Counter Data"
LA-UR-00-5792

Empirical Corrections

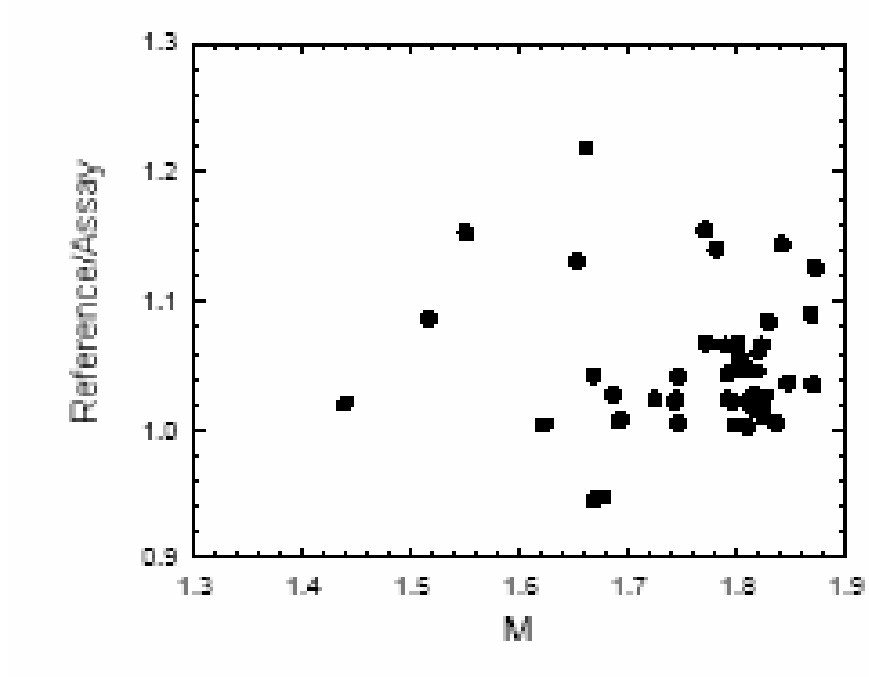
$$m_{240,corr} = m_{240} \cdot CF_M$$

$$CF_M = a + b(M-1) + c(M-1)^2$$

a,b,c empirically determined constants



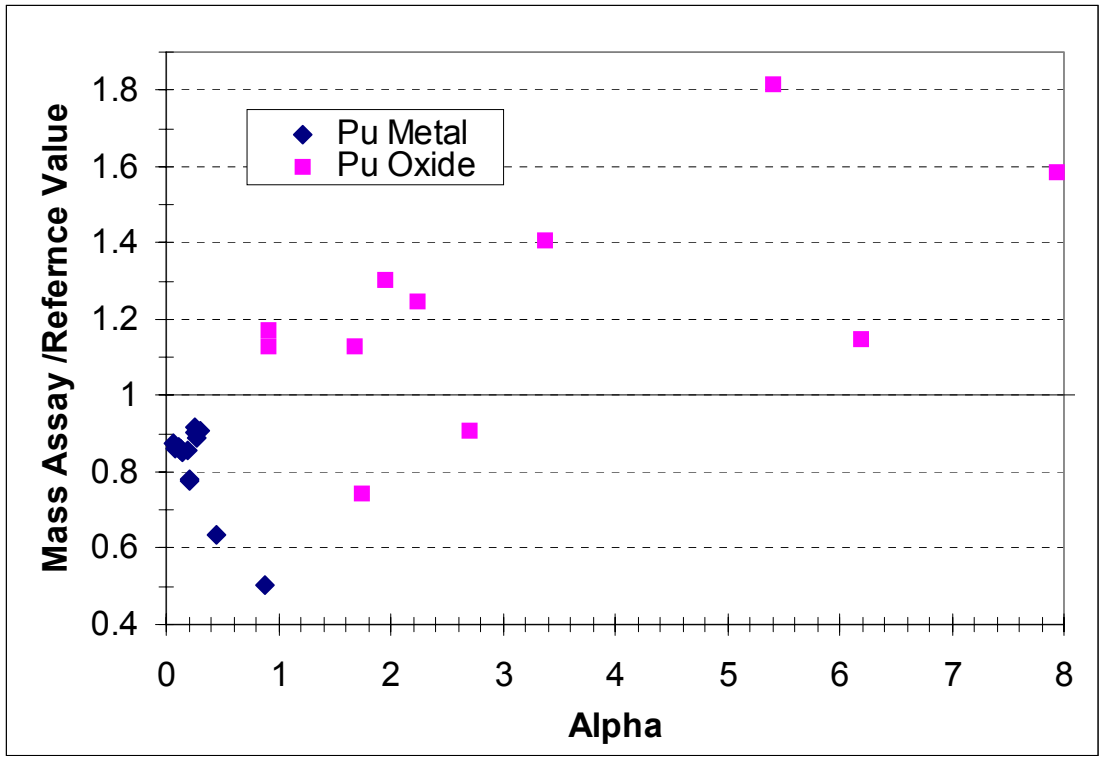
SRS FB Line NMC



W.H Geist, et al.
"Analysis of FB-Line Neutron Multiplicity Counter Data"
LA-UR-00-5792

Impure items

KAMS NMC at SRS



W. Geist (2005)

MCNPX-Version 2.5f

Monte Carlo transport code - simulates transport of particles (neutrons) through given physical setup.

Utilizes point wise cross section data for every material to determine the effects of interactions between the particle and the medium on the motion of the particle.

Spontaneous fission sources which produces neutrons with appropriate multiplicity and energy.

Able to track the time neutrons are born and detected. (coincident rates)

Coincidence capture events can be tallied with either infinite gate length or with practical pre-delay and gate width values. (can now directly calculate S,D,T counting rates as well as doubles and triples gate fractions).

Ideal Analysis

Analysis of S,D,T rates to determine m,α,M with no assumptions in real time.

Ideally, one could use MCNPX to simulate every measurement to match the measured counting rates in order to determine the item properties. (impractical to implement, impossible to verify)

A more useful approach is to build into the multiplicity model corrections which address the critical assumptions based on MCNPX calculations (requires reference materials to benchmark the calculations).

Weighted Point Model

The standard point model multiplicity equations have been modified as follows:

$$S = F\varepsilon\nu_{s1}M(1+\alpha)$$

$$D = \frac{1}{2}F\varepsilon^2\nu_{s2}f_dM^2(f_D+\alpha f_D^{\alpha})$$

$$T = \frac{1}{6}F\varepsilon^3\nu_{s3}f_tM^3(f_T+\alpha f_T^{\alpha})$$

where:

$$f_D = w_D[1+\alpha(M-1)]$$

$$f_D^{\alpha} = w_D^{\alpha}a(M-1)$$

$$f_T = w_T[1+b(M-1)+c(M-1)^2]$$

$$f_T^{\alpha} = w_T^{\alpha}[d(M-1)+c(M-1)^2]$$

$w_D, w_D^{\alpha}, w_T, w_T^{\alpha}$ are variable multiplication weighting factors calculated using MCNPX

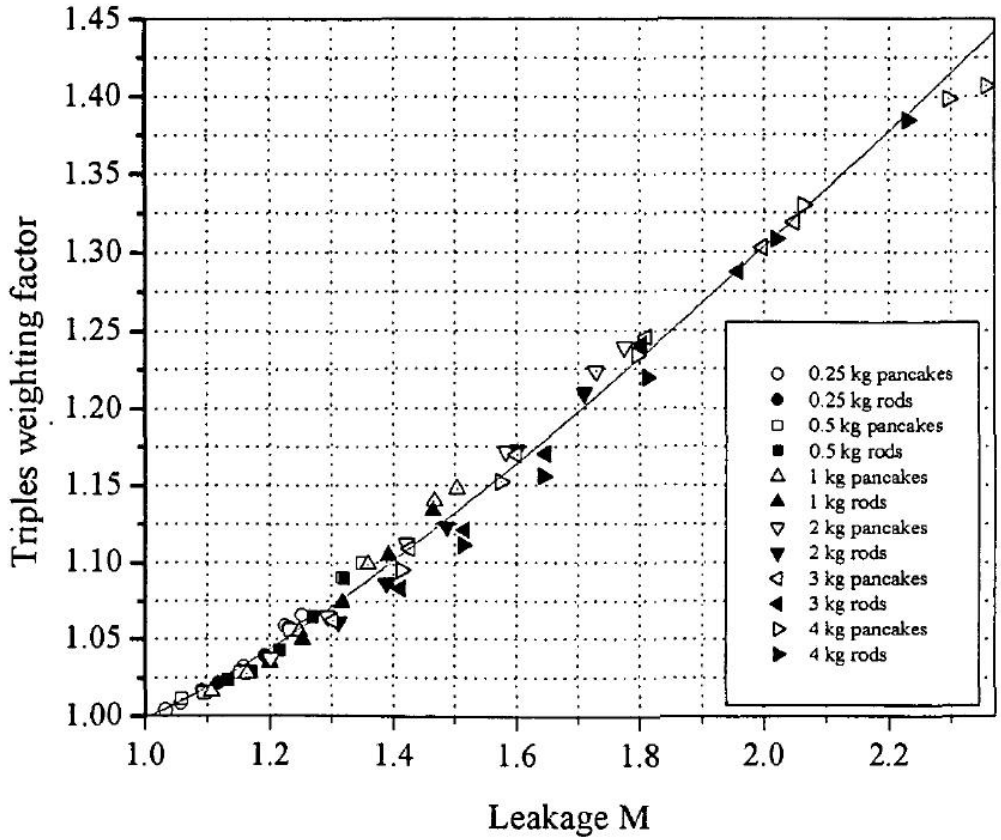
From LA-UR-04-1149 Reduction of Bias in Neutron Multiplicity Assay Using a Weighted Point Model, W.H. Geist, et al., 7th International Conference on Facility Operations-Safeguards Interface, Charleston, SC, February 29-March 5, 2004

Weighting Factor Calculation

Triples weighting factor (w_T) calculated by taking ratio of MCNPX triples rates to standard point model rates.

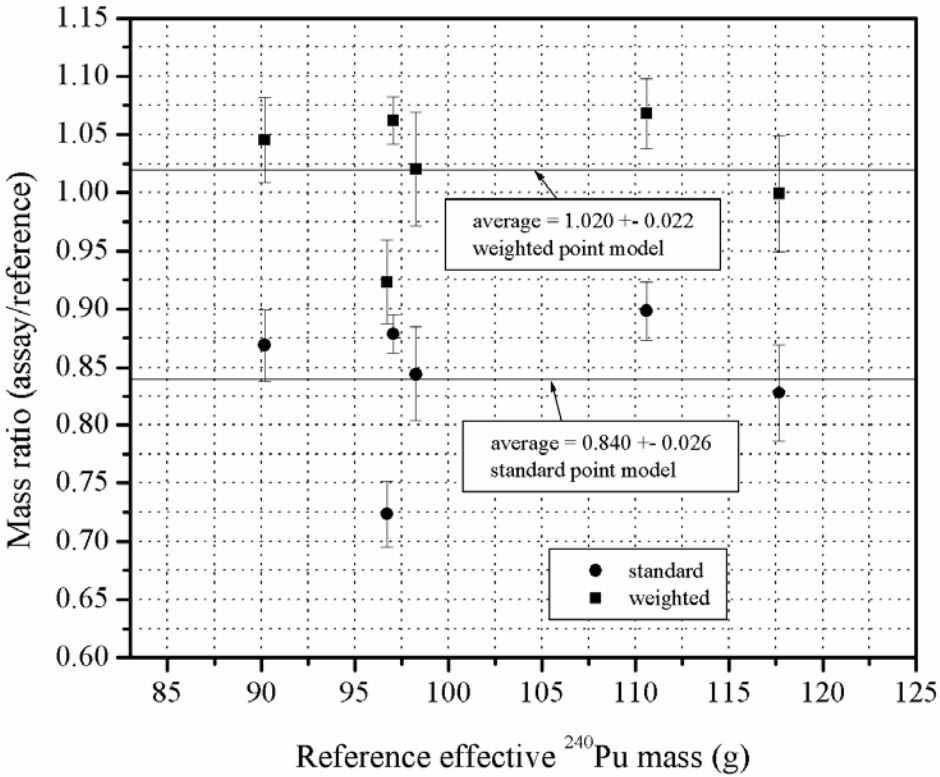
Weighting factors calculated for wide range of cylindrical shaped Pu metal show consistent relationship to leakage Multiplication.

MCNPX Calculations



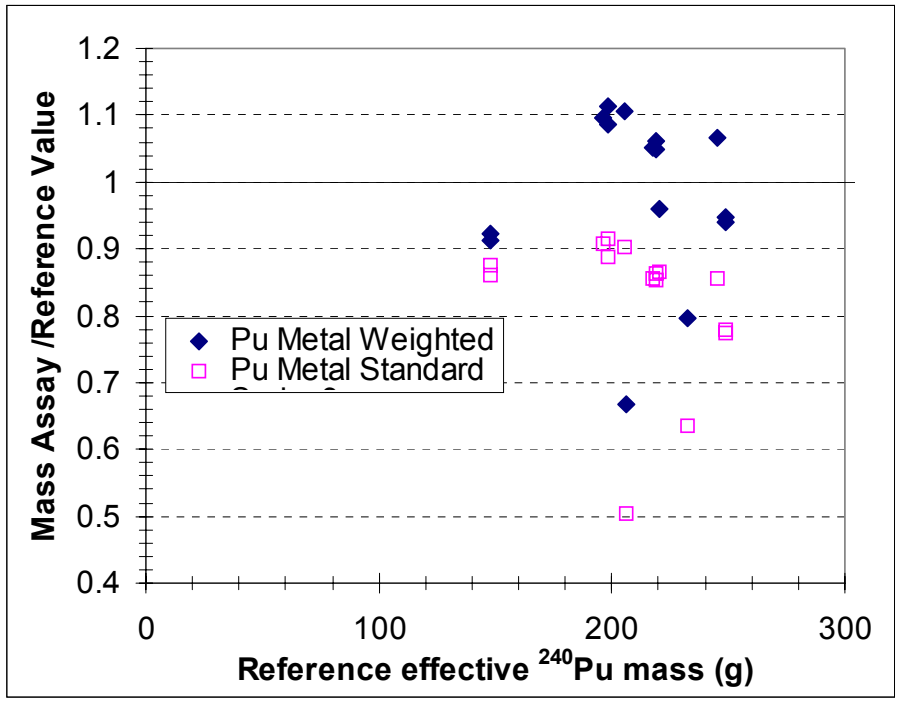
Weighted Point Model Results

SRS FBLine NMC



From LA-UR-04-1149 Reduction of Bias in Neutron Multiplicity Assay Using a Weighted Point Model, W.H. Geist, et al., 7th International Conference on Facility Operations-Safeguards Interface, Charleston, SC, February 29-March 5, 2004

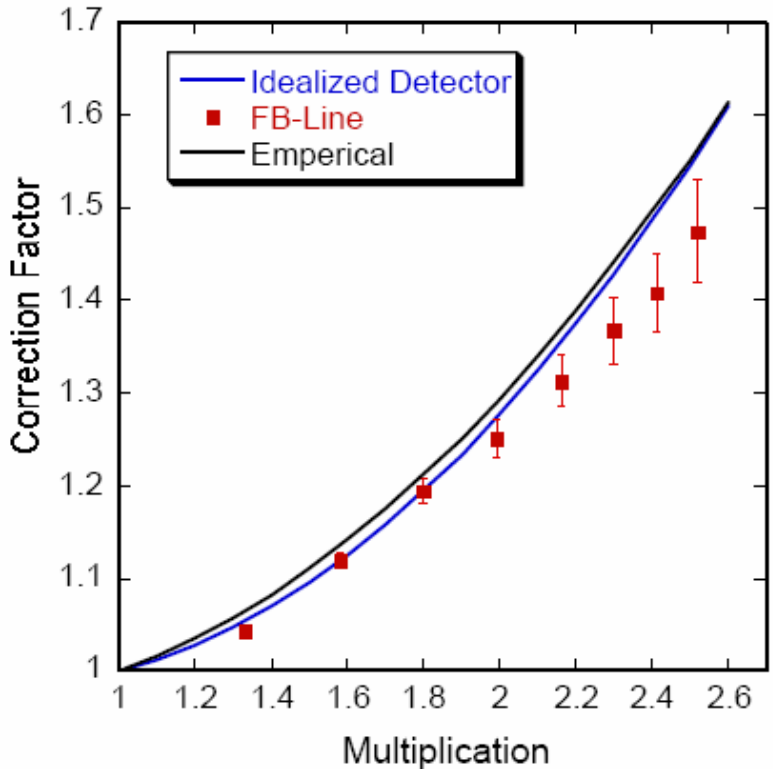
SRS KAMS NMC

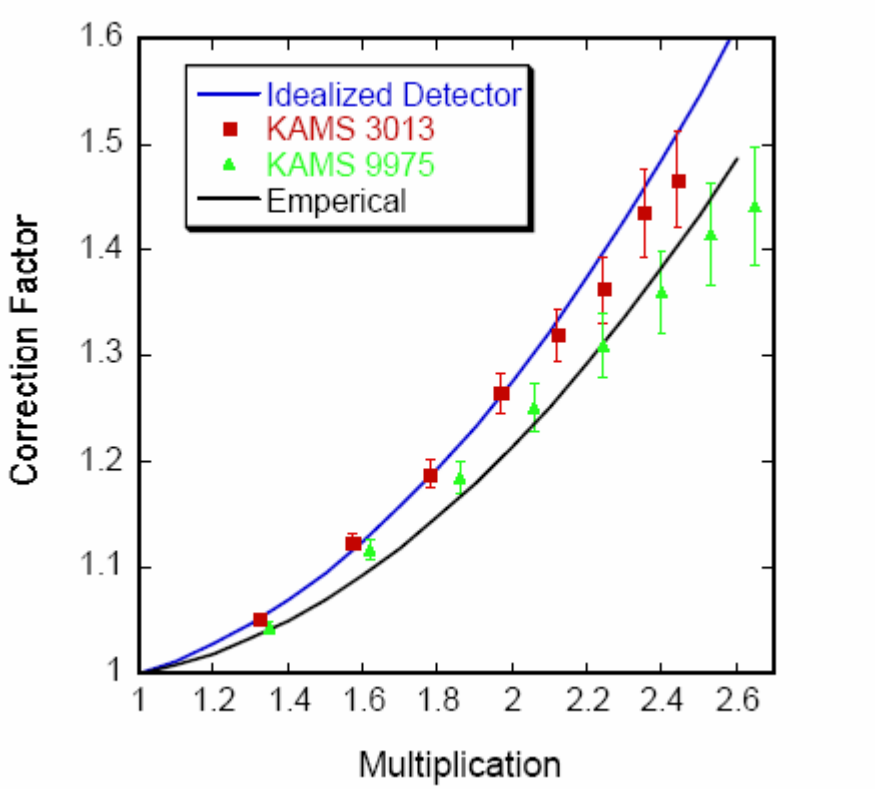


W. Geist (2005)

General Multiplication Correction Factors

MCNPX calculations of correction factors:





W.H Geist,
"Multiplication Dependent Correction Factors for Multiplicity Assay of Plutonium Metal Items"
LA-UR-05-3001

General Multiplication Correction Factors

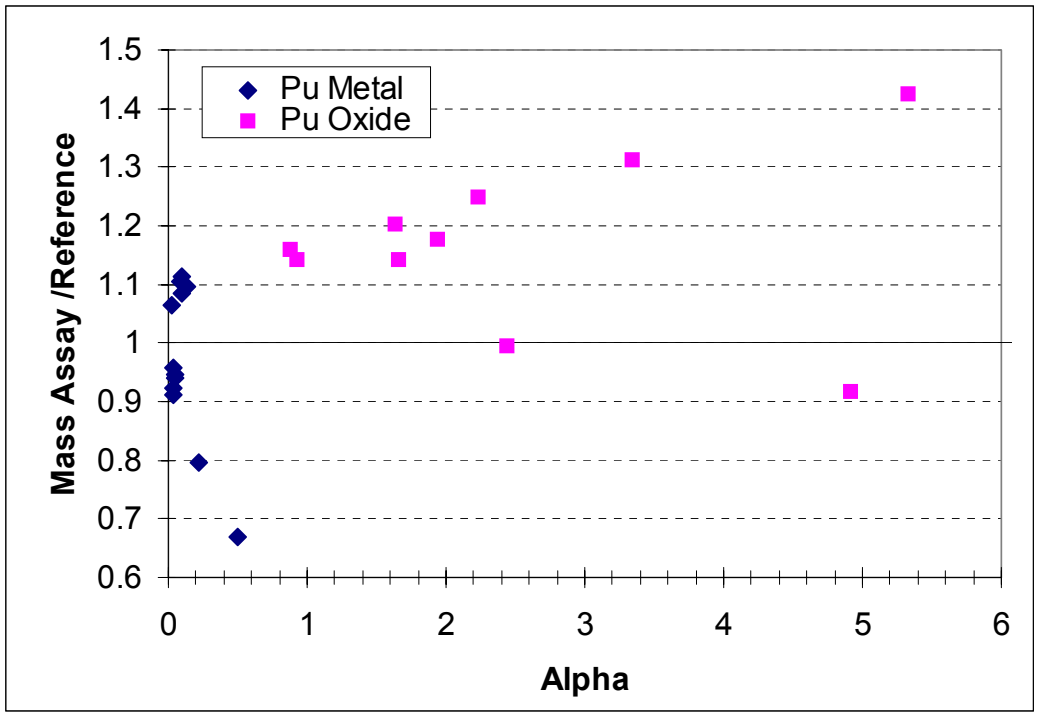
Difference between calculated multiplication dependent correction factors for the ideal detector and various detector systems:

Detector	Percent Difference		
	M = 1.5	M = 2.0	M = 2.5
LNMC	-0.42	-0.22	0.34
LNMC w/ 3013 container	-1.17	-2.25	-3.10
KAMS NMC w/ 3013 container	0.33	-0.55	-2.05
KAMS NMC w/ 9975 container	-1.56	-4.63	-8.18
FB Line NMC	-0.75	-2.15	-3.74
ENMC	-0.46	-1.96	-3.88
10-atm PSMC	0.29	-1.42	-4.14
10-atm PSMC w/ ss container	-1.50	-3.39	-5.20

W.H Geist,
"Multiplication Dependent Correction Factors for Multiplicity Assay of Plutonium Metal Items"
LA-UR-05-3001

Impure Items

SRS KAMS NMC Data analyzed using the Weighted Point Model

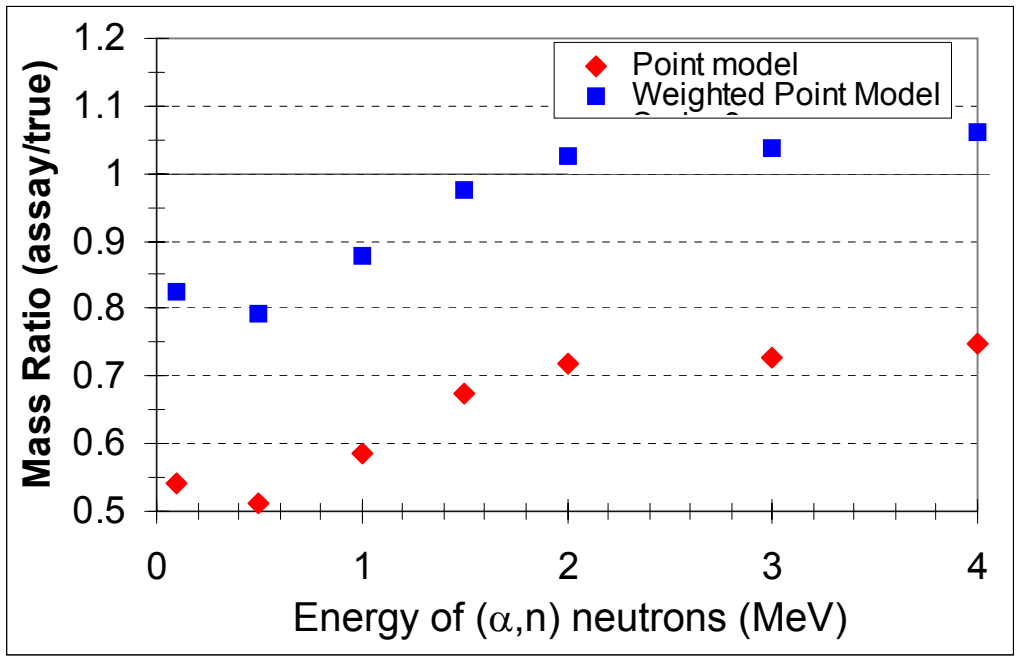


W. Geist (2005)

While use of the Weighted Point Model has successful reduced the bias associated with variable multiplication, assay results still dependent on alpha.

(α,n) Neutron Energy

MCNPX calculations with an ideal detector
(ε=100%, f_d=1, f_t=1)
2 kg Pu metal cylinder with α=1, M = 1.88



Energy Dependent Weighted Point Model

The weighted point model multiplicity equations have been modified as follows:

$$S = mF_0 \varepsilon \nu_{s1} M \left(1 + \alpha \left[\frac{(M\nu_{i1}^{\alpha} + (\nu_{i1} - \nu_{i1}^{\alpha}) - 1)}{(M\nu_{i1} - 1)} \right] \right)$$

$$D = \frac{1}{2} mF_0 \varepsilon^2 \nu_{s2} f_d M^2 (f_D + \alpha f_D^{\alpha})$$

$$T = \frac{1}{6} mF_0 \varepsilon^3 \nu_{s3} f_t M^3 (f_T + \alpha f_T^{\alpha})$$

where:

$$f_D = w_D \left[1 + (M-1) \left(\frac{\nu_{s1}\nu_{i2}}{\nu_{s2}(\nu_{i1} - 1)} \right) \right]$$

$$f_D^{\alpha} = w_D^{\alpha} \left(\frac{\nu_{s1}(M-1)\left[\nu_{i2}^{\alpha}(\nu_{i1} - 1) + (M-1)\nu_{i1}^{\alpha}\nu_{i2}\right]}{\nu_{s2}(\nu_{i1} - 1)(M\nu_{i1} - 1)} \right)$$

$$f_T = w_T \left[1 + (M-1) \left(\frac{3\nu_{s2}\nu_{i2} + \nu_{s1}\nu_{i3}}{\nu_{s3}(\nu_{i1} - 1)} \right) + (M-1)^2 \left(\frac{3\nu_{s1}\nu_{i2}^2}{\nu_{s3}(\nu_{i1} - 1)^2} \right) \right]$$

$$f_T^{\alpha} = w_T^{\alpha} \left[\frac{\nu_{s1}(M-1)}{\nu_{s3}(M\nu_{i1} - 1)} \left(\nu_{i3}^{\alpha} + \frac{(M-1)(3\nu_{i2}^{\alpha}\nu_{i2} + \nu_{i1}^{\alpha}\nu_{i3})}{\nu_{i1} - 1} + \frac{3(M-1)^2 \nu_{i1}^{\alpha}\nu_{i2}^2}{(\nu_{i1} - 1)^2} \right) \right]$$

Changes made to WPM

Ring Ratio

In all multi-ring neutron multiplicity counters, ratio of counts in outer ring to number of counts in inner ring for a given sample is dependent on the neutron energy exiting the sample.

To determine the energy from neutrons from (α,n) reactions, one can utilize the algorithm developed for the International Neutron Coincidence Counting code (INCC):

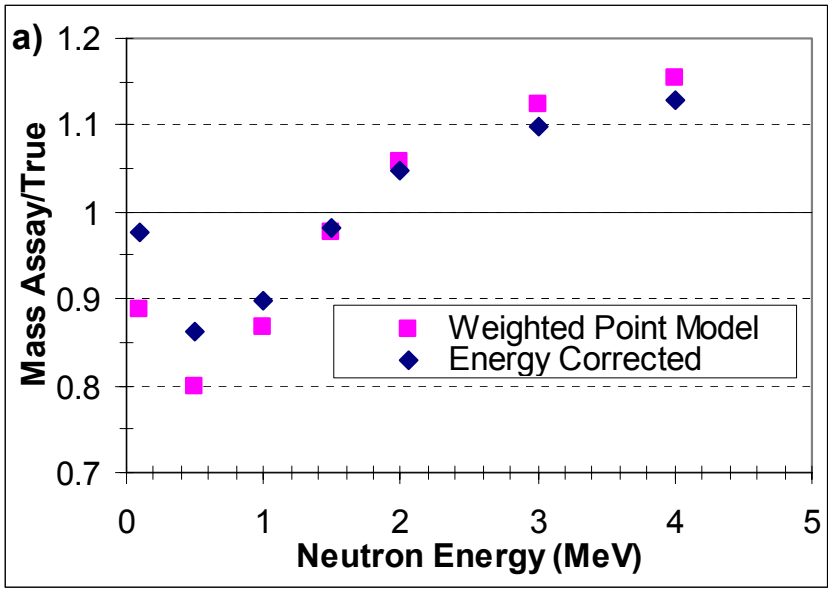
$$S_f = mF_o M\nu_{s1}\left[1+\left(\frac{M-1}{M\nu_{i1}-1}\right)\alpha\nu_{i1}^{\alpha}\right]$$ Total production rate from fission

$$r_r = \frac{S_o - \varepsilon_o S_f}{S_i - \varepsilon_i S_f}$$ Ring Ratio for (α,n) neutrons

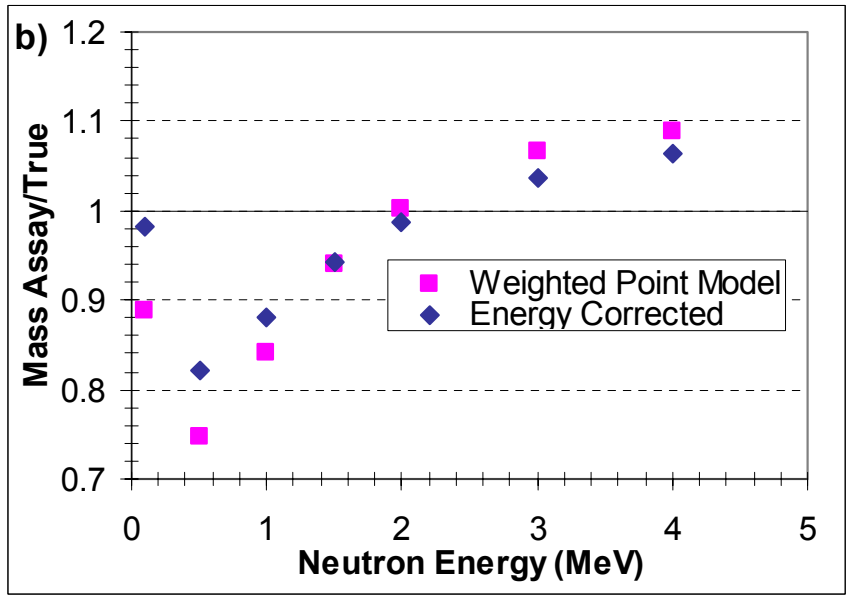
Results with Ring Ratio

MCNPX Calculations

SRS FBLine NMC



SRS KAMS NMC



- Item simulated was a 1.5 kg Pu metal cylinder (α=1 M= 1.75)
- ~25-30% reduction in spread of assay values from 0.5 – 4 MeV

Results with Ring Ratio

MCNPX Calculations

Impure Pu Metal Item			FBLNMC		KAMS NMC	
Mass (g)	Alpha Value	Multiplication	Average Reduction in Bias (%)	Reduction in Spread (%) (0.5 – 4 MeV)	Average Reduction in Bias (%)	Reduction in Spread (%) (0.5 - 4 MeV)
100	0.5	1.08	36.2	35.5	- 1.6	40.0
100	1	1.08	39.8	37.7	-1.1	41.4
1500	0.5	1.75	24.3	18.7	27.0	22.2
1500	1	1.75	31.0	25.6	34.3	29.0
1500	0.5	1.66	24.4	19.8		
1500	1	1.66	31.0	26.5		
1500	0.5	1.5	27.3	22.0	1.7	18.1
1500	1	1.5	32.3	27.0	26.1	31.8
1000	0.5	1.59			27.4	23.8
3581	0.5	1.99			23.8	21.5

In general, ~15-40% reduction in assay dependence on E_n

Quad Parameter

By first solving for m_{eff}, α, and M using the energy-independent weighted point model, one can calculate a quad parameter, Q_P:

$$Q_P = \frac{Q_\alpha}{(Q - Q_{sf})}$$

where Q – measured quad counting rate

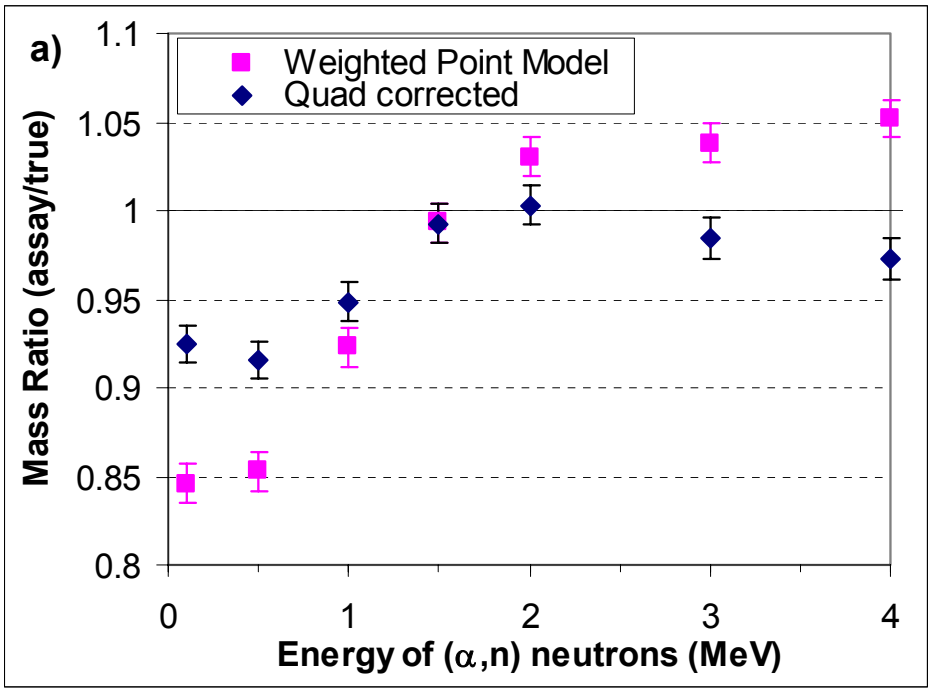
Q_{sf} – calculated quad rate from spontaneous fission

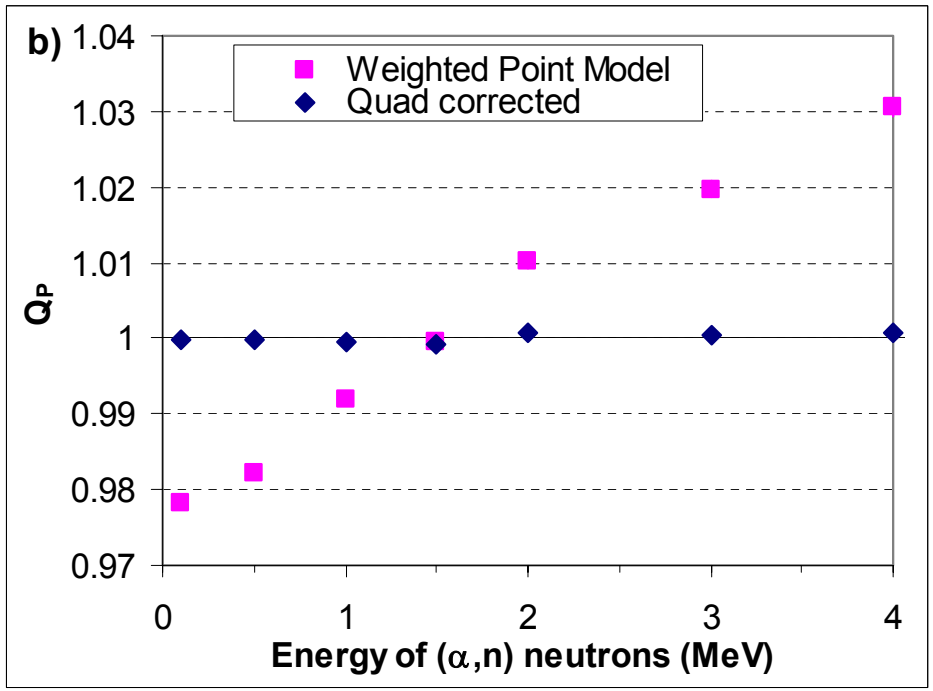
Q_α - calculated quad rate from (α,n) reactions

If energy-independent weighted point model properly describes sample, Q_P equals 1.

Ideal Detector Results

MCNPX calculations for a 1.5 kg Pu metal cylinder with $\alpha = 1$
(Triples statistical uncertainty = 0.2 %)

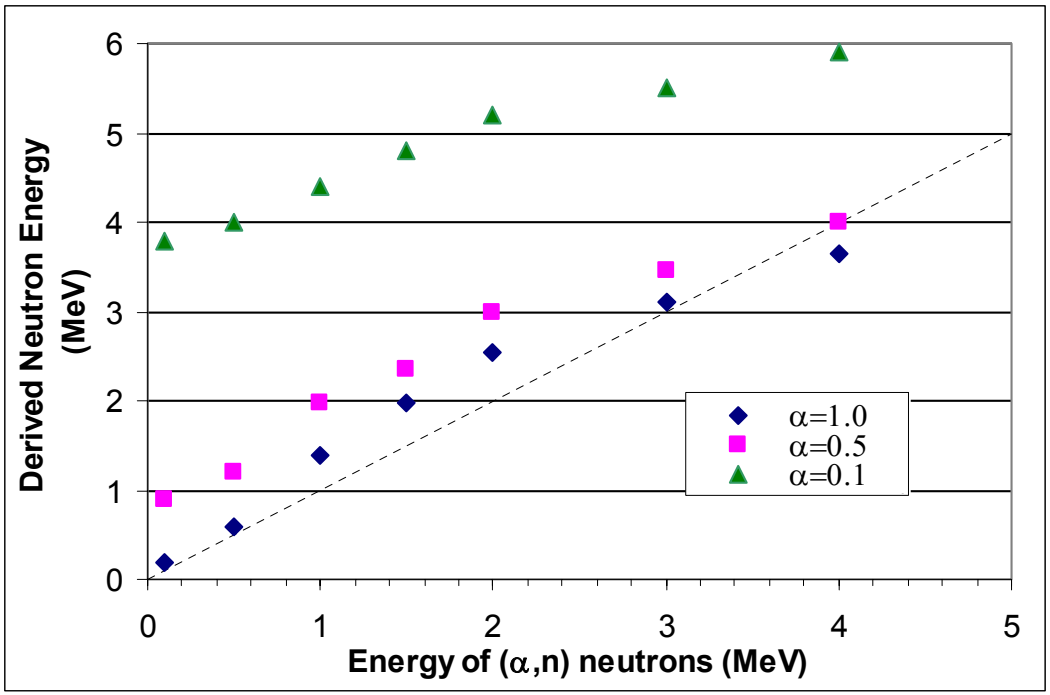




~ 56% reduction in spread of Assay/True ratios from 0.5 to 4 MeV

Ideal Detector Results

Derived E_n for neutrons from (α,n) reactions



Ideal Detector Results

MCNPX Calculations

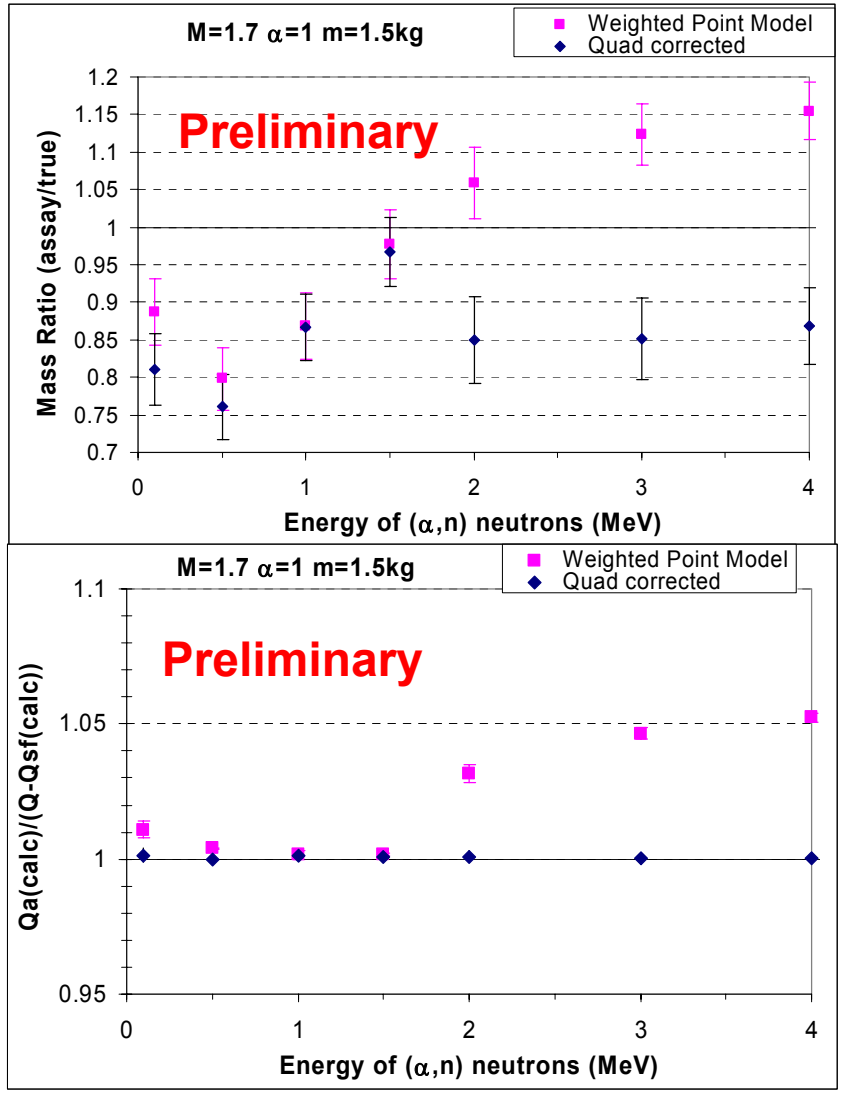
Mass (g)	Alpha Value	Multiplication	Average Reduction in Bias (%)	Reduction in Spread (%) 0.5 – 4 MeV
2000	1.5	1.79	50.6	51.7
2000	1	1.79	52.8	42.3
2000	0.5	1.79	18.0	13.2
2000	0.1	1.79	-61.6	-70.9
2000	1	1.2	51.9	42.8
2000	0.5	1.2	47.2	42.1
2000	0.1	1.2	-14.9	39.0
1000	1	1.51	42.3	49.1
1000	0.5	1.51	5.5	29.1
1500	1	1.45	28.0	55.7
1500	0.5	1.45	5.1	53.4

Minimum value $\alpha \approx 0.5$ needed

Future work with Quads

Test use of Quad parameter with the FBLine NMC and KAMS NMC simulations to see how detection efficiency and quad gate fractions effect results.

Take measurements of Quads with an NMC to test practical usefulness of quads



SRS FBLine NMC

Summary

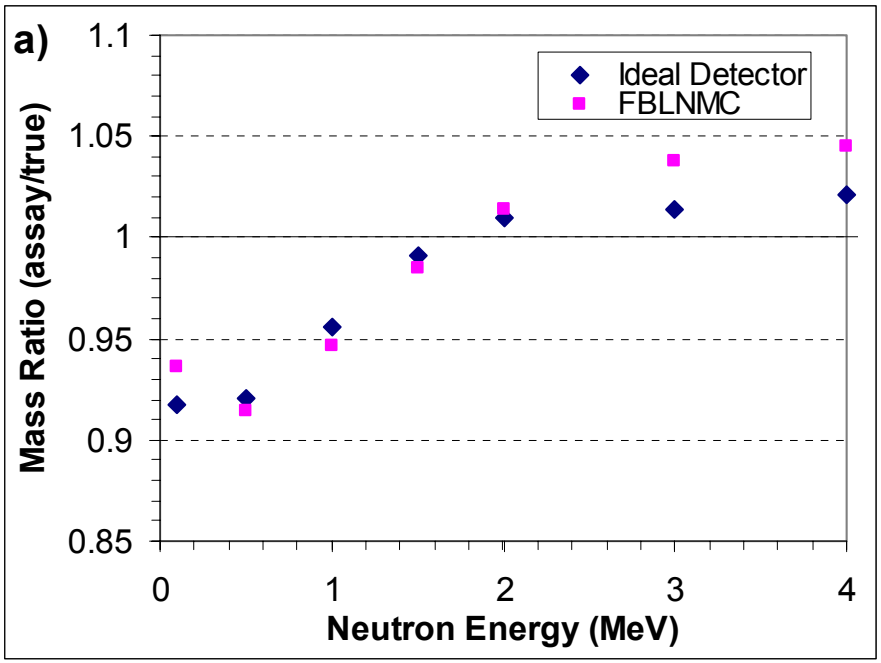
Multiplicity assay using the standard point model is quite applicable for relatively pure Pu metals and oxides. Assumptions in the point model causes bias to occur for highly multiplying and/or highly impure items.

Newly developed features in MCNPX has fostered the development of techniques and methods to address these biases (WPM, general multiplication correction factors, Energy Dependent WPM)

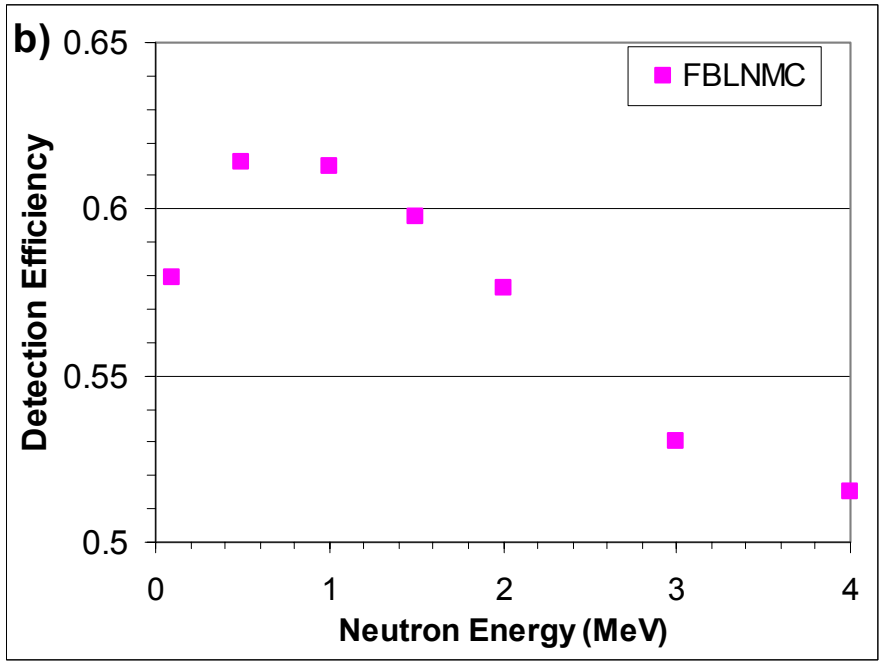
Possible future enhancements to multiplicity counting include use of quad counting rates to ascertain how well model matches item parameters

Detection Efficiency Assumption

MCNPX Calculations of 1.5 kg Pu metal α=0.5



MCNPX Calculated Detection Efficiency

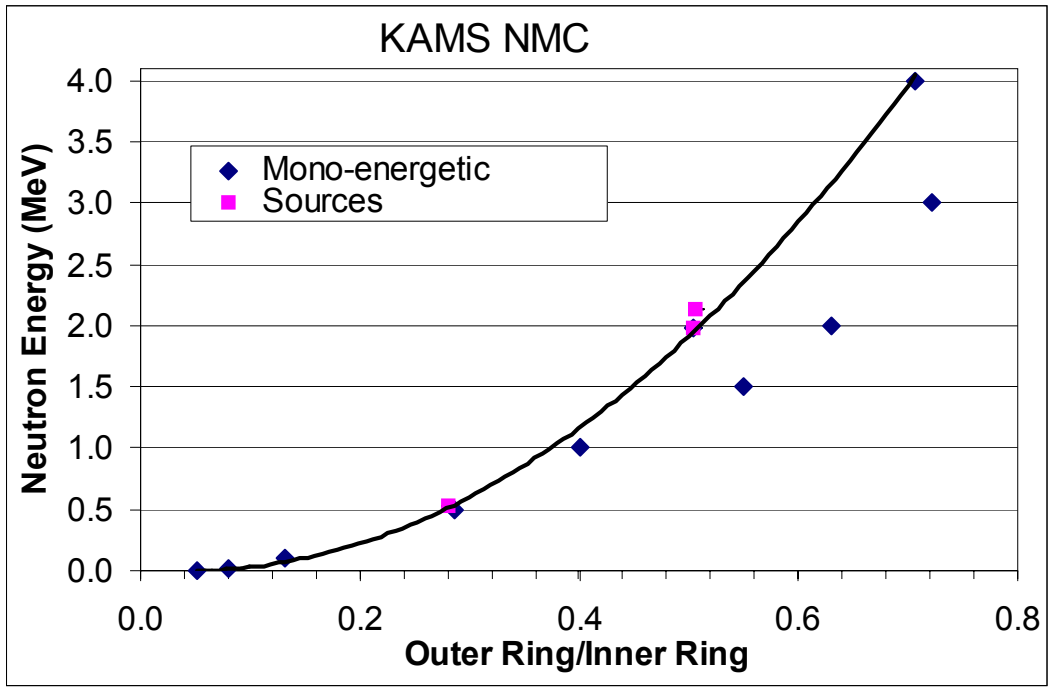


Note: Ideal detector detection efficiency = 1 at all energies

Ring Ratio Calibration

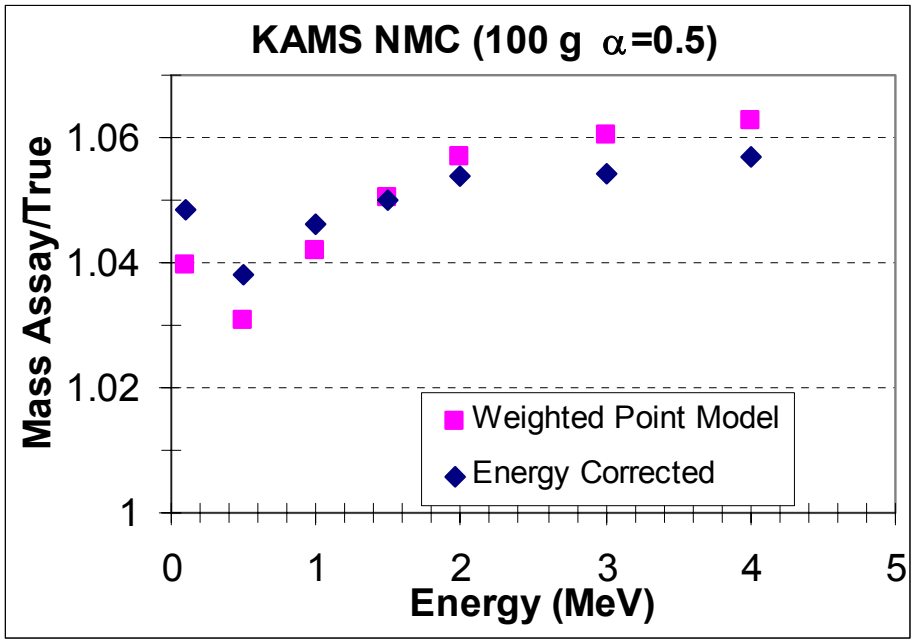
MCNPX calculated Ring Ratio Calibration for SRS KAMS NMC detector

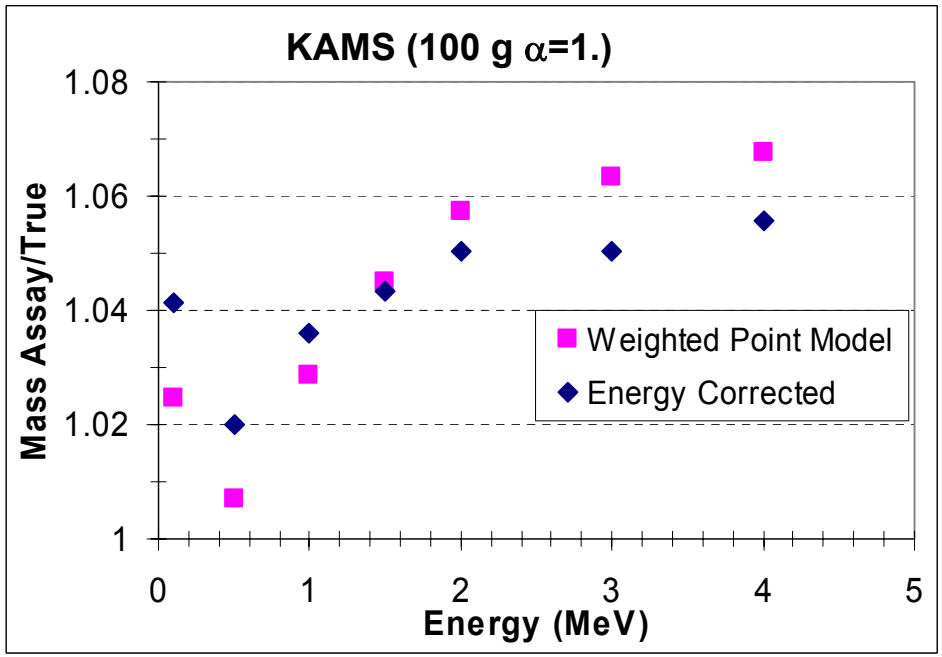
Mono-energetic sources along with ^{252}Cf, ^{240}Pu, AmLi neutron energy spectra used



Shift between sources and mono-energetic neutrons due to sharp drop in inner ring detection efficiency at large neutron energies

Results with Ring Ratio





WPM calculations for 100 g item in KAMS show ~5% bias at all neutron energies.

Quad Counting Rates

An alternative method for determining (α,n) neutron energies utilizes the quad counting rates which are sensitive to the (α,n) neutron energy. The energy dependent weighted point model equation for the quad counting rates is:

$$Q = \frac{1}{24} m F_o \varepsilon^4 \nu_{s4} f_q M^4 (f_Q + \alpha f_Q^\alpha)$$

$$f_Q = w_Q \left[1 + a(M-1) + b(M-1)^2 + c(M-1)^3\right]$$

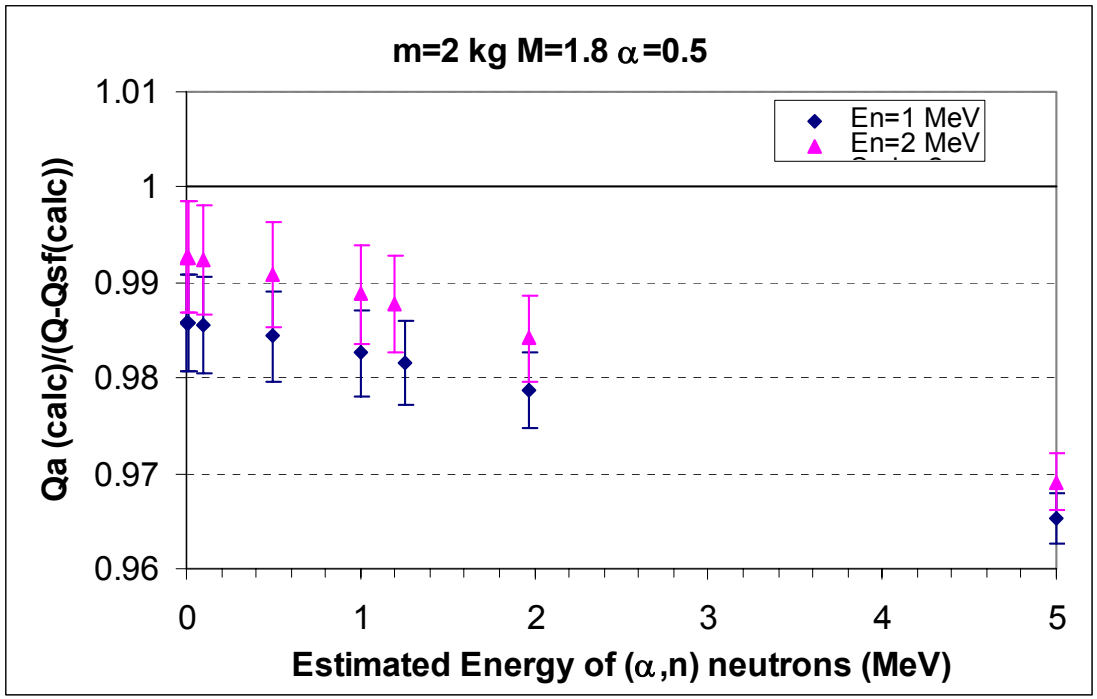
$$f_Q^\alpha = \frac{w_Q^\alpha \nu_{s1}(M-1)}{\nu_{s4}(M\nu_{i1}-1)} \left[\nu_{i4}^\alpha + d(M-1) + e(M-1)^2 + f(M-1)^3\right]$$

a, b, c are groupings of spontaneous and induced fission moments that are constant

d, e, f are groupings of spontaneous and induced fission moments that are dependent on (α,n) neutron energy

Ideal Detector Results

For some items and (α,n) neutron energies, Q_p not consistent with 1



Estimated energy of (α,n) neutrons lowered until Q_P consistent with asymptotic value closest to 1.

Non-Destructive Assay (NDA) techniques and measurements performed in support of nuclear material control and accountancy at the Atomic Weapons Establishment (AWE).

Presented By Tracy Dixon

Overview

- Describe NDA instrumentation used in the NMC&A Assay Suite
- Outline of the software used and the analysis performed
- Briefly describe the new Large Epithermal Multiplicity Counter (LEMC)

NMC&A Assay Suite

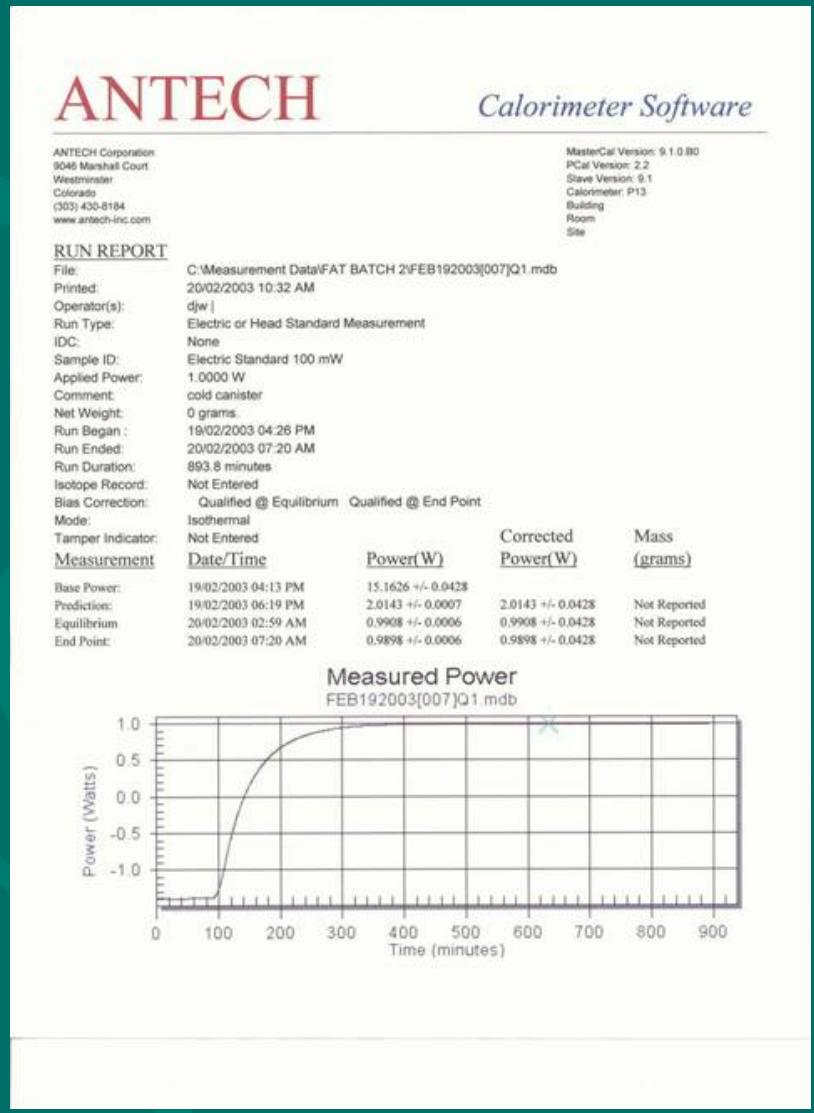
- To quantify isotopic composition and Pu content of the a range of Pu-bearing material for and NMA&C
- Out-of-line Isothermal Calorimeters
- Passive Neutron Coincidence Counter (PNCC)
- High Resolution Gamma Spectrometer (HRGS), Planar and Coaxial
- Future plans to introduce the Large Epithermal Multiplicity Counter (LEMC)
- Re-measurement database

Calorimeters

- AWE has both In-line and Out-of-line calorimeters
- The out-of-line calorimeters are used to measure a range of plutonium-bearing materials.
- Both calorimeters are operated in an isothermal mode, although one has a dual mode (heat flow) capability which increases the precision and accuracy at lower wattages (1mW-15mW).
- Measurement power range from 15mW to 15W.
- Sample canister size (internal diameter) 190mm x 356mm.

Calorimeter Software

- Calorimeters are run using a series of software packages that work as an integrated system. The MS DOS 6.2 Servo control Slave Software and a MS Windows NT4.0 operating platform.
- Software algorithms automatically determine the predicted endpoint, equilibrium endpoint and final end point.
- The prediction endpoint is declared when the measurement is within +/- 2mW.
- The equilibrium endpoint is declared when the measurement is with +/- 0.5mW.



ANTECH Calorimeter Software

ANTECH Corporation
9046 Marshall Court
Westminster
Colorado
(303) 430-8184
www.antech-inc.com

MasterCal Version: 9.1.0.80
PCal Version: 2.2
Slave Version: 9.1
Calorimeter: P13
Building
Room
Site

RUN REPORT

File: C:\Measurement Data\FAT BATCH 2\FEB192003[007]Q1.mdb
Printed: 20/02/2003 10:32 AM
Operator(s): djw |
Run Type: Electric or Head Standard Measurement
IDC: None
Sample ID: Electric Standard 100 mW
Applied Power: 1.0000 W
Comment: cold canister
Net Weight: 0 grams
Run Began : 19/02/2003 04:26 PM
Run Ended: 20/02/2003 07:20 AM
Run Duration: 893.8 minutes
Isotope Record: Not Entered
Bias Correction: Qualified @ Equilibrium Qualified @ End Point
Mode: Isothermal
Tamper Indicator: Not Entered

Measurement	Date/Time	Power(W)	Corrected Power(W)	Mass (grams)
Base Power:	19/02/2003 04:13 PM	15.1626 +/- 0.042$		
Prediction:	19/02/2003 06:19 PM	2.0143 +/- 0.0007	2.0143 +/- 0.042$	Not Reported
Equilibrium	20/02/2003 02:59 AM	0.990$ +/- 0.0006	0.990$ +/- 0.042$	Not Reported
End Point:	20/02/2003 07:20 AM	0.989$ +/- 0.0006	0.989$ +/- 0.042$	Not Reported

Electrical Calibrations

- Out-of-Line calorimeters are electrically calibrated using a traceable 10Ω electric sample
- Weekly automated calibrations for 15mW-15W
- Electrically calibrated due to the absence of certified reference standards

Applied Power (W)	Average Final Power (W)	Accuracy 1σ (%)	Precision1σ (%)	Ratio M/A
0.015	0.0144	5.3541	2.5396	0.9573
0.3	0.3001	0.1374	0.2199	1.0004
1.5	1.5063	0.6996	0.5151	1.0042
10	10.0036	0.0434	0.0265	1.0004
15	15.0006	0.0400	0.0398	1.0000

HRGS

- Two Coaxial HRGS systems
- Crystal size 50x50mm
- Energy Resolution @

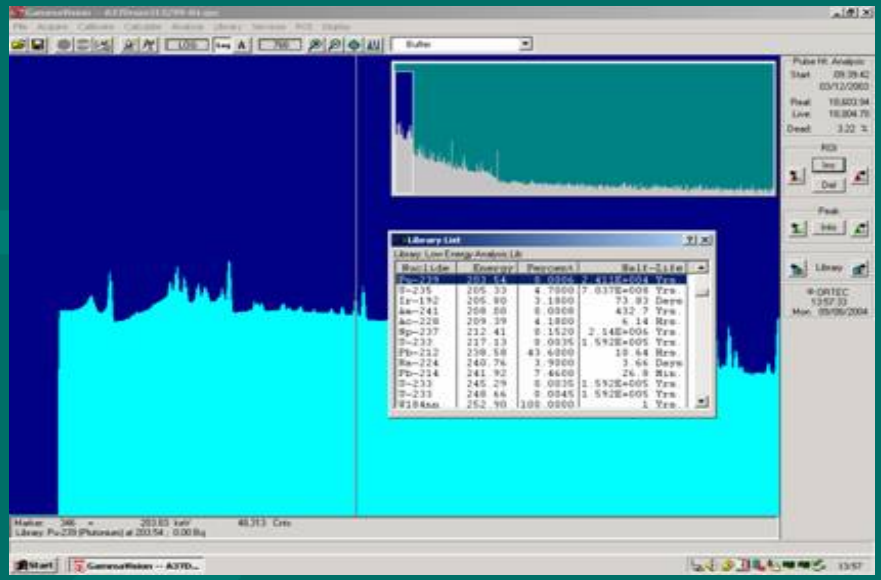
  122keV: FWHM 750eV

  1.33MeV: FWHM 1.75keV
- Two Planar HRGS systems
- Crystal size 25x15mm
- Energy Resolution @

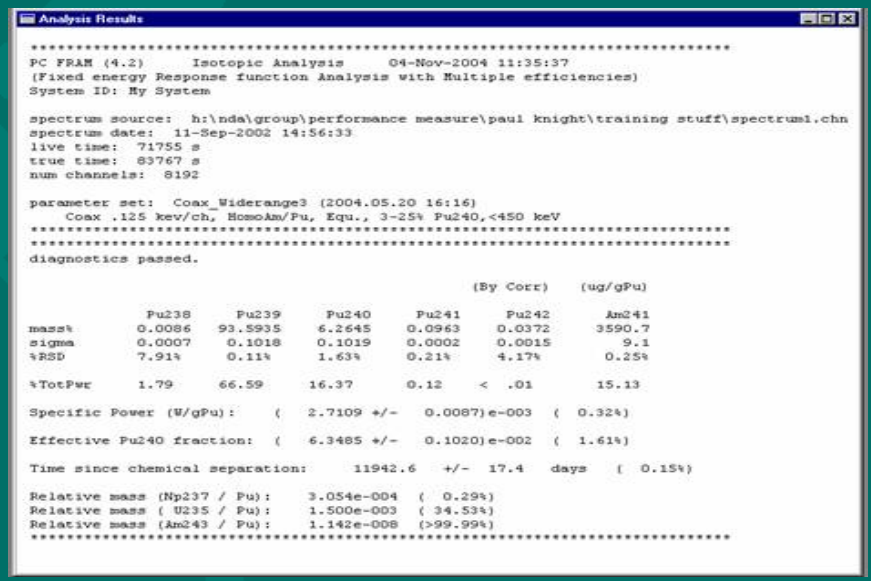
  122keV: 520eV
- Both digital and analogue Pulse Processing Electronics are used.
- Analogue NIM Bins and digital ORTEC DSPEC Plus

HRGS Software

- Gamma Vision – interfaces with PC and detector electronics as a MCA, acquiring a spectrum.



- PCFRAM – the Pu/U isotopic analysis software.



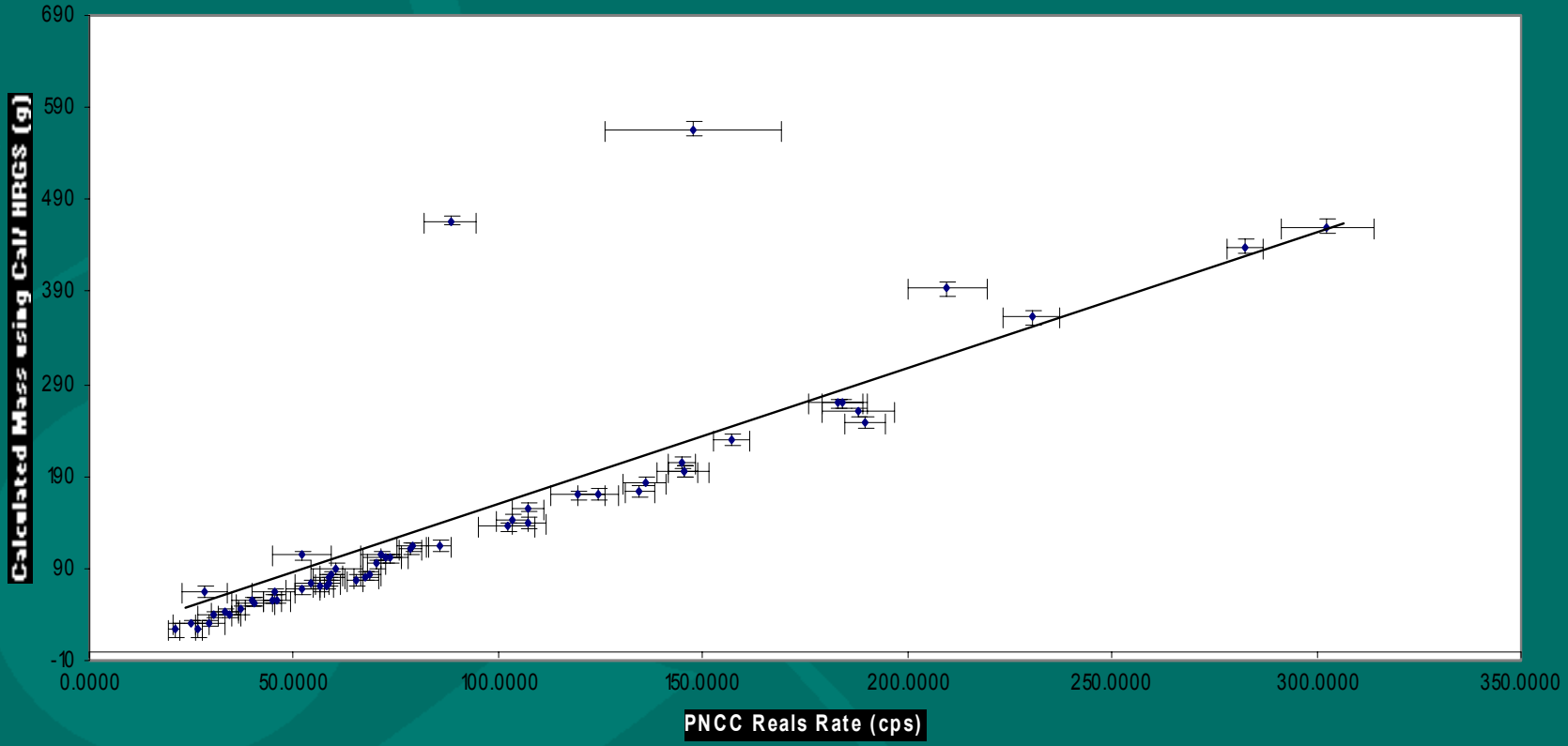
```
Analysis Results

**********************************************************************
PC FRAM (4.2)      Isotopic Analysis      04-Nov-2004 11:35:37
(Fixed energy Response function Analysis with Multiple efficiencies)
System ID: My System

spectrum source:  h:\nda\group\performance measure\paul knight\training stuff\spectrum1.chn
spectrum date:  11-Sep-2002 14:56:33
live time:  71755 s
true time:  83767 s
num channels:  8192

parameter set:  Coax_Widerange3 (2004.05.20 16:16)
    Coax .125 kev/ch, HomoAm/Pu, Equ., 3-25% Pu240,<450 keV
**********************************************************************
**********************************************************************
diagnostics passed.

                                                    (By Corr)   (ug/gPu)

             Pu238      Pu239      Pu240      Pu241      Pu242      Am241
mass%       0.0086    93.5935     6.2645     0.0963     0.0372    3590.7
sigma       0.0007     0.1018     0.1019     0.0002     0.0015       9.1
%RSD        7.91%      0.11%      1.63%      0.21%      4.17%      0.25%

%TotPwr      1.79      66.59      16.37       0.12     <  .01      15.13

Specific Power (W/gPu):     (   2.7109 +/-   0.0087)e-003   (  0.32%)

Effective Pu240 fraction:   (   6.3485 +/-   0.1020)e-002   (  1.61%)

Time since chemical separation:     11942.6   +/-  17.4   days    (  0.15%)

Relative mass (Np237 / Pu):    3.054e-004   (  0.29%)
Relative mass ( U235 / Pu):    1.500e-003   ( 34.53%)
Relative mass (Am243 / Pu):    1.142e-008   (>99.99%)
**********************************************************************
```

Passive Neutron Coincidence Counter

- HLNCC – II consists of 18 He-3 tubes encompassed in a cylindrical polyethylene body.
- Efficiency: 18.01+/- 0.14
- Used as a QC check for calorimeters
- Re-measurement database

Calorimeter and PNCC

A comparison between the measured mass of Pu ER Salts measured on the HLNCC-II, and that calculated using the data collated from the HRGS and Calorimeter.



Reals Rate Equation

$$R = M_{240} F_{Pu_{240}} M^2 \varepsilon^2 fd \frac{1}{2}\left[\nu_{S2} + (M-1)(1+\alpha)\left(\frac{\nu_{I2}\nu_{S1}}{\nu_{I1}-1}\right)\right]$$

M_{240}	Mass of Pu-240
F_{Pu240}	473.5 SF per sec per gram of Pu-240
M	Leakage Multiplication
fd	Gate Fraction
α	Alpha-ratio
v_{S1}	2.154 - 1st fractional moment of the Pu-240 SF prob. distribution
v_{S2}	3.789 - 2nd fractional moment of the Pu-240 SF prob. distribution
v_{I1}	3.163 - 1st fractional moment of the Pu-240 induced prob. distribution
v_{I2}	8.24 - 2nd fractional moment of the Pu-240 induced prob. distribution

Large Epithermal Multiplicity Counter

- Large Epithermal Multiplicity Counter (LEMC) utilizes 126 He-3 proportional tubes.
- Assay Cavity 400mm in diameter and 500mm tall
- Efficiency Pu-240 = 50.52+/-0.4%
- Currently only performed preliminary tests

The Role of the Chemist in Designing New or Renovated Nuclear Laboratory Facilities

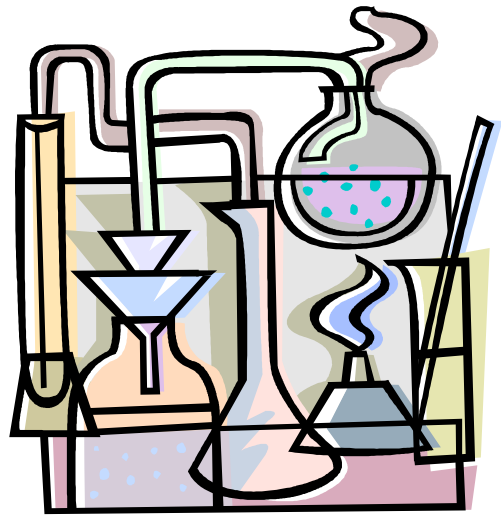
Michael J. Brisson, Michael K. Holland,
and Robin H. Young
Westinghouse Savannah River Company
Aiken, SC 29808

WSRC-MS-2003-00842S

July 9, 2005
Phoenix, AZ

Overview

- What is a laboratory?
  - Depends on whom you ask
- What's the first step?
  - Understand the customer/process
  - Sample Schedule
- What do you need?
  - Space
  - Equipment
  - Containment
  - Ventilation
  - Drain Lines
  - Utilities/Services
- Layout Concepts



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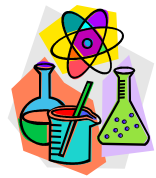
What Is a Laboratory?

Depends on whom you ask ...

- Chemists
  - Think of lab equipment
  - Speak analytical or R&D language
- Engineers
  - Think of systems (HVAC, power, building structures)
  - Speak engineering language(s) based on discipline(s)
- Architects
  - Think of layouts
  - Speak language of dimensions
- Constructors and Project Managers
  - Think of cost and schedule
  - Speak project management metrics
- Customers (direct and indirect)
  - Think of bang for the buck
  - May be affected by external politics
  - Speak language of the bottom line



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The Point Is …

Designing a new or renovated lab space is

- part art
- part science
- but mostly COMMUNICATION
  - getting across what you need to meet your customer's needs in the language(s) "they" understand

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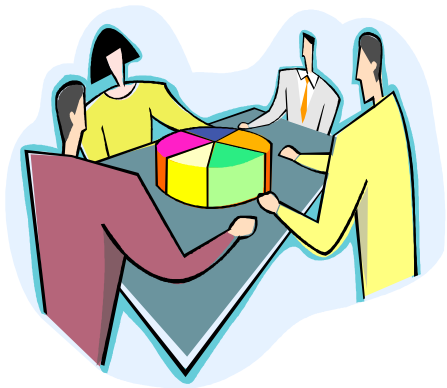
Since Communications is Important …



The bottom line for the chemist is to be

MULTILINGUAL

so the engineers know what you need,

the architects know how it has to be laid out,

the project managers know why it can't be done faster,

and the customers know why they need it,

why it costs that much,

AND what's in it for them.

Understanding the Customer

- Understand their process
  - So you can help make sure their real needs are met by what you do
- Understand the samples they will give you
  - How radioactive are the samples?
  - Physical state of samples (liquid, solid, gas)
  - Sample matrix
  - Representativeness
- Understand how they will use the results (i.e., data) you give them
  - Process control
  - Product quality
  - Nuclear safety
  - Nuclear material safeguards
  - Environment, safety, and health
  - Basis for data quality objectives
- Understand what can (and cannot) be done at-line or “in the field”
- Understand what the customer can (and cannot) afford
- Understand what your customer can sell to his/her customer

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Develop a Sample Schedule

Why do you need a sample schedule?

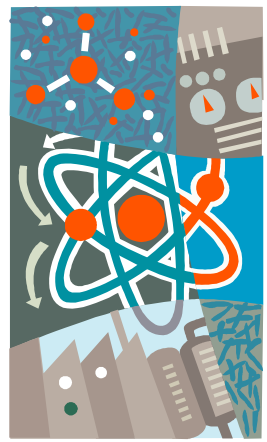
- Provides a documented agreement
  - Avoids misunderstandings
- Provides criteria for needed capabilities
  - (Ex: do I need ICP-MS or will flame AA do?)
- Provides criteria for needed capacity
  - (Ex: do I need two ICP-MS or just one?)
- Provides criteria for needed reliability
  - (Do I need an installed backup or an uninstalled spare?)

Elements of a Sample Schedule

- Sample descriptions
  - Physical state/matrix
  - Volume or mass
  - Radioactivity levels
  - Frequency per unit time
- Analyses required
  - Are certain methods required by order or regulation?
- Expected data range
  - May affect equipment/method selection
- Data quality objectives
  - Accuracy, precision, lower reporting limits
  - Level of uncertainty customer can accept
- Turnaround time
  - Affects method selection, capacity and reliability

Space Requirements

- Instruments/Equipment
- Containment Units
  - Space for containment units
  - Space within containment units
- Counter space
- Sinks
- Safety shower/eyewash stations
- Personnel working space
- Storage (consumables, spares, etc.)
- Computers, file cabinets, etc.



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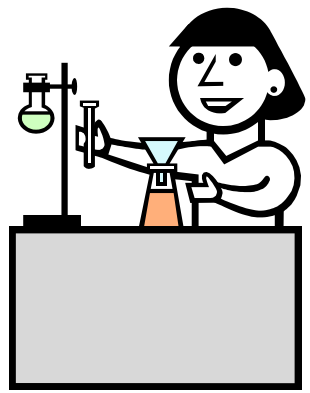
Equipment Requirements

- How many widgets do you need?
- What is their footprint?
  - Length, width, height, shape
- Do they need containment?
- What are the power requirements?
  - Voltage, single-phase or multi-phase
  - UPS
  - Conditioning
- What utilities/services are required?
  - Gases
  - Cryogenics (e.g., liquid nitrogen)
  - Vacuum
  - Special temperature/humidity controls



Containment Requirements

- Chemical Hoods
  - Non-rad applications like reagent preparation
- Radiohoods
  - Flexibility
  - Limits on radioactivity levels
  - High airflow requirement
- Radiobenches
  - Fixed sash
  - Suitable for work while seated
- Gloveboxes
  - More protection but less flexible
  - Lower airflow requirement than hoods/benches
- Enclosures with Manipulators
  - More protection and less flexible than gloveboxes
- Shielded Cells
  - Got beta-gamma?

Containment Requirements

General Considerations

- Select appropriate containment based on activity levels and acceptable risk
- Space to work on contained equipment
- Space for equipment, consumables, sample storage, waste collection
- Utilities and services
- Lighting
- Access (front only, or front and back?)
- Depth (so workers can reach everything)
- Work surfaces
  - Protective coatings where needed
  - Weight loading capacity
- Options for getting things in and out
  - Equipment replacement
  - Waste removal
  - Bag-out ports, airlocks, loading hoods
- Glovebox/Enclosure Atmosphere
  - Options: ambient, dry air, inert

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Ventilation

- ALARA principles
  - Least contaminated to most contaminated to filtration
- Hoods/benches need more airflow than gloveboxes
  - Affects HVAC sizing
  - Avoid too many hoods/benches in a small area (possible "wind tunnel" effect)
- Consider how airflow may affect instrumentation
- Ductwork may need protection from corrosion

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Drain Lines

- Protection against corrosion and radiation effects
  - Stainless steel (good for radiation, not for corrosion)
  - Coatings (e.g., Halar or Kynar)
  - Flushes
- Maintainability
  - Accessibility (trenches are problematic)
  - Replaceability

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Utilities/Services

- Deionized water
  - Got enough? In the right places?
- Instrument air
- Electrical outlets
  - Got enough?
  - Got the right type? (voltage, amperage, etc.)
- Breathing air (if needed)
- Gas storage
  - Cylinders vs. cryogenic (such as for argon)

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Layout Concepts

- Room size
  - SRS “standard” lab module is 12’ by 24’
  - Smaller rooms better than big rooms
    - Use additional wall space for instruments, containment units
    - More adaptable to changing missions
    - Process upsets have less impact on lab operations
- Room groupings
  - Group rooms based on activity levels
- Service chases
- Utility corridors

Layout Concepts

- Room Layouts
  - Assure adequate working/walking space around containment units
  - Ergonomics
  - Ingress/egress
  - Safety equipment (e.g., safety showers)

Acknowledgements

- Sherrod Maxwell (WSRC)
- Lamar Reynolds (WSRC, retired)
- Jim Collins (WSRC)
- Design team members (too numerous to name):
  - Chemists
  - Engineers
  - Project Managers
  - Safety and Health Experts
  - Architects
  - Constructors
- And, most of all, customers!

SRS®

Status of Reference Material Program

Peter Mason
Reference Materials Program Manager

SME Meeting
Phoenix, Arizona
July 9, 2005

Some of our customers in the last 12 months…

United States

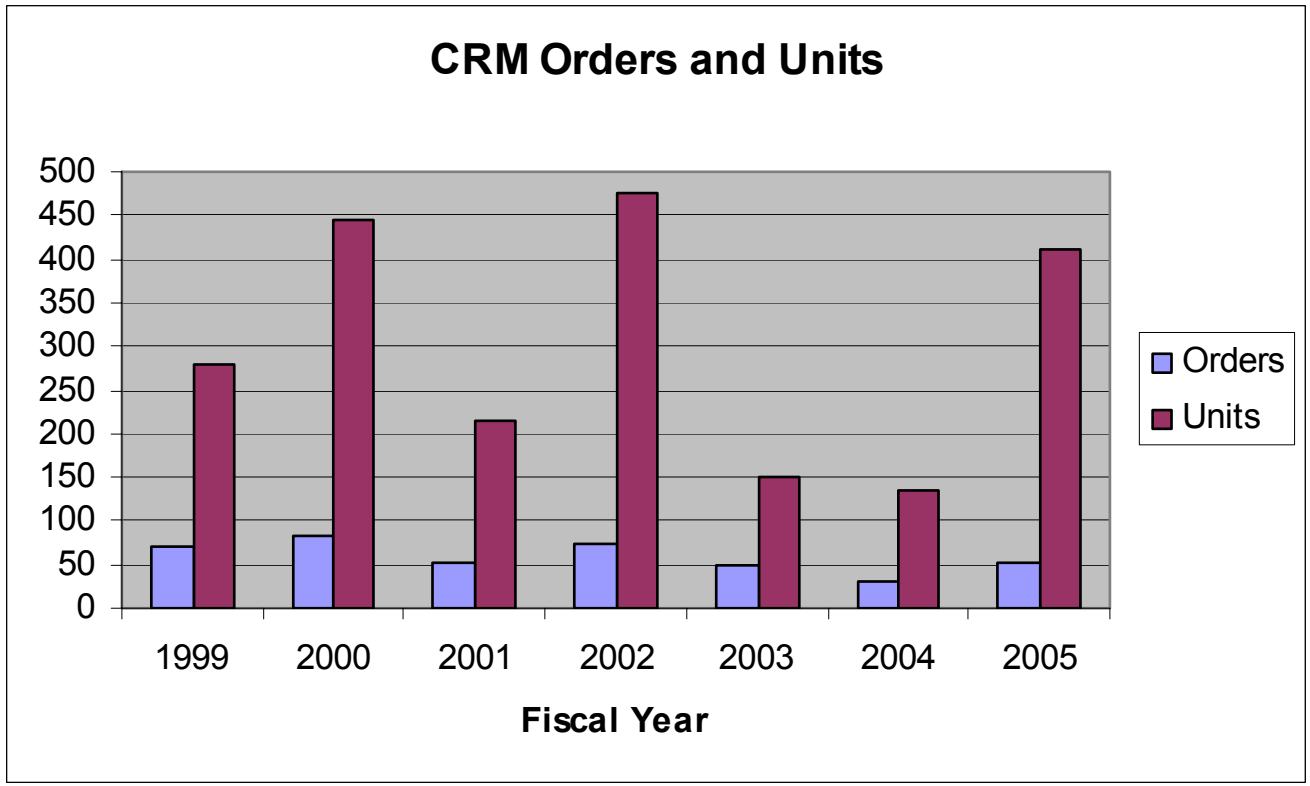
Lawrence Livermore Nat'l Lab
Los Alamos Nat'l Lab
Y-12
BWXT-Nuclear Products Division
Oak Ridge National Lab
Pacific Northwest National Lab
Nevada Test Site
Nuclear Fuel Services
Space and Naval Warfare Systems
US Enrichment Corp
Knolls Atomic Power Lab
Brookhaven National Lab
Wright-Patterson AFB
Global Nuclear Fuels
Framatome ANP
EPA
US Army Corp of Engineers

International and University

IAEA
NMCC-Japan
JAERI-Japan
NNC-Nuclear Division-UK
Institute of Naval Medicine-UK
AWE-UK
Atomic Energy of Canada
Heathgate-Australia (U mine)
Framatome-Belgium/Germany
Various Russian Facilities

San Diego State University
UC Santa Cruz
Univ of Saskatchewan
Univ of Wyoming

Status of RM Program



Recent Journal References to NBL CRM's:

"A comparative evaluation of Pu-238 determination in NIST SRM 947 Pu by alpha spectrometry and thermal ionization mass spectrometry"; Radiochimica Acta, 93, 5, 2005 **CRM 137**

"Determination of uranium isotope ratios by multi-static MIC-ICP-MS: method and implementation for precise U- and Th-series isotope measurements"; Journal of Analytical Atomic Spectrometry, 2005, 20, 5 **CRM 145**

"Determination of the $^{240}Pu/^{239}Pu$ atom ratio in global fallout at two locations in the Northern Hemisphere"; J. of Radioanalytical and Nuclear Chemistry, 263, 2, 2005

"Pu determination in bioassay samples using radiochemical TIMS", J. of Radioanalytical and Nuclear Chem, 263, 2, 2005 **CRM 128**

"Determination of uranium isotopic ratios in biological samples using laser ablation ICP-MS"; Int'l J of MS, 242, 2005 **U020, U350, U930**

"ICP-MS and laser ablation ICP-MS for isotope analysis of long-lived radionuclides"; International Journal of Mass Spectrometry, 242, 2005 **U005, U350, U930**

"Measurement of Pu isotope ratios in nuclear fuel samples by HPLC-MC-ICP-MS"; Int'l J. of MS, 242, 2005 **CRM 138**

"Determination of ^{90}Sr and Pu isotopes in contaminated groundwater samples by ICP-MS"; Intl J of MS, 242, 2005 **U020**

"Ultratrace determination of U and Pu by nano-volume flow injection sector field ICP-MS (nFI-ICP-SFMS)" J of Anal Atomic Spec, 2005, 20 **U350**

"Detection of depleted U in urine of veterans from the 1991 Gulf war"; Health Physics, 2004; **CRM U010**

Status of RM Program

- CRM U045 Issued
  - 4.5% enriched standard
  - 5 mg uranyl nitrate in solution
  - Made from CRM 113-B
  - Replacement for U050

	234	235	236	238
Atom %:	0.038720	4.5143	0.027655	95.4193
95% CI:	0.000029	0.0023	0.000025	0.0023

Status of RM Program

- Acquired base materials for future RM's
  - Off-normal oxide and UF_6
  - "virgin normal" UF_6
  - 1.5% enriched oxide and UF_6
  - CRM 113-B in P-10 tubes w/ impurity analysis
- All CRM 126-A work completed
  - 200 units reserved in storage at LANL
  - NBL will participate in intercomparison of C126A with French MP-3 in 2006

Status of RM Program

- CRM U630
  - One gram U_3O_8 isotopic standard
  - Issued next month

	^{234}U	^{235}U	^{236}U	^{238}U
Atom Percent	0.61894 ± 0.00038	63.353 ± 0.020	0.962296 ± 0.000051	35.066 ± 0.020
Weight Percent	0.61354 ± 0.00038	63.069 ± 0.020	0.962065 ± 0.000051	35.355 ± 0.020

$^{234}U/^{235}U$	$^{236}U/^{235}U$	$^{238}U/^{235}U$
0.0097698 ± 0.0000030	0.0151895 ± 0.0000046	0.55351 ± 0.00049

Status of RM Program

Two to four month time-frame

- Repackage and verify isotopics:
  - U0002 1 gram & 10 mg oxide, 5 mg nitrate sol'n
  - U030A
  - U500 1 gram & 10 mg oxide; future dilutions
  - U970

- CRM 116 Re-issue
  - U Metal, 93% enriched
  - Verify isotopics and assay
  - Maintain interim supply until new certification

Status of RM Program

- Cf shuffler standards
  - 93% HEU 100-400 grams
  - Sampling complete, awaiting shipment and analysis
- CRM 124 replacement
  - Impurities in normal U_3O_8
  - CRM 124: 7 levels of 24 elements
  - Material spec survey being conducted

Certified Reference Material Specification Survey
CRM 124: Uranium Oxide Impurity Standard

1. What impurity elements would your facility deem most important for inclusion in a new CRM?
2. At what concentrations should each element be present and certified.
3. What is a target uncertainty desired by your facility for each element?
4. What is your desired unit size?
5. Please provide an estimate of your facilities annual need for sets of the new CRM.
6. If possible, please indicate the purpose and the measurement method(s) employed when using CRM 124.
7. Are there other aspects of the proposed CRM that would require certification or inclusion on the certificate for informational purposes (e.g. particle size characterization, isotopic composition of the uranium or impurities, etc).
8. Do you have specific requirements or suggestions for how the material is packaged?

Status of RM Program

- Gadolinia in UO_2
  - 0 – 10 (?) wt % Gd in $U0_2$
  - Domestic and international fuel suppliers
  - Material specification survey being conducted

Certified Reference Material Specification Survey
Gadolinium Oxide in Uranium Oxide CRM

1. At what concentrations should the material be certified?
2. What is a target uncertainty desired by your facility for the CRM?
3. Does your facility have a desired enrichment for the uranium?
4. What is your desired unit size? For example, each unit should consist of three bottles, each containing 25 grams of material certified for Gd/U mole ratio at 0, 5 and 10% nominal.
5. Please provide an estimate of your facilities annual need for sets of the new CRM.
6. If possible, please indicate the purpose and the measurement method(s) employed when using the CRM.
7. Are there other aspects of the proposed CRM that would require certification or inclusion on the certificate for informational purposes (e.g. impurities analysis, uranium isotopic composition, particle size characterization, etc).
8. Do you have specific requirements or suggestions for how the material is packaged?

Status of RM Program

- Calorimetry standards (CalEx II)
  - 2 kg, 12% Pu-240, 6 watt
  - Isotopics complete, awaiting Pu amount certification

Status of RM Program

- Release CRM 144 as Isotopic Standard
  - 2 mg Pu nitrate in Teflon
  - ~8 ppt ^{241}Am
  - Approx. isotopics as of 2005:

	238	**239**	**240**	**241**	**242**	**244**
Atom %:	0.191	2.189	33.06	1.06	46.01	17.48

Status of RM Program

- New CRM made from C126A solutions
  - Solution or dried nitrate form
  - Assay and Isotopics certified
  - 10-100 mg sample size
- Re-certify CRM 136, 137, 138 series
  - Use existing materials
  - CRM 128 1:1 $^{242}Pu/^{239}Pu$ traceability
  - Target $^{240}Pu/^{239}Pu$ uncert of <0.03%
  - Considering assay certification
- Dilutions of above (including CRM 130?)
  - Dilute to µg to pg range
- Material specification survey on-going

Certified Reference Material Specification Survey
Plutonium Isotopic and Assay CRMs

1. In addition to isotopic certification, do you need plutonium content certified? If so, indicate a target uncertainty for the plutonium content, and please indicate how the standards will be used.
2. At what concentration(s) should the standards be produced? Initial plans are to offer each standard at two different plutonium contents (e.g. 10 mg Pu and 10 µg Pu per unit).
3. Please indicate a preferred form for the material (e.g. dried nitrate, sulfate, nitrate solution, etc).
4. Do you have specific requirements or suggestions for how the material is packaged and/or produced?
5. Please provide an estimate of your facilities annual need for the new CRMs.
6. If possible, please indicate the purpose and the measurement method(s) employed when using these reference materials.
7. Are there other aspects of the proposed CRM that would require certification or inclusion on the certificate for informational purposes?

Future RM Plans

- Uranium calibration mixes
  - Acquiring base materials
  - Use for all future U isotopic certifications
  - Reduce U-series major ratio uncerts from ~0.10% to <0.03% and minor ratio uncerts by one to two orders of magnitude
  - Collaboration with IRMM on some RM certifications leading to international U series standards
- Recertify U metal standards
  - CRM 112 normal U metal
  - CRM 116 HEU metal
  - High-purity metals (<100 ppm total)

Future RM Plans

- MOX standards for LWR/PWR
- U and Pu double spikes
- Np standard
- Am standard

Other Activities

- Publish certification reports
  - CRM 129-A and 126-A
- Update and expand NBL website
  - CRM catalog posting on-line next month
  - Certificates available via website
  - Technical reports on new RM's
  - Interface for RM needs
  - Constant values (1/2 life, atomic masses)