NEW BRUNSWICK LABORATORY

July 16, 2011
Meeting Organized by P. Mason

U.S. Department of Energy – Office of Science
9800 South Cass Ave
Argonne, Illinois 60439

MEASUREMENT EVALUATION PROGRAM ANNUAL MEETING MINUTES

New Brunswick Laboratory: History and Mission

NBL was established by the Atomic Energy Commission in 1949 in New Brunswick, NJ. It was initially staffed by scientists from the National Bureau of Standards that had contributed to the measurement science of nuclear materials for the Manhattan Project. NBL's initial mission was to provide a Federal capability for the assay of uranium-containing materials for the nation's developing atomic energy program. Over the years NBL expanded its capabilities, developing newer and improved methods and procedures, and certifying additional reference materials for use around the world. The capability for plutonium measurements was implemented at NBL in 1959. NBL was relocated from New Jersey to the site at Argonne National Laboratory during the period 1975-77.

Since its beginning, NBL has maintained a Center of Excellence in the analytical chemistry and measurement science of nuclear materials. In this role, NBL continues to perform state-of-the-art measurements of the elemental and isotopic compositions for a wide range of nuclear materials.

NBL has expanded from its initial mission by improving methods and procedures and developing new ones for actinide analytical chemistry, added the capacity to certify and globally distribute nuclear reference materials and operated a number of interlaboratory measurement exercises to determine state-of-the-art and state-of-the-practice for many analytical techniques and actinide material forms. NBL also does work in highly enriched uranium transparency monitoring, assists in Material Control and Accountability surveys and inventories at laboratories nationwide, maintains a cadre of scientists capable of responding to nuclear emergencies, and collaborates with local, national, and international laboratories in the areas of Safeguards and nonproliferation.

NBL’s Primary Functional Groups:

- Reference Materials Program
- Measurement Evaluation Program
- Nuclear Safeguards and Nonproliferation Support Program
- Measurement Services
- Measurement Development

Further details may be found at our website at www.nbl.doe.gov or by contacting us via telephone at 630-252-2446.

Opening Statement from Acting Laboratory Director

Dr. Usha Narayanan

Dear Colleagues,

Welcome to the 2011 New Brunswick Laboratory Measurement Evaluation Program Annual Meeting. We have some updates that we would like to share with you. Mr. Jon Neuhoff whom you knew as the New Brunswick Laboratory (NBL) Director has accepted a position in the private sector and his last day at NBL was June 21, 2011. I have been appointed to serve as the Acting Laboratory Director until a permanent NBL Director is selected.

Dr. Chino Srinivasan who coordinated this Program for nearly six years is now detailed within the laboratory to develop analytical procedures that would be used for certification efforts. I thank both Jon and Chino for their contributions and wish them the best.

Mr. Pete Mason is coordinating the NBL Measurement Evaluation Program. Pete's experience includes nuclear chemistry, mass spectrometry and coordinating the NBL Reference Materials Program. He is eager and willing to make the measurement evaluation program an effective and useful tool for the nuclear community. Please communicate with him about your needs and support him in this new role.

I apologize for not being here at this meeting. The Laboratory has been undergoing many changes over the past six years, and as we near the end of a long road to full operations, NBL management is focused on pushing the lab the 'final mile'. However, two NBL staff members Dr. Steven Goldberg (Nuclear Forensics) and Dr. Richard Essex (Reference Materials) are also in attendance at the INMM meeting. All three NBL staff will be available to talk to you regarding NBL status and services.

Thanks for your presence and participation, we are looking forward to a productive meeting here and would like to continue our communication beyond this meeting to strengthen the measurement capabilities of the safeguards community.

Best wishes for a successful meeting.

Usha Narayanan, Acting Laboratory Director

NBL Contact Information:

Website/Addresses	
Website	www.nbl.doe.gov
CRM Prices & Certificates	www.nbl.doe.gov/htm/price_list.htm
CRM Ordering Information	www.nbl.doe.gov/htm/ordering.htm
General (sales, shipping, general inquiries)	usdoe.nbl@ch.doe.gov
Reference Materials (technical questions, special requests, projects)	crm.nbl@ch.doe.gov
Measurement Evaluation (ME participation, data requests)	sme.nbl@ch.doe.gov

Staff Contacts		
Chief Operations Officer	Rock Aker	rock.aker@ch.doe.gov
Program Manager (Forensics Program)	Steven Goldberg	steven.goldberg@ch.doe.gov
Facility Operations Division Director	Robert Koedam	robert.koedam@ch.doe.gov
Standards and Evaluation Division Director	Margaret Legel	margaret.legel@ch.doe.gov
Measurement Services	Margaret Legel	margaret.legel@ch.doe.gov
Reference Materials Program Coordinator	Richard Essex	richard.essex@ch.doe.gov
Measurement Evaluation Program Coordinator	Peter Mason	peter.mason@ch.doe.gov
Domestic Safeguards Assistance	Paul Croatto	paul.croatto@ch.doe.gov

Attendee's:

Name	Facility	E-mail
Peter Mason	NBL	Peter.mason@ch.doe.gov
R. Chris Robinson	Y-12	YCR@y12.doe.gov
Thomas Sampson	-	tesampson@cox.net
Steven Goldberg	NBL	Steven.goldberg@ch.doe.gov
Jeff Gross	LLNL	Gross15@llnl.gov
Bud Marsh	LLNL	bud@llnl.gov
Greg Schaafe	Y-12	schaaffeg@y12.doe.gov
Joe Giaquinto	ORNL	giaquintojm@ornl.gov
Jane Poths	IAEA	J.Poths@iaea.org
Steve Balsley	IAEA	s.d.balsley@iaea.org
Maureen Bernard	SRNS	Maureen.bernard@srs.gov
Steven Bakhtiar	INL	Steven.bakhtiar@inl.gov
Kevin Norbash	INL	Kevin.norbash@inl.gov
Tamara Keever	ORNL	keevertj@ornl.gov
Debra Bostick	ORNL	Bostickda@ornl.gov
Russ Johns	PNL	Russell.johns@pnnl.gov
Bill Hopwood	ORNL	hopwoodwhjr@ornl.gov
Jeff Sanders	INL	Jeff.sanders@inl.gov
Veronica Sviridova	VNITA	Veronica.sv@mail.ru
Gary Kodman		kodmang@comcast.net
D.L.Whaley	DOE-HQ	D.L.Whaley@hq.doe.gov
Lynne Preston	DOE-HQ	Lynne.preston@hq.doe.gov
Lisa Colleti	LANL	lcolletti@lanl.gov
Terri L. Welsh	Hanford	Terri_L_WelshL@RL.gov
Katherine Hales	Urenco UK	Katherine.hales@urenco.com
Orpet Peixoto	ABACC	Orpet@abacc.org.br
Stephan Richter	IRMM	Stephan.richter@ec.europa.eu
Roger Wellum	-	r.wellum@gmail.com
Olivio Pereira	IPEN	oliviojr@usp.br
Erwin Galdoz	ABACC	galdoz@abacc.org.br
Claudio Devida	CAE-CNEA	devida@cae.cnea.gov.ar
Carlos Rodriquez	ABACC	Rodriguez@abacc.org.br
Stephan Croft	LANL	scroft@lanl.gov

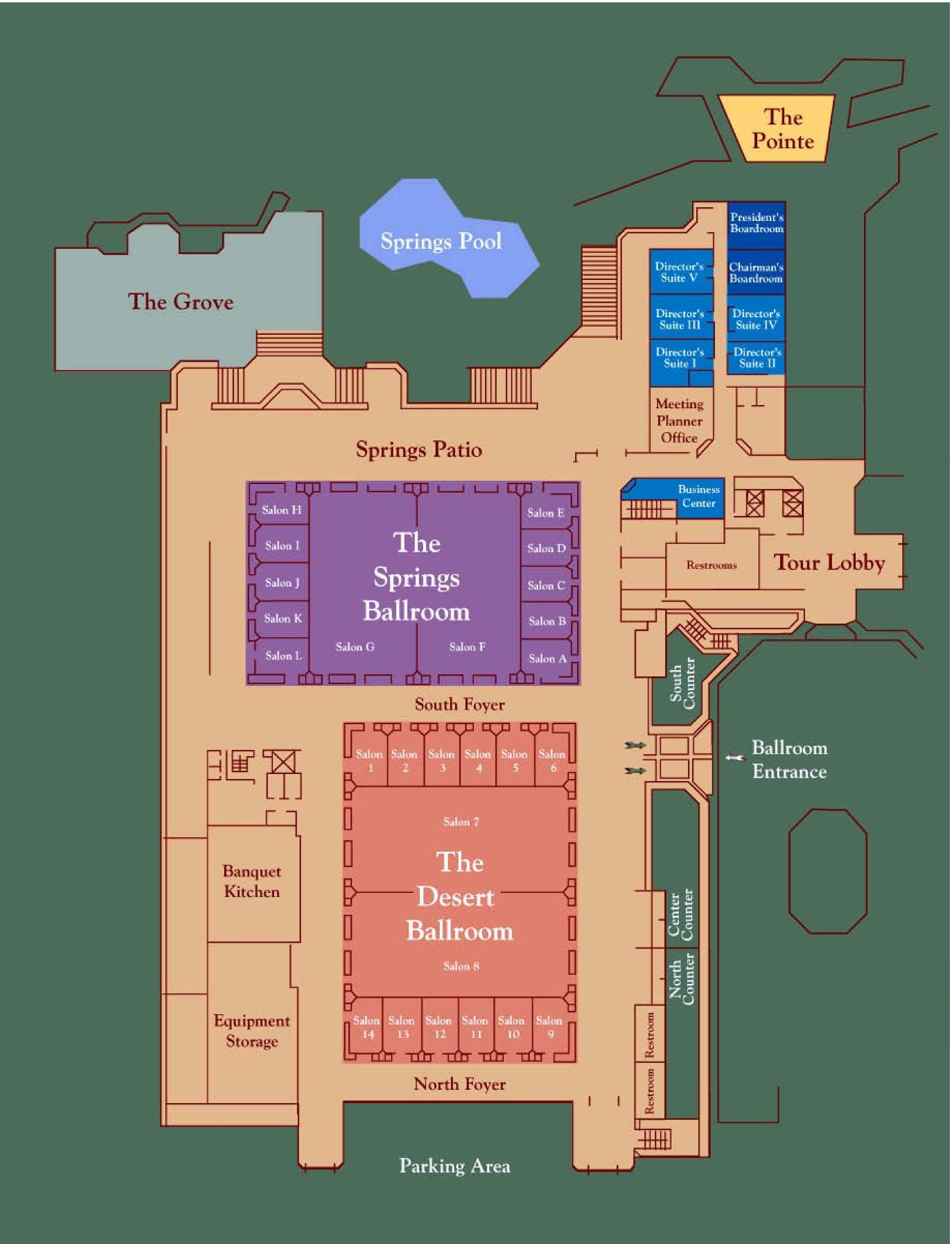
2011 Safeguards Measurement Evaluation Meeting

AGENDA

July 16, 2011 JW Marriott Desert Springs Resort Palm Desert, California

Desert Ballroom, Salons 1-3

9:00 am	**Introductions & Message from NBL Director**	**P. Mason, NBL**
9:30 am	**SME Program: History Review & 2010 Data Evaluation**	**P. Mason, NBL**
	BREAK 10:30 – 10:45	
10:45 am	**Measurements for Nuclear Safeguards and Improvement of Analytical Techniques**	**C. Devida, CNEA**
11:10 am	**Improvements in the Measurements of Uranium Concentration and Isotope Amount Ratio for Nuclear Safeguards**	**O. Pereira, IPEN**
11:35 am	**Uncertainty Estimation Procedures at CNEN's LASAL Laboratory**	**F. C. Dias, CNEN**
	LUNCH 12 -1:30 pm	
1:30 pm	**Measurement Evaluation Programmes at IRMM**	**S. Richter, IRMM**
1:55 pm	**An Independent Analysis Protocol for Thermal Ionization Mass Spectrometric Measurement of LEU in Blend-Down Process Solutions**	**M. Bernard, SRS**
2:20 pm	**UF_4 Base Material for a Certified Reference Material**	**G. Schaff, Y12**
2:45 pm	**Importance of U-234 and U-236 in Nuclear Material Samples**	**J. Poths, IAEA**
	BREAK 3:10 – 3:25 pm	
3:25 pm	**Wrap-up of Data Evaluation (if necessary) Discussion of Possible Changes to SME: A. Samples B. Analysis/Evaluation Scheme C. Reporting GUM Uncertainties, minor isotopes, etc D. Annual Report/Meeting Suggestions E. Open discussion/suggestions/meeting evaluation** Map of JW Marriott Desert Springs Resort on next page	**ALL**



The Pointe
Springs Pool
The Grove
President's Boardroom
Director's Suite V
Chairman's Boardroom
Director's Suite III
Director's Suite IV
Director's Suite I
Director's Suite II
Meeting Planner Office
Springs Patio
Business Center
Salon H
Salon E
The Springs Ballroom
Salon I
Salon D
Salon J
Salon C
Salon K
Salon B
Salon L
Salon G
Salon F
Salon A
Restrooms
Tour Lobby
South Counter
South Foyer
Salon 1
Salon 2
Salon 3
Salon 4
Salon 5
Salon 6
Ballroom Entrance
Salon 7
The Desert Ballroom
Salon 8
Banquet Kitchen
Center Counter
North Counter
Equipment Storage
Salon 14
Salon 13
Salon 12
Salon 11
Salon 10
Salon 9
Restroom
Restroom
North Foyer
Parking Area

Meeting Summary:

The 2011 SME Annual meeting was held in Palm Desert, California on Saturday July 16th. Approximately 40 people were in attendance. After introductions, an overview and status of the New Brunswick Laboratory was given, followed by a presentation of the CY2010 measurement evaluation data. There were general discussions and comments during the data presentation.

One request was that, in the future, NBL issue 'certification reports' and values and uncertainties for new SME materials. P. Mason, SME Program Coordinator, confirmed that that is the plan for future materials, and that in fact the new samples produced in FY11 have a report and values/uncertainties associated with them.

Plans for the program were presented, including NBL's commitment to continue to offer training in:

- Chemical handling for high-accuracy measurements
- Davies & Gray titrimetry
- High Precision titrimetry
- TIMS techniques
- Measurement uncertainty workshops to ensure ISO compliance

Additionally, NBL management has expressed a need to expand participation in the SME program and do a better job of maintaining current customers. New materials to be added to the program in the future were mentioned, including new LEU fuel pellets and the preliminary plans to offer an 'impurities in uranium' round-robin campaign later in the year.

At the end of the day, an open discussion was held to solicit ideas and suggestions from participants. NBL presented the idea of changing how data evaluation and sample analyses are currently conducted, from an intense, multi-day and multi-replicate analysis scheme to simple reporting of value(s) and uncertainties. There seemed to be some agreement that this would be a good idea. NBL will not eliminate its current procedure of performing ANOVA (requiring multi-day and multi-replicate analyses) to look for day-to-day and analyst-to-analyst variabilities, but will allow individual participants to decide how they wish to perform analyses and report results.

Input on new sample types or properties was solicited. In general NBL seems to be meeting the needs of the DA community in terms of uranium materials. When plutonium is returned to the program new materials will need to be utilized.

One significant oversight at the meeting was the lack of discussion concerning NDA in the SME program. This has been an escalating problem over the past few years. At next years meeting NBL will make an effort to raise the issue of NDA materials and usage in intercomparison programs. NBL will also look to revive some NDA measurements using already-existing samples such as the CRM 149 SME containers at most major DOE sites.

The need for low-level materials was re-iterated, particularly of low enough U content to allow introduction into clean-lab-type conditions.

The arrangement and scheduling of the meeting was discussed. The vast majority of participants were happy with having the meeting in July and having it cover the previous years data. Having the annual report issued before the meeting would be useful.

2010 SME Annual Evaluation Presentation:

The data and information on the following slides was given as a presentation by Peter Mason of NBL at the annual meeting, and the slides summarize the performance of all participating laboratories for CY2010. This includes uranium content and isotopic determinations performed on a variety of uranium material types. Please refer to the 2010 SME Annual Report for complete details on program performance, or feel free to contact the NBL SME Program Coordinator (P. Mason) at peter.mason@ch.doe.gov or 630-252-2458 should you have any additional questions.

Please note that the slides presented here were originally appended to an additional set of slides. The first set of slides, included in this report in the "Presentations" section, give an overview of the New Brunswick Laboratory and its current operations. The set of slides included here discuss the actual SME performance results.

Due to animations in the original slideshow, the presentation as illustrated here differs somewhat from as given, in order to avoid the loss of information or clarity associated with slide animations.

Measurement Evaluation Program
Annual Meeting

CY2010 SME PROGRAM

P. Mason
July 16, 2011
Palm Desert, California

Measurement Evaluation Program

Provides DOE with the ability to

- Independently assess measurement performance
- DOE's 'quality control program'
- Provide measurement support to labs
- Monitor method performance over time, new methods conformity

Participation

- Mandatory for DOE labs
- Cost free for DOE
- Voluntary for non-DOE facilities
- Provided on a cost-recovery basis

History

Facility	Location	Facility	Location
British Nuclear Fuels, Ltd	1. Capenhurst 2. Springfield	Laboratorio Chemica Industriale	14. Rome, Italy
Commissariat a L'Energie Atomique	3. Pierrelatte 4. Grenoble 5. Gif-sur-Yvette 6. Narbonne	GE	15. Wilmington, NC 16. Morris, IL 17. Pleasanton, CA
Bureau Centrale de Measures Nucleaires	7. Geel, Belgium	Reactor Centrum	18. Petten, Netherlands
Centro Commune Di Ricerca	8. Ispra, Italy	New Brunswick Lab	19. New Brunswick, NJ
Exxon Nuclear	9. Richland, WA	Uran-Isotopentrennungs	20. Julich, Germany
Union Carbide	10. Paducah, KY 11. Oak Ridge, TN	Westinghouse	21. Columbia, SC
Ultra-Centrifuge	12. Alemlo, Netherlands	Goodyear Atomic	22. Piketon, OH
Avco	13. Tulsa, OK		

History

- General Analytical Evaluation (GAE)
  - 1952-1984
  - Typically U.S. Participants (6-9 labs), with exceptions
  - Uranium measurements (HEU scrap, metal, UF_6)
  - E.g. UF_6 program in 1974-1977
    - Determine state-of –the-art capability for U assay and isotopic msmts
    - 3 phases: U purity & U-235, lab sampling (from 1S), impurities
    - Phase 1: 6 samples monthly (3 assay/3 iso) for 12 consecutive months
    - 22 labs in US and Europe participated
    - 4 purity samples into P-10 tubes, 4 isotopic (0.7-1.7%) into PE 'pigtails'
    - Gravimetry, D&G titration, coulometry; GSMS (9), TIMS (9)
      - Assay: most labs consistently measured to within 0.1% of the reference value
      - Isotopics: only 10 of 18 labs could differentiate materials of similar composition, and 4 of them exhibited significant bias

Assay	% SE	Wt% 235U	% SE
99.977	0.025	0.7109	0.0001
99.934	0.025	1.7229	0.0002
99.954	0.021	1.7124	0.0002
99.976	0.026	0.7092	0.0001
Mean: 99.968	0.016		

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History

- Grand Junction Interlaboratory Exercise (circa 1982)
  - National Uranium Resources Evaluation (NURE)
  - Part of US effort to encourage U mining development/resource discovery
  - Run from AEC's Grand Junction, CO office responsible for estimating domestic U reserves
  - Interlaboratory exercise to:
    1. provide a reference data base for comparison of various methods used on ores
    2. Establish 'consensus' values for these CRM's (verify)
    3. Document traceability of NURE measurements to the national measurement base
  - Seven laboratories
  - Use CRM's 101A - 105A for U & radium assay (pitchblende ore + silica: 1% - 0.001% U)
  - Use CRM's 106A - 110A for Th assay (monazite sand + silica: 1% - 0.001% Th)

- Results:
  - Used DA methods for verifying reference values (lack of NDA cal standards)
  - Most U results verified the reference values
  - Many Th results did not verify the reference values (poor precision on Th methods)

Bendix	Texas A&M
EG&G Idaho	Union Carbide (Oak Ridge)
Eldorado Nuclear	RESL
LANL	

Fluorometry	Colorimetry
XRF	Neutron Activation
ICP-OES	Delayed Neutron
Alpha Spec	Passive Gamma (both GeLi/NaI)

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History

- Safeguards Analytical Laboratory Evaluation (SALE)
  - 1970-1984: total of >26,000 measurements
  - Demonstrate and monitor ability of DOE, the nuclear industry, and the international nuclear community to determine the quantities of nuclear materials being stored, handled, processed or transported.
  - U.S. and International (at times >70 participants)
  - Uranium and plutonium, analysis on a bi-monthly basis
  - Final three years of the program: 1982-1984
    - Five materials certified for this 'campaign'
    - 50 facilities provided over 6,000 assay and isotopic measurements
    - 22 different analytical methods employed
    - Tests of lab-to-lab, method-to-method, day-to-day variations
    - Test of laboratory/method compatibility

Material	Quantity	Container	Atmosphere	Measurement	Characterization Methods
UNH solution	5-20 mL	Flame-sealed amp	air	U conc U-235 abundance	D&G TIMS
UO_2 powder	25 g	Heat sealed jar	nitrogen	U conc U-235 abundance	D&G, Gravimetry TIMS
UO_2 pellet	20 g	Glass vial	air	U conc U-235 abundance	D&G, Gravimetry TIMS
PuO_2 powder	1 g	Screw-cap glass vial	air	Pu conc Pu-239, Pu-241	Coulometry TIMS
$(Pu,U)O_2$ pellet	~1 g	Sealed glass tubes	argon	Pu & U conc Pu-239, Pu-241, U-235	Coulometry, D&G TIMS

History

- SALE Results (% of labs reporting means within 0.05% and 0.10% of reference)

Measurement	n	1982 % within		n	1983 % within		n	1984 % within	
		0.05%	0.10%		0.05%	0.10%		0.05%	0.10%
UNH Assay	34	53	79	30	57	83	31	58	74
UNH U-235	27	48	71	27	41	74	28	43	64
$U0_2$ assay	45	71	84	35	86	97	41	73	90
$U0_2$ U-235	30	33	57	31	42	65	32	25	56
$(Pu,U)0_2$ U assay	6	17	17	5	40	60	6	17	50
$(Pu,U)0_2$ U-235	5	0	20	6	33	33	6	0	33
$(Pu,U)0_2$ Pu assay	9	22	44	11	27	36	10	50	60
$(Pu,U)0_2$ Pu-239	7	71	100	8	88	100	8	100	-
$Pu0_2$ Pu assay	9	56	67	15	20	33	14	24	64
$Pu0_2$ Pu-239	8	88	100	12	100	-	11	100	-

History

SALE 1982-1984 Study Conclusions

- Uranium:
  - Favorable measurement trends from 1970's for UNH and UO_2
  - Gravimetry w/ impurities and NBL-modified D&G - all labs had good results: methods of choice
  - IDMS showed a greater spread than the uncertainty on the spikes used and no improvement in performance over time
  - $U0_2$ assay measurements better than UNH: sampling ease of solids over liquids? Evaporation/storage?
  - U-235 in UNH more accurate than in $U0_2$ partially due to inhomogeneity in $U0_2$
  - U conc in Pu,U oxides difficult (sample size?)
  - U-235 in MOX less accurate due to composition (0.72% U-235) vs 2.8% and 4.3%
- Plutonium:
  - Coulometry appeared to be the most precise and accurate method, though a few laboratories exhibited control problems, particularly with MOX
  - Silver oxide-ferrous titrations (amp & potentiometric) yielded good results also
  - Very good results for Pu-239 abundance
  - There was improvement in Pu-241 (not shown) and no bias indicating superior Am-241 removal vs 1970's
- Compatibility – "the mean value of a set of measurements must lie within the pooled uncertainties of the reference and measured values for compatibility to exist"
  - # of labs falling outside of the major groupings for homogeneity of means decreased from 20 in 1981 to only 2 in 1984
  - At the same time between 1981 and 1984 precisions increased significantly
  - **Therefore, "apparent shipper-receiver differences due to analytical variation had become less likely during this period".**

History

- Safeguards Measurement Evaluation Program (SME)
  - SALE discontinued 1984
  - SME instituted 1986 – present
  - Initial focus entirely domestic - DOE and NRC labs
  - At times 6 labs participating
  - Typical SME construct:
    - Labs identify material types (oxides, solutions, etc)
    - NBL and Labs agree upon analysis schedule
    - Typical scheme includes enough samples/analyses for day-to-day and analyst-to-analyst variability determinations (?)
    - 1 annual shipment of samples (Sept/Oct)
    - Labs submit results on a CY quarterly basis (Jan-Mar, Apr-Jun, Jul-Sep, Oct-Dec)
    - NBL submits evaluation after each data submittal
    - Outlier test, ANOVA on day-to-day/analyst-analyst, mean %RD, precision
    - Comparison to ITV random and systematic uncertainty components

Results

2010 Annual Report & Data Evaluation

Test Samples

Uranium test samples for mass fraction and isotopic abundance determinations

- Uranyl nitrate solutions for mass fraction and NU, LEU, HEU isotopes
- UO_2 pellets for mass fraction and LEU isotopes
- UO_3 powder for mass fraction and NU isotopes
- U_3O_8 powder for mass fraction and NU isotopes
- UF_6 for mass fraction and NU and LEU isotopes

Plutonium test samples still not available – coming soon

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Material/Method Specific Evaluation

- Enter material/method specific measurement results into SMES database
- Verify data entry is correct
- Test for outliers; evaluate and reject outliers
- Calculate % RD of each result with respect to characterized value

$$\% \, RD = 100 \left(\frac{M - A}{A} \right)$$

- Calculate mean % RD and standard deviation for the set of results
- Test for day to day variation
- Calculate standard uncertainty, degrees of freedom, and 95% C.L.
- Compare mean % RD and standard deviations against ITVs for systematic and random uncertainty components, u(s) and u(r)
- Send evaluation report to participant

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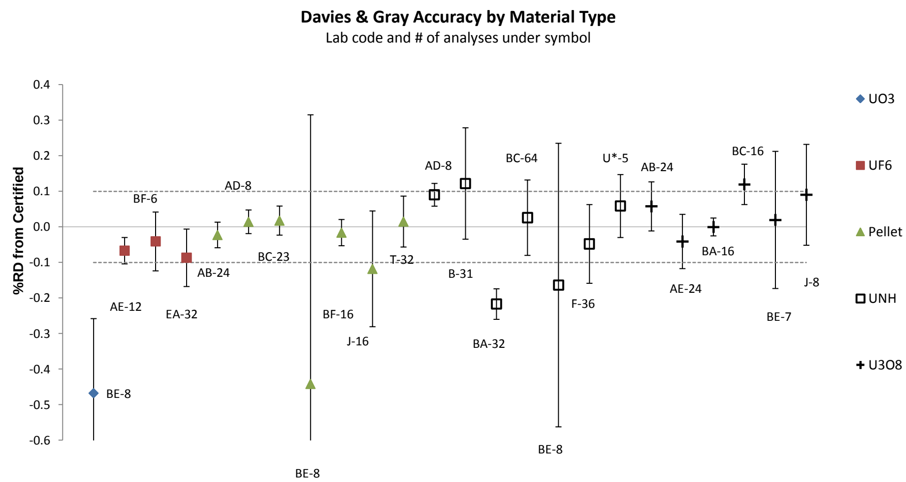
Measurement Results Evaluation: Uranium Mass Fraction

Lab Code	UNH	U3O8	UO2 PELLET	UF6	UO3
A	IDMS, XRF				
AB		D&G	D&G		
AD	D&G		D&G		
AE		D&G		D&G	
B	D&G, IDMS				
BA	D&G	D&G			
BC	D&G	D&G	D&G		
BE	D&G	D&G	D&G		D&G
BF			D&G	D&G	
EA				D&G	
F	D&G				
J		D&G, IDMS	D&G, IDMS		
SA	XRF				
T			D&G		
TH			GRAV		
TO			GRAV		
TP			GRAV		
TR			GRAV		
U	D&G				

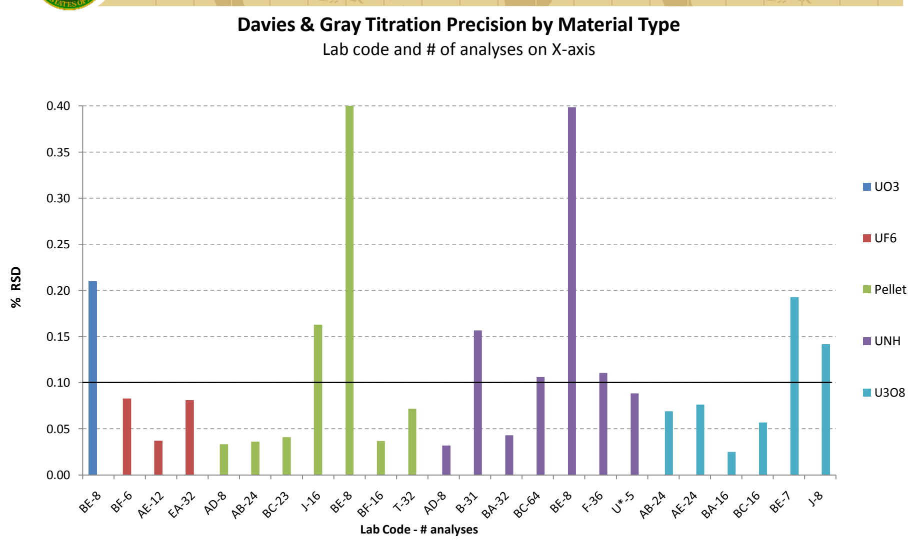
- 19 Labs
- 611 measurements
  - 13 labs D&G
  - 4 labs Gravimetry
  - 3 labs IDMS
  - 2 labs XRF

- D&G Titration Msmts (456):
  - UF6 – 50
  - Pellet – 127
  - UNH – 184
  - U3O8 - 95

D & G by Material



D&G by Material



UNH Solution Performance

1982-1984 SALE data

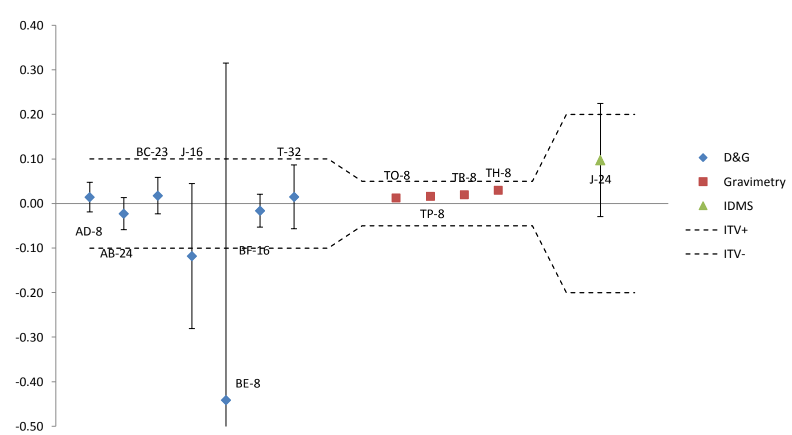
Measurement	n	1982 % within 0.05%	1982 % within 0.10%	n	1983 % within 0.05%	1983 % within 0.10%	n	1984 % within 0.05%	1984 % within 0.10%
UNH Assay	34	**53**	79	30	**57**	83	31	**58**	74
UNH U-235	27	48	71	27	41	74	28	43	64
$U0_2$ assay	45	**71**	84	35	**86**	97	41	**73**	90
$U0_2$ U-235	30	33	57	31	42	65	32	25	56
MOX U assay	6	17	17	5	40	60	6	17	50
								0	33
								50	60
								100	-
								24	64
								100	-

2010 SME Data	% within 0.05%	% within 0.10%	# of means
UNH Soln	22%	57%	9
UO_2, UF_6, U_30_8	59%	82%	22

Small data-set, but is evaporation/storage/handling of solutions still an issue?

Uranium assay: Fuel Pellets

U Assay Accuracy on Fuel Pellets by Method



Uranium Assay: Other Methods

Pellet IDMS

Lab Code	%RD	ITV	Std Dev	ITV	N
J	0.098	0.2	0.127	0.2	24

UNH IDMS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
B	**-0.78**	0.2	0.20	0.2	31
A	-0.15	0.2	0.19	0.2	16

U3O8 - IDMS

Lab Code	%RD	ITV	Std Dev	ITV	N
J	0.11	0.20	0.12	0.2	8

UNH X-Ray

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
SA	1.51	2	1.01	2	20
A	0.23	2	0.17	2	16

Uranium Enrichment

Lab	UNH	U_30_8	Pellet	UF_6	$U0_3$
A	TIMS				
AA	TIMS	TIMS			TIMS
AD	ICP-MS		ICP-MS		
B	TIMS				
BC	TIMS	TIMS	TIMS	GSMS	
EA	ICP-MS			ICP-MS	
EB				GSMS	
F	TIMS				
G	TIMS				
J		TIMS	TIMS	TIMS	
SA	TIMS				
SF				ICP-MS	
T			TIMS		
TH			TIMS		
TO			TIMS		
TP			TIMS		
TR			TIMS		

- 17 Labs
- 615 measurements

- 13 TIMS: 352 msmts
- 2 GSMS (1 quadrupole)
- 3 ICP-MS (1 quad, 2 MC)

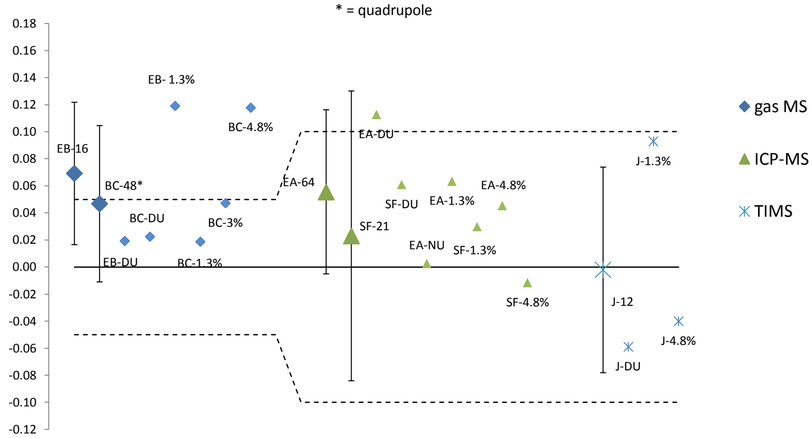
- EA = 144 msmts on 2 MC-ICP-MS's (UNH & UF_6)

U-235 in UF_6

Accuracy of UF_6 U-235 Abundance

DU-5%, three methods, by enrichment

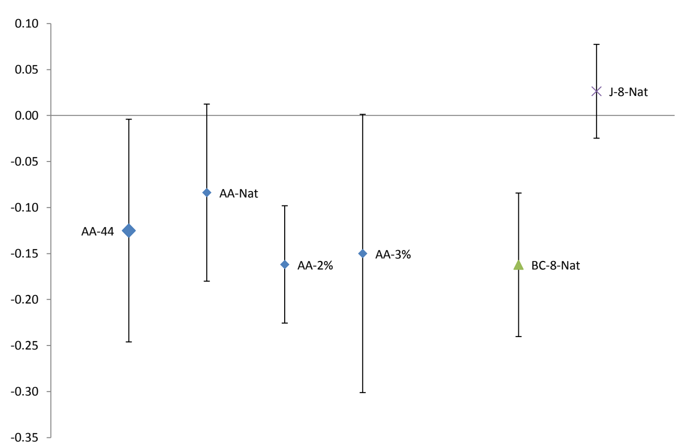
* = quadrupole



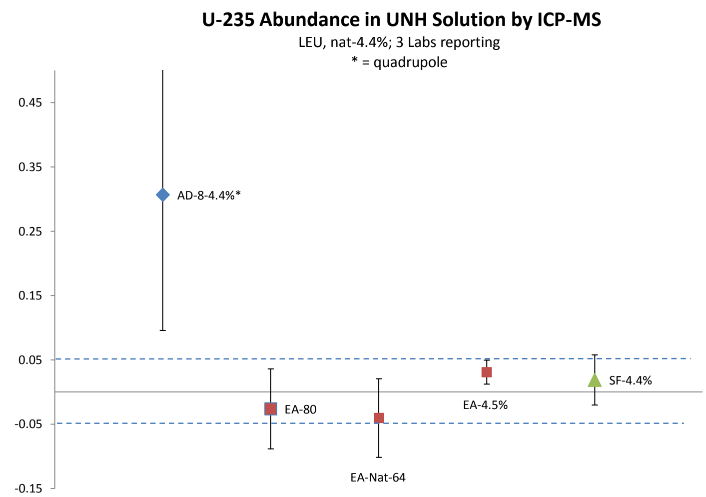
U-235 Abundance in U_30_8 by TIMS

Nat & LEU, 3 laboratories

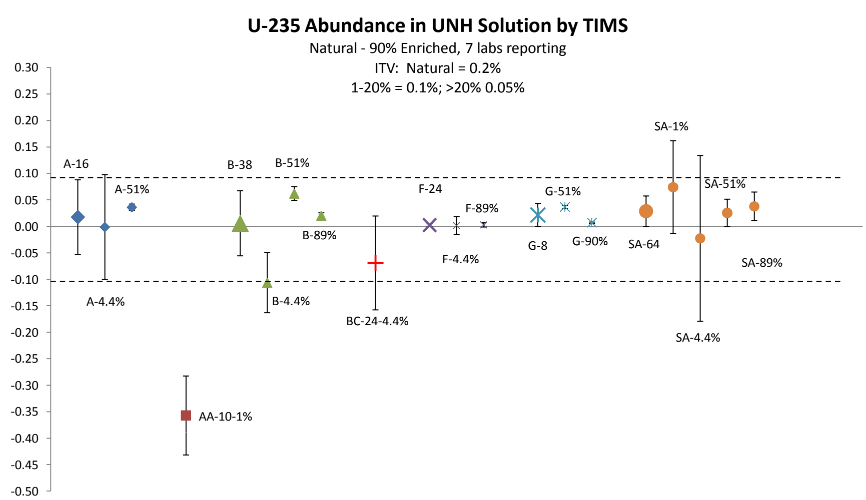
ITV: 0.2% for natural, 0.1% for >1%



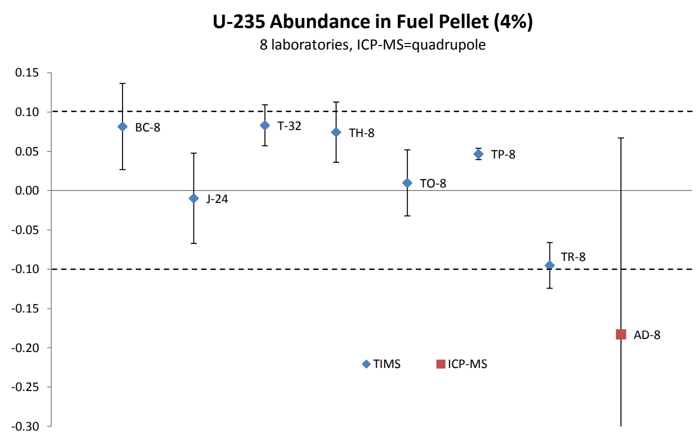
U-235 in UNH Solution by ICP



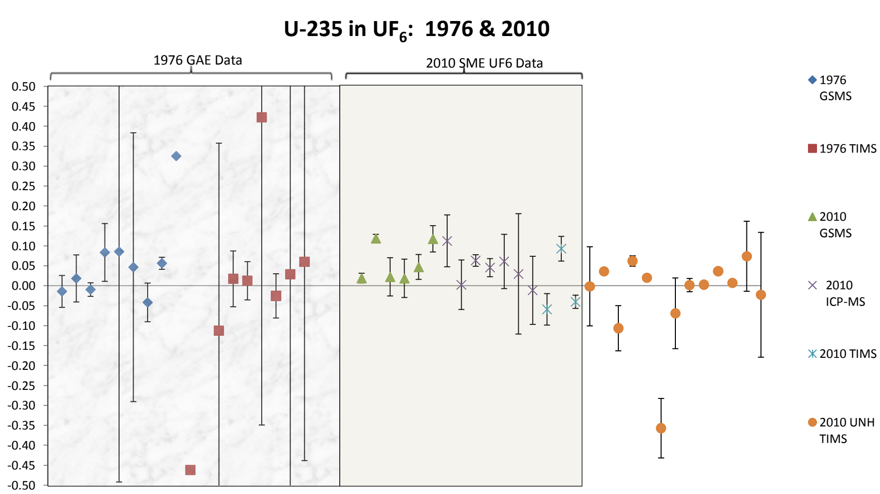
U-235 in UNH Solution by TIMS



U-235 in UO_2 pellets



U-235 in UF_6 History



Detailed Data Tables

UF6 - gas MS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
EB	0.069	0.05-0.10	0.053	0.05-0.10	16
BC	0.047	0.05-0.10	0.058	0.05-0.10	48
EB-DU	0.019	0.10	0.012	0.10	8
EB- 1.3%	**0.119**	0.05	0.010	0.05	8
BC-DU	0.022	0.10	0.048	0.10	12
BC-1.3%	0.019	0.05	0.048	0.05	12
BC-3%	0.047	0.05	0.031	0.05	12
BC-4.8%	**0.118**	0.00	0.033	0.05	12

UF6 ICP-MS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
EA	0.056	0.1-0.2	0.061	0.1-0.2	64
SF	0.023	0.1-0.2	0.107	0.1-.02	21
EA-DU	0.113	0.20	0.065	0.20	16
EA-NU	0.003	0.20	0.062	0.20	15
EA-1.3%	0.063	0.10	0.014	0.10	16
EA-4.8%	0.045	0.10	0.023	0.10	16
SF-DU	0.061	0.20	0.068	0.20	6
SF-1.3%	0.030	0.10	**0.151**	0.10	7
SF-4.8%	-0.011	0.10	0.085	0.10	8

UF6 TIMS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
J	-0.002	0.1 -0.2	0.076	0.1-0.2	12
J-DU	-0.059	0.2	0.039	0.2	4
J-1.3%	0.093	0.1	0.031	0.1	4
J-4.8%	-0.040	0.1	0.017	0.1	4

Detailed Data Tables

U3O8 TIMS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
AA	-0.125	0.1-0.2	0.121	0.1-0.2	44
BC	-0.162	0.2	0.078	0.2	8
J	0.026	0.2	0.051	0.2	8
AA-Nat	-0.084	0.2	0.096	0.2	18
AA-2%	**-0.162**	0.1	0.064	0.1	8
AA-3%	**-0.150**	0.1	**0.151**	0.1	18
BC-Nat	-0.162	0.2	0.078	0.2	8
J-Nat	0.026	0.2	0.051	0.2	8

UNH ICP-MS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
AD-4.4%	0.306	0.1	0.211	0.1	8
EA	-0.026	0.1-0.2	0.062	0.1-0.2	80
EA-Nat	-0.041	0.2	0.061	0.2	64
EA-4.5%	0.031	0.1	0.019	0.1	16
SF-4.4%	0.019	0.1	0.039	0.1	16

Detailed Data Tables

UNH TIMS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
A	0.017	0.05-0.1	0.071	0.05-0.1	16
AA 1%	**-0.357**	0.2	0.075	0.2	10
B	0.006	0.05-0.1	0.061	0.05-0.1	38
BC-4.4%	-0.069	0.1	0.089	0.1	24
F	0.002	0.05-0.1	0.002	0.05-0.1	24
G	0.022	0.050	0.022	0.05	8
SA	0.029	0.05-0.1	0.029	0.05-0.1	64
A-4.4%	-0.001	0.10	0.099	0.10	8
A-51%	0.036	0.05	0.006	0.05	8
B-4.4%	**-0.11**	0.10	0.057	0.10	7
B-51%	0.062	0.05	0.013	0.05	8
B-89%	0.020	0.05	0.005	0.05	23
AA 1%	**-0.357**	0.20	0.075	0.20	10
BC-4.4%	-0.069	0.10	0.089	0.10	24
F-4.4%	0.002	0.10	0.017	0.10	8
F-89%	0.003	0.05	0.004	0.05	16
G-51%	0.036	0.05	0.003	0.05	4
G-90%	0.007	0.05	0.001	0.05	4
SA-1%	0.074	0.20	0.088	0.20	16
SA-4.4%	-0.023	0.10	0.157	0.10	16
SA-51%	0.025	0.05	0.026	0.05	16
SA-89%	0.038	0.05	0.027	0.05	16

Detailed Data Tables

Pellet TIMS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
BC	0.082	0.1	0.055	0.1	8
J	-0.010	0.1	0.057	0.1	24
T	0.083	0.1	0.026	0.1	32
TH	0.074	0.1	0.038	0.1	8
TO	0.010	0.1	0.042	0.1	8
TP	0.047	0.1	0.007	0.1	8
TR	-0.095	0.1	0.029	0.1	8

Pellet ICP-MS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
AD	-0.18	0.10	0.25	0.1	8

UO3 TIMS

Lab Code	Avg %RD	ITV	Std Dev	ITV	N
AA	-0.27	0.20	0.15	0.2	18

Conclusions

- Uranium content determination
  - ✓ D&G is still the preferred method of analysis in a majority of labs
  - ✓ IDMS and XRF techniques are used by fewer
  - ✓ Powders seem to be more easily handled than solutions (?)
  - ✓ Most labs in conformity to ITVs
  - ✓ Are labs calculating GUM-compliant uncertainties for customers?
- Uranium isotopes abundance
  - ✓ TIMS is the method of analysis in a majority of labs
  - ✓ >90% labs are making measurements in conformity to ITVs
  - ✓ Increasing number of labs are using MC ICP-MS
  - ✓ Most labs in conformity to ITVs
  - ✓ GUM?

Plans for 2012 & beyond

Continue to offer hands-on training in:

- Chemical handling for high accuracy (weighing, solution handling, aliquanting, dissolution, etc)
- D&G titration
- High precision titration (better than 0.05% total uncertainty)
- TIMS techniques
  - Conventional fractionation correction
  - Total evaporation with minors abundances corrected
  - Modified TE for highly accurate minor determination
  - Minor isotope using internal mass-fractionation correction and Faraday-Ion counter calibration

Continue to offer GUM workshops on uncertainty determinations

Add new participants to the SME program & maintain current customers

Add new materials and occasional 'campaigns'

At least two new pellets coming this fall (LEU

Hope to do impurities in U campaign early next year

- Discuss changes to the program -

Discussion Points

- Samples:

Material	Assay Certification?	Isotopic Certification?
UF_6	Theoretical stoichiometry only	0.5% - 4.8%
UO_2 fuel pellet	Yes	4%
UO_3 powder	Yes	0.9%
U_3O_8 powder	Some yes, some no	0.7%, 2%, 3%
UNH Solution	Most yes	0.7% - 90%
Dry UNH	No	1.5%
Dry Pu nitrate	No	77%, 85%, 91% ^{239}Pu

Discussion Points

- Samples
  - UF_6 vital and will continue, but expensive to produce
  - UF_4
  - U metal
  - Two new fuel pellet types coming in late '11 or early '12
  - Ores or synthetic ores?
  - More challenging properties (minor isotopes, matrices, sizes)?
  - Pu possibility in 2012, definitely by 2013
  - Suggestions or comments:

Discussion Points

- Analysis scheme-
  - Bimonthly (SALE), quarterly, once a year?
  - Large # of analyses/days (ANOVA): is it useful?
  - Push towards single GUM uncertainty reporting?
  - Other suggestions/comments?

Discussion Points

- Measurement campaigns-
  - Single shipment, reporting date
  - One material type per campaign
  - Comparative report issued at end of campaign
    - Impurities in U
    - U assay, isotopics and impurities in an oxide or ore

Discussion Points

- Annual Meeting & Schedule
  - Currently analysis schedule supposed to follow CY
  - Report to be issued in 2nd quarter (April-May) of following year
  - ME meeting in July
  - Is this a good plan/schedule?
  - Annual Meeting – more talks, mix of talks and workshop(s), other?

Presentations:

The following pages contain the slides as given by the presenter's at the 2011 NBL SME Annual Meeting. Presenters included:

- Dr. Olivio Pereira De Oliveira JR, of the Nuclear and Energetic Research Institute in Sao Paolo, Brazil
- Dr. Claudio A. Devida of the Argentinean National Atomic Energy Commission's Ezeiza Atomic Center
- Dr. Roger Wellum, formerly of the Institute for Reference Materials and Measurements in Geel, Belgium
- Dr. Stephan Richter of the Institute for Reference Materials and Measurements in Geel, Belgium
- Greg Schaaff of the Y-12 National Security Complex, Oak Ridge, TN
- Maureen Bernard of Savannah River Nuclear Solutions, Aiken, SC

NBL offers sincere thanks to each speaker. The presentations were well-received and given in a clear and concise manner. Questions regarding the content of the presentations may be directed towards the speakers listed above, via their email addresses given earlier in this report.

Improvements in the measurements of uranium concentration and isotope amount ratio for nuclear safeguards

Olivio Pereira de Oliveira Jr.

SMEP - NBL Annual Meeting
Palm Desert, USA
July 16th 2011

IPEN and CTMSP facilities

IPEN

Nuclear and Energetic Research Institute

- Civilian federal research center focused in applied sciences
- Holds the first nuclear research reactor (IEA-R1) built in South America (1958)
- Just 10% devoted to nuclear energy topics
- Runs a very successful posgraduation program (800 master and PHD students)

CTMSP

Brazilian Navy Technological Center

- Nuclear research center managed by the Brazilian navy
- Developed the uranium isotope enrichment process by ultracentrifugation
- About 600 employees working in two facilities within the Sao Paulo state

CTMSP provides analytical services for

- Brazilian uranium enrichment facilities
- Brazilian fuel manufacturer INB
- Brazilian nuclear institutes
- ABACC regional safeguards agency
- Universities and industry

Analytical services provided

- Uranium concentration measurement
- Uranium isotope amount ratios
- Volatile impurities in UF_6
- Metallic impurities in UF_6 and UO_2
- UF_6 hydrolysis

- Reconversion from UO_2 to UF_6
- Development of UF_6 sampling method with alumina with CNEA colleagues
- Residual gas analysis
- Leak testing in

vacuum instruments, valves and pumps
uranium enrichment facilities

Uranium concentration measurements

- **Technique selected:**
  Potentiometric titration
- **Method applied:**
  NBL modified Davies and Gray
- **Instrument used:**
  Titrino S Metrohm (Herisau, Switzerland)
- **CRM used**
  NBL CRM 112A, CRM 129

Year	ITV 2010		Results for UO_2	
	Bias	Precision	Bias	Precision
	(%)	(%)	(%)	(%)
2010	0.10	0.10	0.009	0.045
2009	0.10	0.10	0.039	0.021
2008	0.10	0.10	-0.032	0.085
2007	0.10	0.10	0.157	0.111
2006	0.10	0.10	-0.010	0.055
2006	0.10	0.10	-0.077	0.065
2002	0.10	0.10	-0.178	0.305
1998	0.10	0.10	0.025	0.238

Uranium isotope ratio measurements

- **Technique selected:**
  Thermal ionization mass spectrometry (TIMS)
- **Method applied:**
  External calibration
- **Instrument used**
  THQ, Finnigan MAT (Bremen, Germany)
- **CRM used**
  NBL CRM isotopic series

Year	Y (%)	ITV 2010		Results for UO_2	
		Bias (%)	Precision (%)	Bias (%)	Precision (%)
2010	4.0	0.10	0.10	0.082	0.055
2009	4.0	0.10	0.10	0.020	0.055
2008	0.7	0.10	0.10	-0.011	0.083
2008	4.0	0.10	0.10	0.119	0.079
2007	4.0	0.10	0.10	-0.010	0.075
2006	4.0	0.10	0.10	0.029	0.092
2006	4.0	0.10	0.10	-0.005	0.060
2002	0.7	0.10	0.10	0.547	0.251
2000	4.0	0.10	0.10	-0.410	0.178

UF_6 isotope ratio measurements

- **Technique selected:**
  Electron impact mass spectrometry (GSMS)
- **Methods applied:**
  Single and double standard
- **Instrument used:**
  IMU 200, IPI Instruments (Bremen, Germany)
- **CIRM used**
  MRI 0.5 to 20.0 (Brazilian CIRM)
  IRMM 019 - 028

Year	Y (%)	ITV 2000		Results for UF_6	
		Bias (%)	Precision (%)	Bias (%)	Precision (%)
2010	0.5	0.10	0.10	0.047	0.031
	1.29	0.05	0.05	0.019	0.048
2009	1.29	0.05	0.05	0.039	0.094
2008	1.29	0.05	0.05	-0.086	0.073
	0.49	0.10	0.10	0.016	0.114
	0.71	0.10	0.10	-0.025	0.086
2007	2.98	0.05	0.05	0.139	0.063
	3.19	0.05	0.05	0.162	0.083
	4.79	0.05	0.05	0.004	0.076
2006	3.19	0.05	0.05	0.017	0.250
	3.19	0.05	0.05	0.093	0.121

Non-volatile impurities in UO_2

Technique selected:

Inductively coupled plasma mass spectrometry (ICPMS)

Method:

Matrix matching method

Instrument used:

PQ II, VG Elemental (Winsford, Cheshire, UK)

CRM used

NBL CRM 124

Volatile impurities in UF_6

Technique selected:

Fourier transformed infrared spectrometry (FTIR)

Method applied:

Calibration curves of pure gases mixed with UF_6

Instrument used:

Spectrum One Perkin Elmer (Shelton, CT, USA)

CRM used:

Pure gases (HF, BF_3, PF_5, SiF_4) from Matheson (Newark, CA, USA)

Residual gas analysis

Technique selected:

Quadrupole mass spectrometry (QMS)

Method applied:

Partial pressure measurements

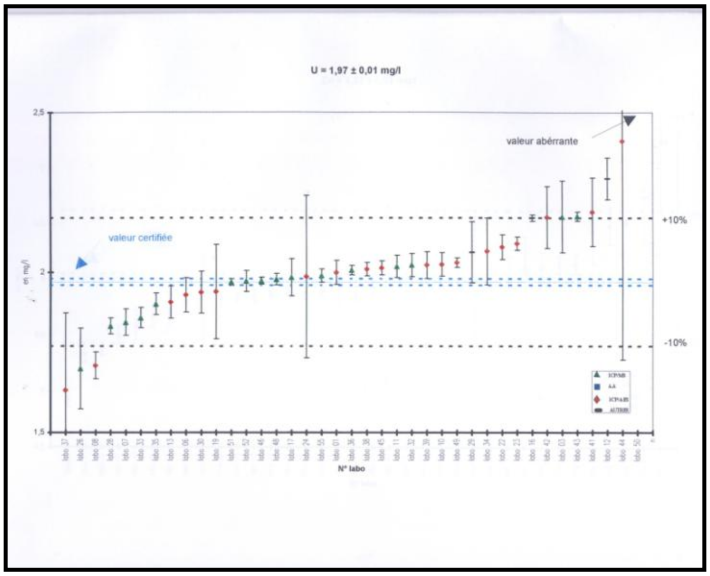
Instrument used:

Prisma QMS 200 (Pfeiffer Vacuum, Assler, Germany)

Participation in other international interlaboratorial comparison programs

CETAMA

Analyse de Traces nº 4



REIMEP 15

REIMEP-15 : Uranium hexafluoride isotopic ratios

$n(^{235}U)/n(^{238}U)$ certified range ($\pm U=2u_c$): 0.034131 - 0.034165

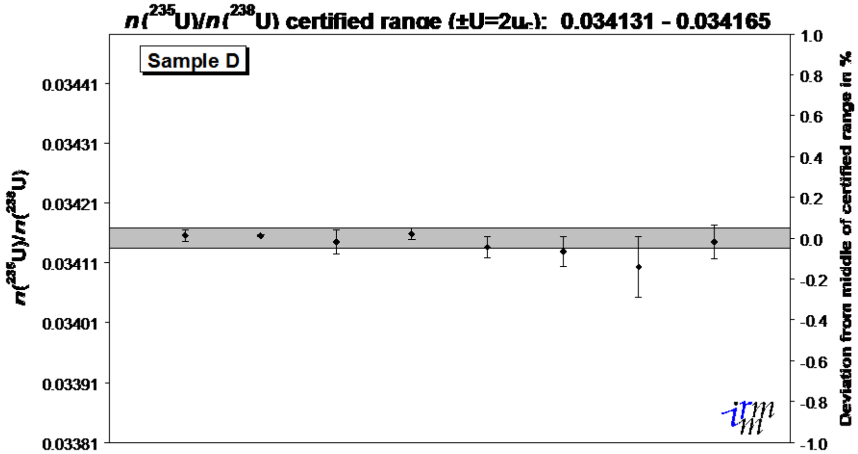
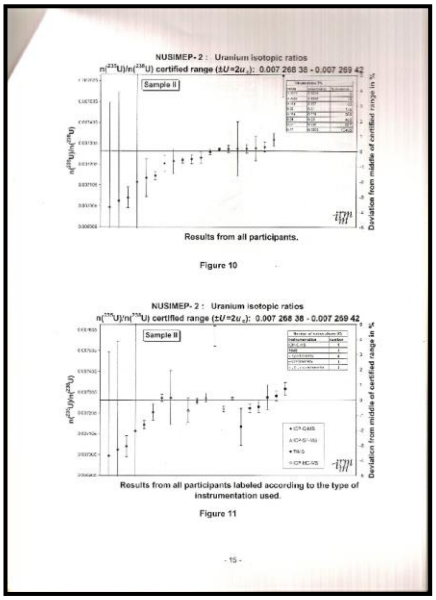


Fig. 4: Results from all participants.

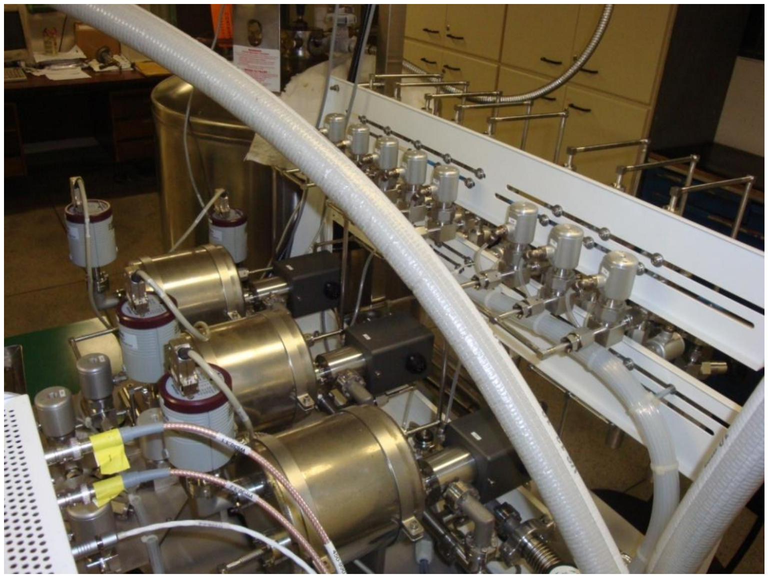
NUSIMEP 2



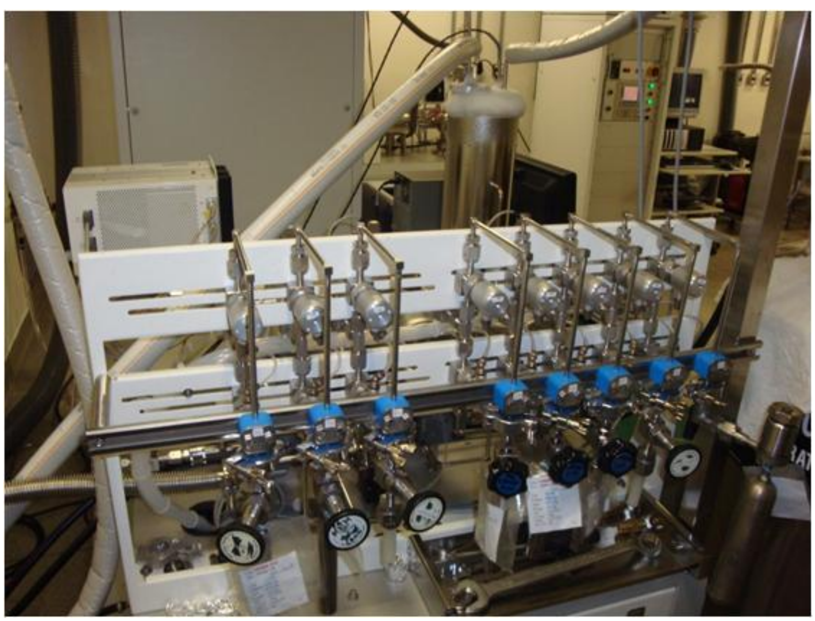
What is really new in our laboratory?

a mass spectrometer for UF_6 isotope ratio measurements

- special designed instrument for direct UF_6 isotope ratio measurements
- three inlet tanks for D, N and E samples
- electron impact ion source
- quadrupole analyzer
- faraday cup & electron multiplier detectors
- can also detect volatile impurities in UF_6



3 sample inlet tanks
3 MKS Baratron pressure manometers



8 inlet connections for UF_6 ampoules

Typical precison and bias values

Isotope ratios	Isotopic ratio range	Precision (%)	Bias (%)
n(^{234}U)/n(^{238}U	1.0e^{-5}	5.0	3.0
	1.0e^{-4}	5.0	2.0
	1.0e^{-3}	5.0	0.5
	1.0e^{-3}	0.05	0.05
n(^{235}U)/n(^{238}U)	1.0e^{-2}	0.05	0.05
	1.0e^{-1}	0.05	0.05
	1.0e^{-7} & 1.0e^{-6}	LOD	LOD
	1.0e^{-5}	0.5	40
n(^{236}U)/n(^{238}U)	1.0e^{-4}	0.5	30
	1.0e^{-3}	0.5	20

Conclusions

Destructive measurements (DA)

- CTMSP is performing well the basic measurements for nuclear safeguards

ITV 2010

- within a decade a considerable improvement has been made regarding the IAEA target values

New analytical instruments & procedures

- Very important developments in the measurement of n(^{234}U)/n(^{238}U) and n(^{236}U)/n(^{238}U) ratios

MEASUREMENTS FOR NUCLEAR *SAFEGUARDS AND* IMPROVEMENT OF ANALYTICAL TECHNIQUES. .

Claudio A. Devida

Argentinean National Atomic Energy Commission (C.N.E.A .)
UAM y CN. Ezeiza Atomic Center(CAE)
Presbítero Luis González y Aragón Nro.15. Ezeiza
Provincia de Buenos Aires
CP: B1802AYA - Argentina
devida@cae.cnea.gov.ar

The National Atomic Energy Commission, (CNEA) is the Argentine government agency in charge of nuclear energy research and development.

The agency was created on May 31, 1950 with the mission of developing and controlling nuclear energy for peaceful purposes in the country.

GOALS

The Analytical Laboratory located at EZEIZA ATOMIC CENTRE (CAE), was established by the CNEA to provide service in chemical analyses to:

-Facilities that supply nuclear-grade purified uranium employed in the production of nuclear fuel elements and irradiation target for Mo-99 production.
- Research laboratories.
-Measurement of trace element in samples from CNEA and outside companies and organizations .

The aims has always been to provide fast, accurate, a reliable services to customers, using analytical methods and procedures that are accepted as international standards.
The analytical capacity of the laboratory was upgraded with the incorporations of Quadrupole Inductively Coupled Plasma Mass Spectrometry (Q-ICPMS) .Among other advantages, this addition extended the capacity of the lab for safeguard methods used to uranium isotopic abundance measurements in different compounds.

LABORATORY'S CURRENT ACTIVITIES

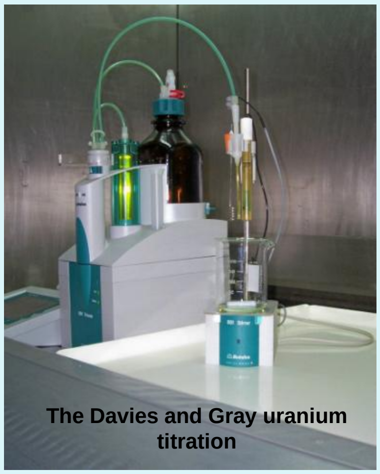
Chemical control for purposes of nuclear material accounting of radiochemical facility LTA which to recover, down-blend to low-enriched uranium containing <20 wt % ^{235}U (LEU) and purify fresh highly-enriched uranium containing ≥ 20 wt % ^{235}U (HEU) inventories remaining as scrap from fuel and target production of the fuel fabrication facility.

We are working on measurement of trace impurities in uranium dioxide pellets (used in the fuel elements for power reactors) by ICPMS spectrometry.

As safeguards titrimetric method (Davies and Gray) is applied for the accurate measurements of non-irradiated enriched uranium in various physical form and chemical compositions and isotopic analysis of uranium materials by Q-ICPMS for Uranium Down blending process.

NUCLEAR SAFEGUARDS ANALYTICAL METHODS

Destructive analysis (DA)



The Davies and Gray uranium titration

Uranium isotopic compositions by Q-ICPMS

ABACC network laboratories

The Brazilian-Argentine Agency for Accountability and Control of Nuclear Materials (ABACC), as administrator of the Common System of Accountability and Control, whenever necessary during safeguards inspections, has to analyze samples of nuclear materials

Since the ABACC does not have its own analytical laboratory for performing the necessary analyses, the Agency makes use of a network composed by laboratories in Brazil and Argentina, which participate in the nuclear programs of these countries.

International partnerships ABACC-NBL

In order to verify the quality of DA and, at the same time, to identify eventual problems in the analyses, one of the activities of the ABACC's Technical Support Sector is a program for intercomparison of measurements, involving the participation of the laboratories in the network.

By means of an agreement for technical cooperation with the United States Department of Energy (DoE), the Agency has also developed projects, coordinated with the New Brunswick National Laboratory (NBL), training, workshops and NBL's Safeguard Measurement Evaluation (SME) /intercomparison program.

NBL- SAFEGUARD MEASUREMENT EVALUATION

Since 1995 the laboratory has participated in ABACC Round Robin .

Uranium mass fractions of Uranyl nitrate hydrate (UNH) solution and Uranium dioxide (UO_2) pellet by Davies & Gray titrations.

In 2008 the laboratory was involved in the analysis of uranium isotopic abundance in LEU.

NBL SAFEGUARD MEASUREMENT EVALUATION PROGRAM, DATA EVALUATION REPORT-%U

NBL sends each participant a report about the errors and bias, providing them with feedback for improvement of methods, techniques and procedures.

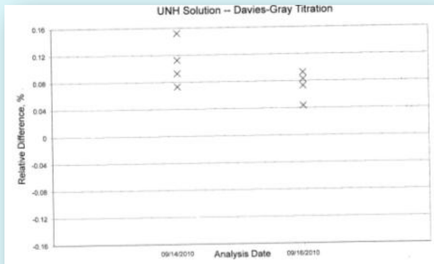
NBL-Training workshop

- In June 2004 , Quality Assurance (QA) Workshop presented in Rio de Janeiro, Brazil.
- In Septiembre 2005 , NBL hosted training workshop on destructive analytical techniques.
- NBL-modified Davies and Gray method and Uranium Thermal Ionizations Mass Spectrometry (TIMS) .
- Software tool developed by NIST - based on R-statistics application with Excel interface – for uncertainty estimations according to GUM (Guide to the Expression of Uncertainty in Measurement).

NBL-Training workshop

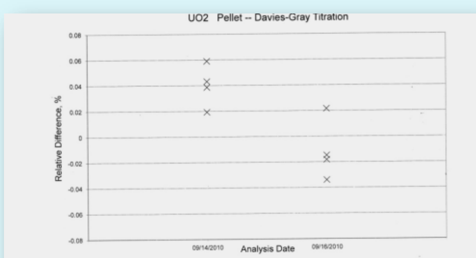
- These workshops and training in laboratories NBL were very useful to improve the techniques applied to safeguards.
- environmental conditions of laboratory and temperature of the reagent which affect the results of the analysis.
- Sample volume and interference.
- Preparation of uranium standard solutions, using glass bottles caps seal with a Polycon, without loss of analyte.
- Indicating electrode wire pt.
- Quality assurance.

Evaluation summary of uranium mass fractions. UNH



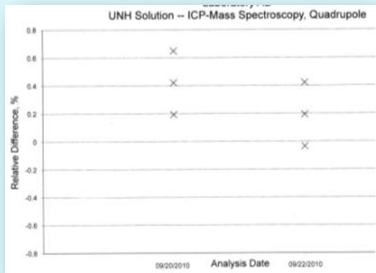
	Uranium mass fraction	ITV
No. of results (n)	8	
Outlier	None	
Mean % Difference	0.090	u(s): 0.1
Standard Deviation	0.032	u(r): 0.1
95% C.L. of Mean (df = 7)	0.027	
Day-to-day variation: Statistical Significance	Not significant; 86.6%	
Bias	Negative bias	

Evaluation summary of uranium mass fractions. UO_2



	Uranium mass fraction	ITV
No. of results (n)	8	
Outlier	None	
Mean % Difference	0.014	u(s): 0.1
Standard Deviation	0.033	u(r): 0.1
95% C.L. of Mean (df = 1)	0.326	
Day-to-day variation: Statistical Significance	Highly significant; 98.8%	
Bias	Inconclusive	

Evaluation summary of ^{235}U abundance. LEU



	^{235}U abundance	ITV
Number of results (n)	8	
Outlier	None	
Mean % Difference	0.306	u(s) = 0.1
Standard Deviation	0.211	u(r) = 0.1
95% C.L. of Mean (df = 7)	0.176	
Day-to-day variation: statistical significance	Not significant, 86.6%	
Bias	Positive bias	

FUTURE IMPROVEMENTS

- Sample introduction system
- Ultra-sonic nebulizer coupled with membrane desolvation system.
  - BENEFITS
  - Improved signal stability. less drift.
  - Sesitivity enhanced up to 10x greater for ICPMS.
  - Oxide reductions.
  - To provide maximum signal with minimal sample uptake. Lower volume of radioactive waste

Thank you for your attention!!

Proposal for a new type of LSD spike

R. Wellum

Why LSD spike?

The main problem area when measuring the uranium and plutonium isotopic amounts in spent nuclear fuel is in handling the dissolved fuel solution.

Large sized dried spikes were developed to allow a simple process in the hot-cells and still yield excellent measured values.

IRMM has been one of the world’s centres of excellence for LSD spikes.

Present LSD spike

- A mixture of 20% ^{235}U-enriched uranium and ^{239}Pu; ratio ~ 50:1; ~ 50 mg U per spike
- Sample of dissolved fuel is spiked directly, chemically homogenized and a small sample is taken
- A dilute sample of the dissolved fuel also needed without spiking

Proposal

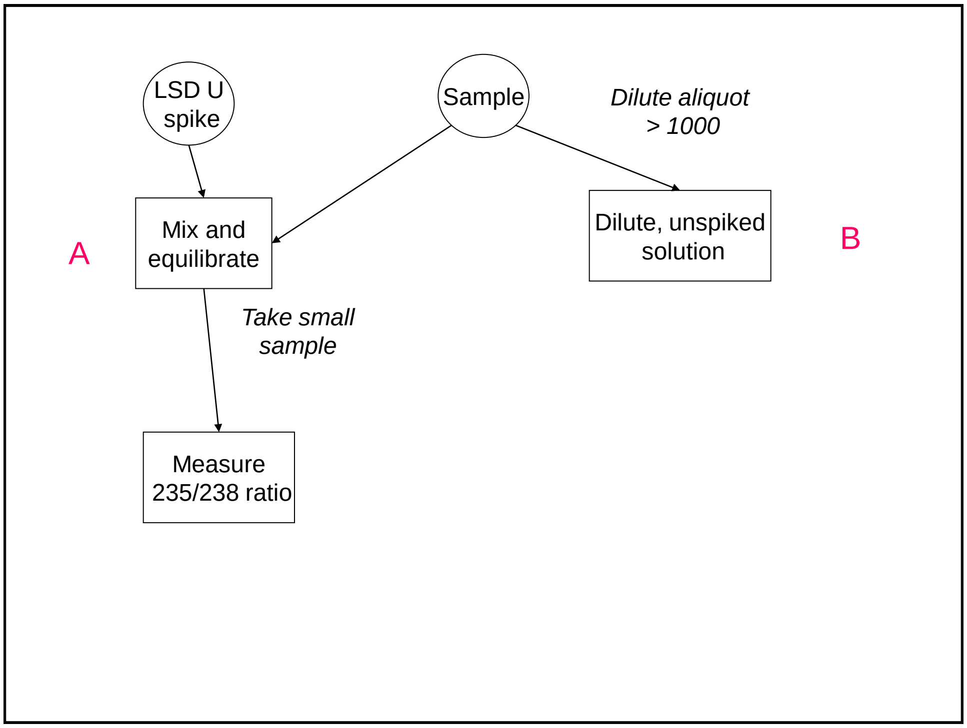
By separating the 2 functions of the LSD spike:
a) measurement of U and Pu isotopic concentrations and
b) relating these to the concentrated solution, we can modify the traditional LSD spike and use uranium alone as spike and measure Pu concentration relative to that of uranium

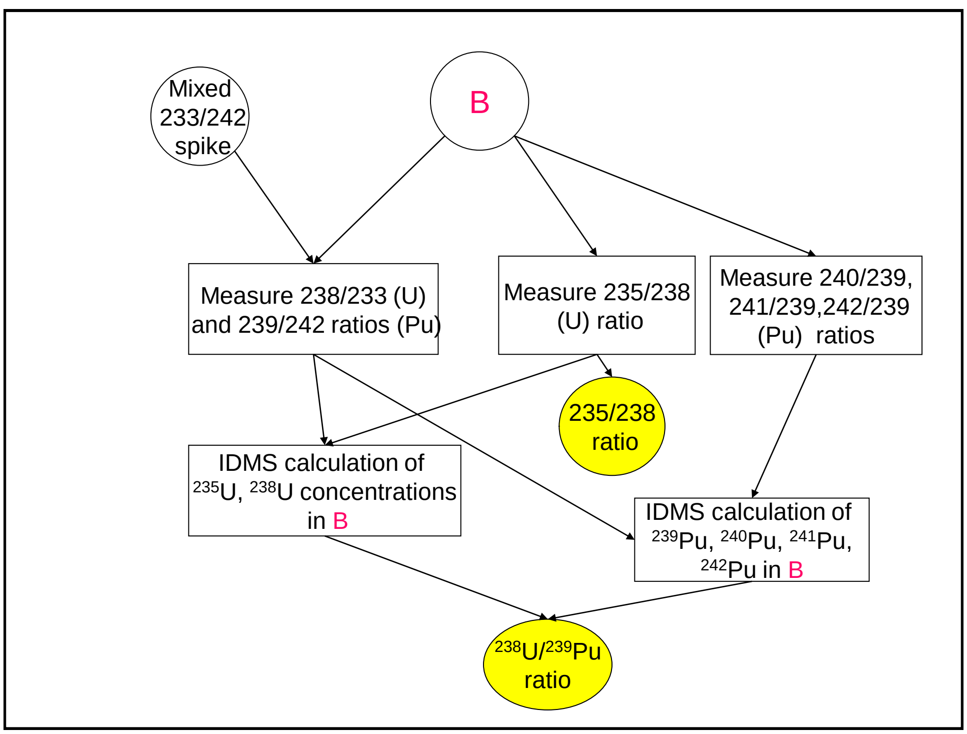
Basis of new scheme

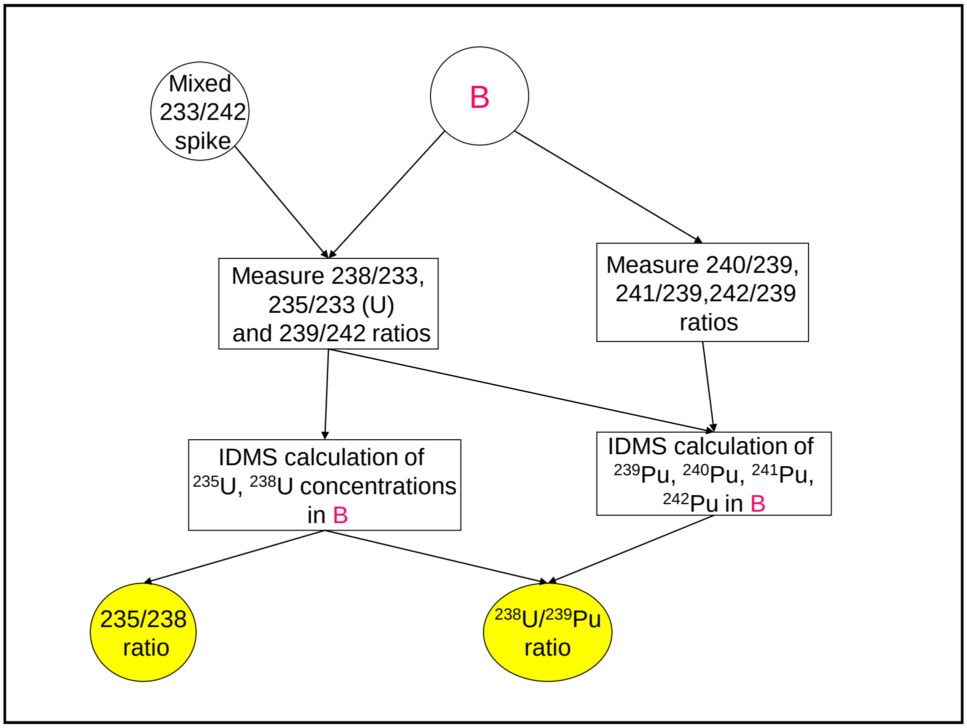
- Only uranium LSD spike is used
  - The concentration of uranium in the sample is fixed with this spike
- An aliquot of the sample is diluted as required (e.g. x1000) and the uranium and plutonium isotopic concentrations are measured by IDMS using a mixed U/Pu spike

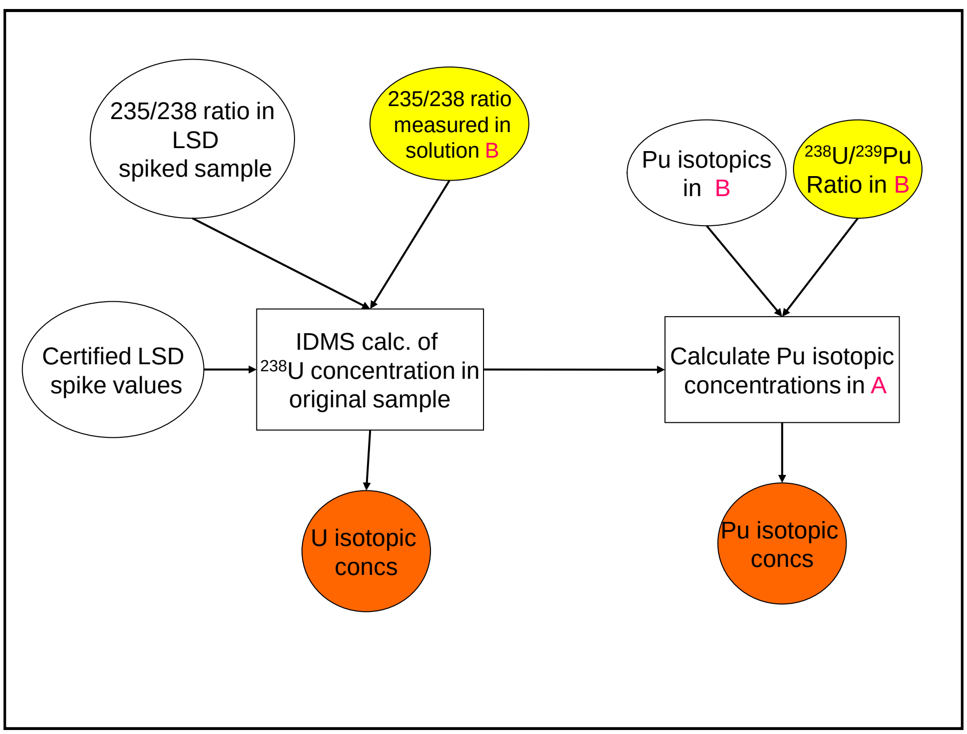
Advantages

1. No large amounts of ^{239}Pu are required
   - Transport problems avoided
   - Equilibration and stability problems of Pu can be dealt with in dilute solution
2. Flexibility of measurement
   - Spiking of dilute solution can be done with a mixed U/Pu spike or by separate spikes
3. If a mixed spike is used $(^{233}U/^{242}Pu)$, no extra measurements are needed


LSD U spike
Sample
Dilute aliquot > 1000
Mix and equilibrate
Dilute, unspiked solution
A
B
Take small sample
Measure 235/238 ratio


Mixed 233/242 spike
B
Measure 238/233 (U) and 239/242 ratios (Pu)
Measure 235/238 (U) ratio
Measure 240/239, 241/239,242/239 (Pu) ratios
235/238 ratio
IDMS calculation of ^{235}U, ^{238}U concentrations in B
IDMS calculation of ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu in B
$^{238}U/^{239}Pu$ ratio


Mixed 233/242 spike
B
Measure 238/233, 235/233 (U) and 239/242 ratios
Measure 240/239, 241/239,242/239 ratios
IDMS calculation of ^{235}U, ^{238}U concentrations in B
IDMS calculation of ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu in B
235/238 ratio
$^{238}U/^{239}Pu$ ratio


235/238 ratio in LSD spiked sample
235/238 ratio measured in solution B
Pu isotopics in B
$^{238}U/^{239}Pu$ Ratio in B
Certified LSD spike values
IDMS calc. of ^{238}U concentration in original sample
Calculate Pu isotopic concentrations in A
U isotopic concs
Pu isotopic concs

Measurement Evaluation Programmes at IRMM

S Richter, H Kühn, J Truyens, E Stefaniak, Y Aregbe, F Kehoe, J Bouwens, R Bujak, R Eykens, A Vergruggen, R Wellum

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

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

Introduction

- REIMEP= Regular European Inter-Laboratory Measurement Evaluation Program
- NUSIMEP: Nuclear Signatures Interlaboratory Measurement Evaluation Programme
- Rules:
  - a) External quality control tools for laboratories from nuclear safeguards, nuclear industry but also from the environmental, geochemistry field and academia
  - b) Laboratories receive well-characterised samples with undisclosed values
  - c) References values are provided, independent of the participants' results
  - d) Full confidentiality is guaranteed (result vs. identity)

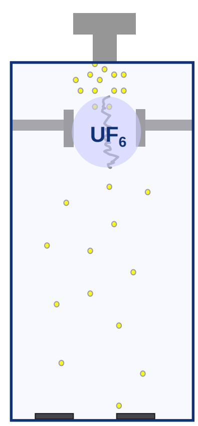
REIMEP-17

- U/Pu synthetic input solution prepared from dissolved MOX fuel with addition of NU (U:Pu = 100:1)
- REIMEP-17 samples will be prepared and distributed by ITU
- REIMEP-17 samples will be certified by IRMM: IRMM provides the reference values for U and Pu amount contents and isotopic compositions
- <u>3 different concentrations for nuclear laboratories:</u>
  a) *high* – (200 mg U, 2 mg Pu) addition of inactive fission products - spiking is possible with IRMM-1027 LSD spike
  b) *medium* – *(*about 5 mg U, 50 µg Pu)
  c) *low* - (500 ng U, 5 ng Pu) for environmental labs

- Start foreseen: end of 2011!

NUSIMEP-7

- Uranium isotope amount ratios in uranium particles
- Graphite planchet
- Measurement of $^{234}U/^{238}U$, $^{235}U/^{238}U$ & $^{236}U/^{238}U$, 2 enrichments !
- Routine measurement procedure, SIMS, FT-TIMS, LA-ICPMS,…
- Preparation of “real life” U particles:



$UF_6 + 2\,H_2O \rightarrow UO_2F_2 + 4\,HF$

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NUSIMEP-7

- Contact for NUSIMEP-7
  JRC-IRMM-NUSIMEP@ec.europa.eu
- Sample mailing end of May
- Deadline for result reporting extended to 1 September

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A New UF_6-Gas Source Mass Spectrometer for Certification of Reference Materials and Nuclear Safeguards Measurements at IRMM

S Richter, H Kühn, J Truyens, M Kraiem, E Stefaniak, Y Aregbe

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

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

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Content

- Introduction about UF_6-gas source mass spectrometry
  1. Role of UF_6 in nuclear fuel cycle
  2. Need for accurate isotopic measurements of UF_6 samples
  3. Preparation of basic gravimetric mixtures, certification of first UF_6 isotope reference materials
- UF_6-gas source mass spectrometry at IRMM
  1. Installation of MAT511 at IRMM
  2. Replacement of 39-year old MAT511 by URANUS
  3. Design of URANUS
  4. Measurement performance for "major" ratios $^{235}U/^{238}U$
  5. Measurement performance for "minor" ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$
- Conclusions

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Introduction about UF_6-gas source mass spectrometry (GSMS)

- Gaseous UF_6 is primary form of U in nuclear fuel cycle
- Reason: used in isotope enrichment process
- Accurate isotopic measurements of UF_6 samples necessary
- Isotopic reference materials needed !
- Isotopic measurements of UF_6 samples are performed at:
  a) Enrichment facilities
  b) Safeguards authorities (Euratom, IAEA, etc)
  c) Reference material providers (IRMM[1], NBL[2], IPEN[3], etc)

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Introduction about UF_6-gas source mass spectrometry (GSMS)

Measuring $^{235}U/^{238}U$ ratios by UF_6-gas source mass spectrometry:

- Unprecedented level of reproducibility for $^{235}U/^{238}U$ ratio measurements using UF_6-gas-MS: RSD = ca. 0.003%
  TIMS total evaporation still limited to RSD = ca. 0.015%
  MC-ICP-MS still limited to RSD = ca. 0.030%
- For all instruments & all methods: isotopic reference materials needed !

Applications for UF_6-gas source mass spectrometry at IRMM:

- Preparation of *tailor made* isotopic RMs on demand, for external customers and IRMM, measurement campaigns (REIMEP)
- Measurement service for external customers and European Safeguards Authorities
- Production of U-oxide reference particles made from UF_6

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Basic gravimetric mixtures & primary UF_6 isotope reference materials

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- Started with gravimetrically mixing of highly enriched ^{235}U and ^{238}U
- 10 mixtures prepared with accuracy of 0.01% for $^{235}U/^{238}U$
- Conversion from U-oxide into UF_6
- 5 new U materials prepared, each 30kg of U_3O_8:
  1. EC171/IRMM-031: $^{235}U/^{238}U \cong 0.003$ ($\pm$0.03%)
  2. EC171/IRMM-071: $^{235}U/^{238}U \cong 0.007$
  3. EC171/IRMM-194: $^{235}U/^{238}U \cong 0.020$
  4. EC171/IRMM-294: $^{235}U/^{238}U \cong 0.030$
  5. EC171/IRMM-446: $^{235}U/^{238}U \cong 0.045$
  - 500 units of U-nitrate solution, 1g U each: IRMM-183-187
  - 6 g converted to UF_6 for GSMS measurement against the 10 gravimetric mixtures, using MAT511 & double standard method
- IRMM-021 to IRMM-027 series ($\pm$0.05%), using MAT511

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UF_6-gas source mass spectrometry at IRMM: since almost 40 years

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Reasons for replacing the old MAT511:

- Difficult or even impossible to get certain spare parts for MAT511
- Impossible to measure minor isotopes ^{234}U and ^{236}U on MAT511
- Manual operation, 1 sample per day (double standard method)

vacuum system

mercury pump for ion source (replaced by ion getter pump)

old electronics

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Replacement of the MAT511 by the URANUS from Thermo Fisher

- Based on well proven technology from TRITON-TIMS and NEPTUNE-ICPMS
- Magnet, amplifier housing and Faraday-multi-collector identical (except for triple cup)
- Ion source similar to MAT511
- Sample introduction system from MAT281

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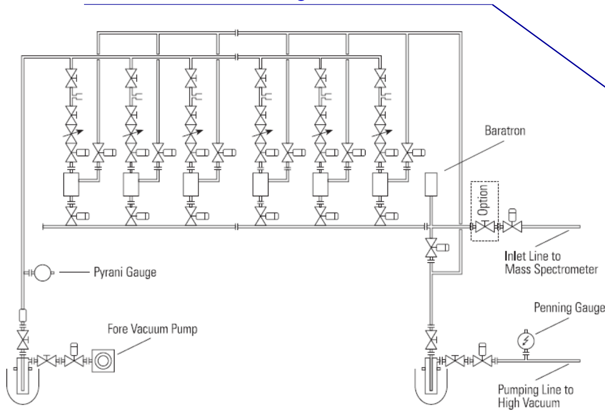
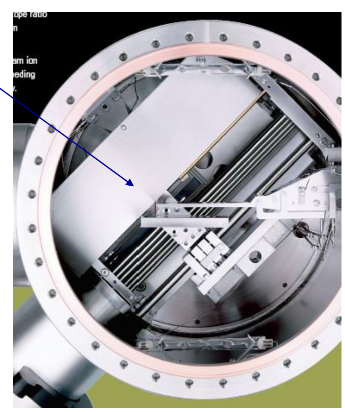
Design of the URANUS

- Measuring minor isotopes ^{234}U, ^{236}U simultaneously with ^{235}U, ^{238}U
- Triple-Faraday collector for masses 329 ($^{234}U^{19}F_5^+$), 330 ($^{235}U^{19}F_5^+$) and 331 ($^{236}U^{19}F_5^+$)





- Sample introduction system (9 inlets at IRMM) for automatic sequences, e.g. for using double standard method

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Performance for "major" ratios $^{235}U/^{238}U$

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- Investigation of methods & corrections done using a set of 6 working standards
- Characterized for major and minor ratios by TIMS-MTE (modified total evaporation), relative to new gravimetric standard IRMM-074
- $^{235}U/^{238}U$: agreement between TIMS/MTE and UF_6 GSMS
- TIMS/MTE data used

Working Standard No.	IRMM ID	$^{235}U/^{238}U$	U (k=2)	Rel. U (k=2)
5	IRMM-2396	0.0058943	0.0000013	0.023%
6	IRMM-634	0.0072586	0.0000017	0.023%
7	IRMM-2397	0.0084305	0.0000022	0.026%
8	IRMM-714	0.0155608	0.0000031	0.020%
9	IRMM-026	0.0256780	0.0000050	0.020%
10	IRMM-029	0.0440481	0.0000093	0.021%

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Corrections for "major" ratios $^{235}U/^{238}U$

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- Despite the excellent reproducibility for UF_6 GSMS (0.003%): reference materials are needed to calibrate instrument & method
- Single standard method, using 1 standard, called S1:

$$R_{SA-corrected} = R_{SA-measured} \frac{R_{S1-certified}}{R_{S1-measured}}$$

- Double standard method (DS): use 2 standards S1 and S2, calculate average, weighted by "isotopic distances" between sample and standards:

$$\alpha_1 = \frac{R_{SA-measured}}{R_{S1-measured}} \qquad \alpha_2 = \frac{R_{SA-measured}}{R_{S2-measured}}$$

$$R_{SA-corrected-DS} = \frac{\alpha_1 - \alpha_2}{\frac{1}{R_{S1-certified}}(1-\alpha_2) + \frac{1}{R_{S2-certified}}(\alpha_1 - 1)}$$

Colour for plot:

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Corrections for "major" ratios $^{235}U/^{238}U$

- What about memory effects ?
  a) Depends on instrumental design, e.g. vacuum tubes
  b) Depends on "isotopic distances" between sample and standards
- Definition:

$$M_{S1vsS2} = \left(\frac{R_{S1-certified}}{R_{S2-certified}} - 1\right) \Big/ \left(\frac{R_{S1-measured}}{R_{S2-measured}} - 1\right)$$

$\Rightarrow$ Always 2 standards needed to measure memory effects

- Memory-corrected "single" standard method:

$$R_{SA-corrected-S2} = \left[M_{S1vsS2}\left(\frac{R_{SA-measured}}{R_{S2-measured}} - 1\right) + 1\right] R_{S2-certified}$$

$$R_{SA-corrected-S1} = \left[M_{S2vsS1}\left(\frac{R_{SA-measured}}{R_{S1-measured}} - 1\right) + 1\right] R_{S1-certified}$$

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Corrections for "major" ratios $^{235}U/^{238}U$

- Memory-corrected double standard method (MCDS)
  Similar to DS, but α-values are memory-corrected:

$$\alpha_{1-corrected} = [M_{S2vsS1}(\alpha_1 - 1) + 1]$$

$$\alpha_{2-corrected} = [M_{S1vsS2}(\alpha_2 - 1) + 1]$$

$$R_{SA-corrected-MCDS} = \frac{\alpha_{1-corrected} - \alpha_{2-corrected}}{\frac{1}{R_{S1-certified}}(1 - \alpha_{2-corrected}) + \frac{1}{R_{S2-certified}}(\alpha_{1-corrected} - 1)}$$

- "Normal" double standard method (DS): only works…
  a) if memory effects cancel out, or
  b) if "isotopic distance" similar between sample and standards, or
  c) if memory effects are small
- …otherwise: significant deviations observed for DS

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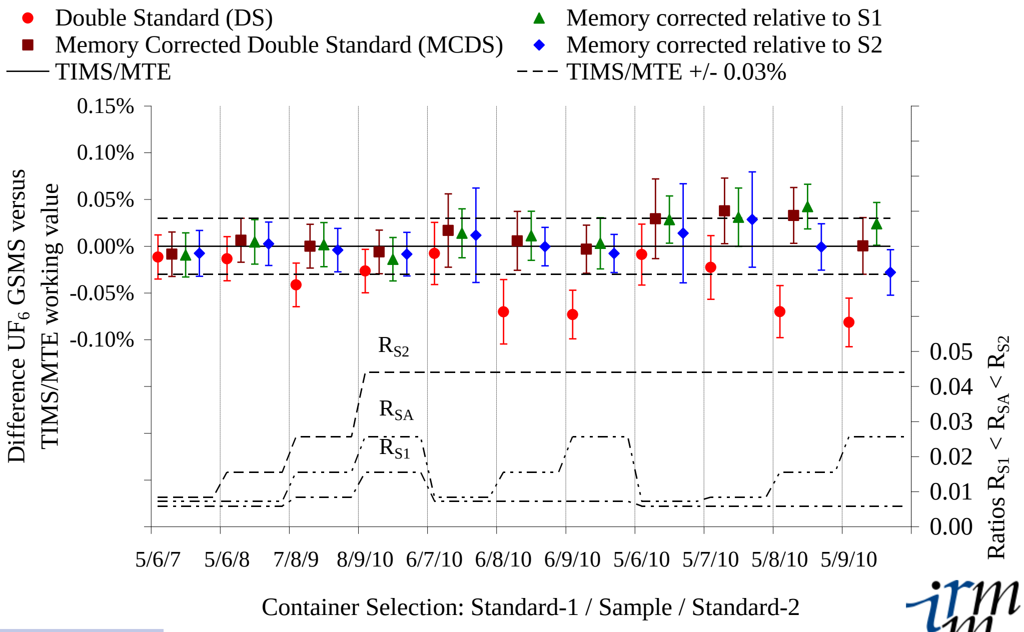
Performance for “major” ratios $^{235}U/^{238}U$



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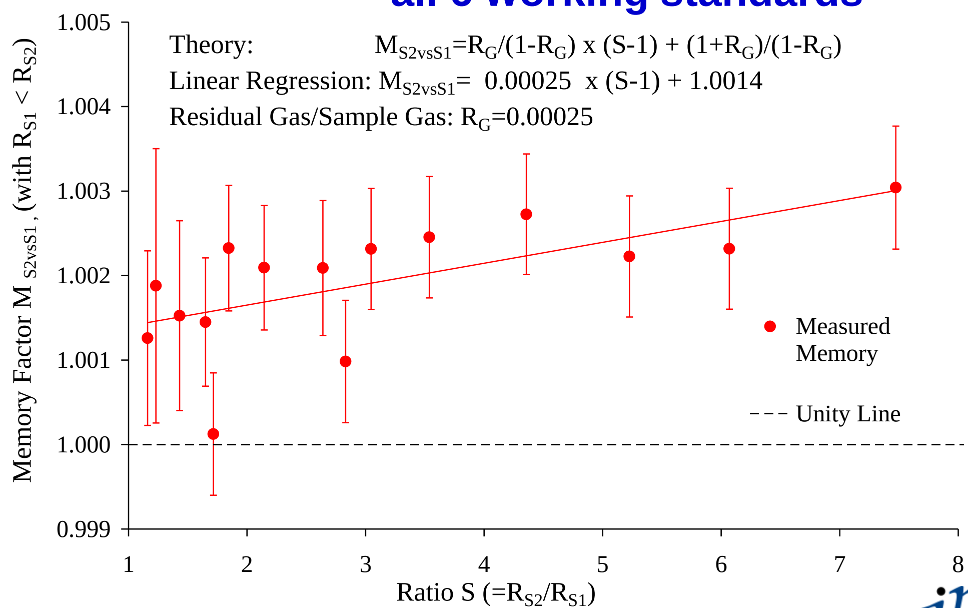
Memory effects measured between all 6 working standards



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Minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$

- Smaller relative mass differences between masses 329 ($^{234}U^{19}F_5^+$), 330 ($^{235}U^{19}F_5^+$) and 331 ($^{236}U^{19}F_5^+$) compared to 234, 235 and 236
- Construction of new "triple cup": 3 graphite Faraday cups from TRITON-TIMS mounted inside the same housing
- Shielding between cups not as good as for single cups, scattering of ions into neighboring cups possible
- Peak tailing effects from major beams (mainly ^{238}U) towards ^{234}U and ^{236}U are 10x higher compared to TIMS: "abundance sensitivity"
- Choice of standards difficult, e.g. for DS method
- Memory effects to be considered
- So far uncertainties about 10x higher compared to TIMS/MTE, but performance satisfactory for purpose
- Method optimization / validation still ongoing

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Conclusions

- New UF_6 GSMS installed at IRMM
- 40 years old MAT511 replaced by URANUS
- Necessary to guarantee the high quality supply of IRMM UF_6 reference materials and reference measurements in the future
- Advantages of URANUS:
  a) Measurement of major & minor ratios
  b) Automatic measurement sequences
- Performance for "major" ratios $^{235}U/^{238}U$ satisfactory (±0.03%), correction for memory effects necessary: MCDS !
- Validation ongoing for "minor" ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$
- New UF_6 GSMS guarantees IRMM's role as a leading provider of high quality UF_6 reference materials and measurements to European and international safeguards authorities and other customers

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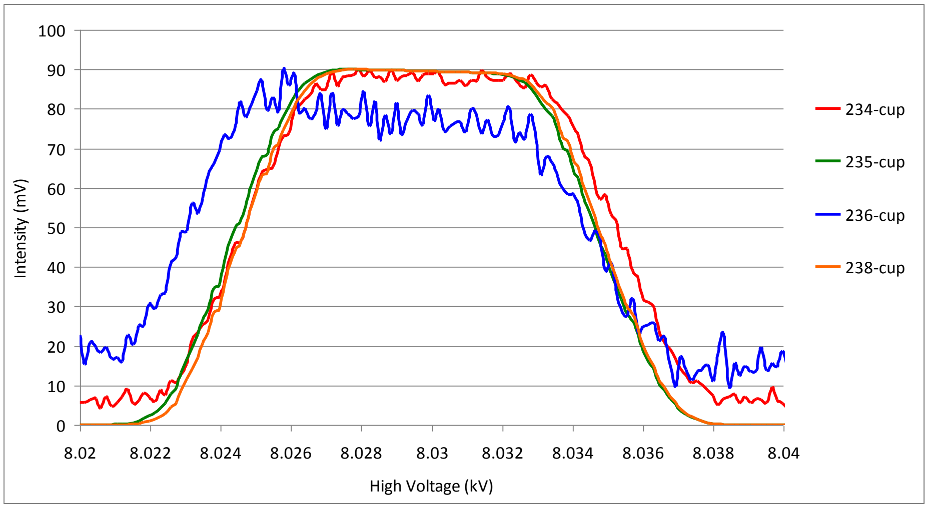
Scattering on ^{234}U and ^{236}U cups

Natural U, 333 ($^{238}U^{19}F_5^+$) scanned through 238-cup (mass 333)
(normalized to so same maximum intensity for all cups)



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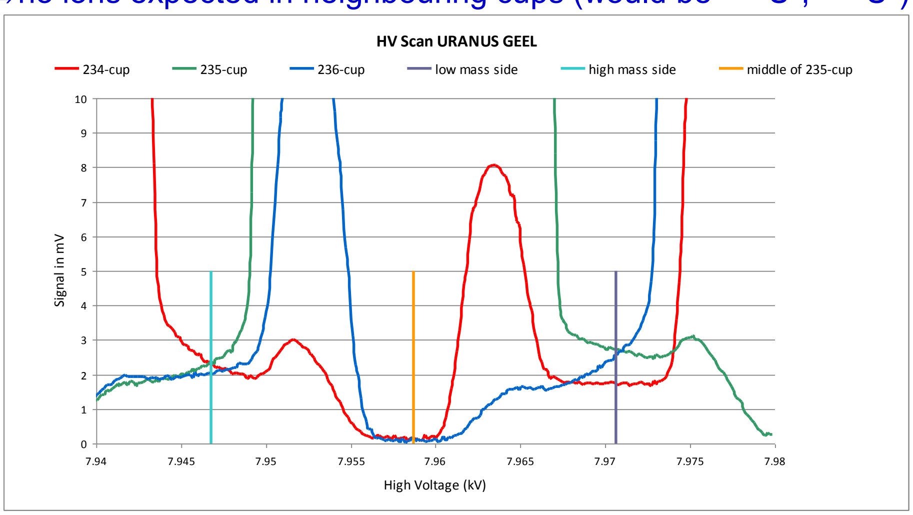
Scattering on ^{234}U and ^{236}U cups

Mass 333 ($^{238}U^{19}F_5^+$) scanned through 235-cup (mass 330)
⇒no ions expected in neighbouring cups (would be "^{237}U", "^{239}U")



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UF4 Base Material for a Certified Reference Material

Greg Schaaff
Technology Fellow, Y-12 National Security Complex

Annual NBL Safeguards Meeting, Palm Desert
July 16, 2011

Acknowledgements

- **NBL** for input for this talk
  - Chino Srinivasan and all others that contributed to the draft report and initial proposal work
  - Gary Sowell, Paul Croatto: Sending information pertinent to this presentation and continued work to keep this rolling
- **Y-12** Analysts for Compiling Data at the last minute
  - John Barry: lead analyst for green salt work
  - Sophie Bobrowski: lead chemist for green salt work
  - Joe Oswald: chemist for oxalate extraction

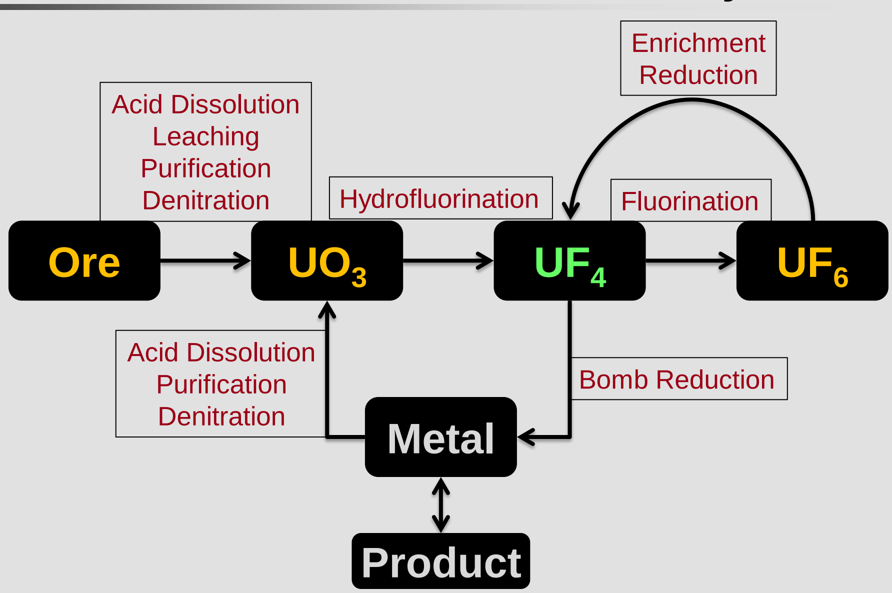
UF4 CRM 17B Overview

- UF4 Chemistry
- Need and History for CRM 17B
  - NMC&A
  - Production Sites
- Proposed Study
  - Approach and challenges
  - Independent methods

Image from Wikipedia.com

- Current Y-12 Methods and QC Data for CRM 17B
  - %-UO2F2
  - Uranium Content

Central Role of UF4 in Uranium Cycle



Why is a UF4 standard necessary???

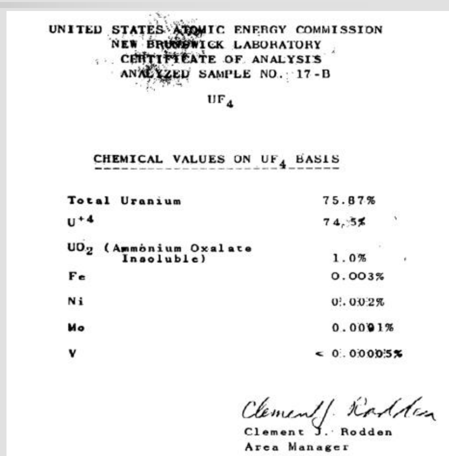
- **NMC&A:** Critical at uranium production sites
  - Processes are typically contained in different MBAs
  - One U.S. standard available: CRM 17B
    - Certified values from 1961
    - Needs to be reevaluated

- **Production Sites:** Critical for monitoring production streams and quality of final product
  - Moisture/O2 in-leakage during UF6 reduction or storage of UF4
    - UO2F2
  - Incomplete reduction to tetravalent state during solid recycle
    - Impure oxide contamination
    - UO2.12, U3O8, UO3, etc.
  - Issues with casting and metal working

CRM 17B Uranium Tetrafluoride

- Originally certified in 1961
  - 200g units at NBL
  - Certified for:
    - g-U/g
      - Titration, Gravimetry
    - UO2 content
      - Oxalate Extraction
    - 4 additional elements
      - Emission Spec
  - ***1.9% of weight unaccounted***
  - ***No certified value for isotopic***

- Repackaged in 1997 to 50g units



UNITED STATES ATOMIC ENERGY COMMISSION
NEW BRUNSWICK LABORATORY
CERTIFICATE OF ANALYSIS
ANALYZED SAMPLE NO. 17-B

UF_4

CHEMICAL VALUES ON UF_4 BASIS

Total Uranium	75.87%
U^{+4}	74.5%
UO_2 (Ammonium Oxalate Insoluble)	1.0%
Fe	0.003%
Ni	0.002%
Mo	0.0001%
V	< 0.00005%

Clement J. Rodden
Area Manager

- Quite different requirements and measurement technologies today
  - Uncertainties are needed for adequate NMC&A
  - New techniques used to monitor uranium production

Overall CRM 17B Goal

- Recertifying CRM 17B UF4 for:
  - Isotopic Content
  - g-U/g
  - UO2, UO2F2, (other uranium oxides)
  - All metallic impurities
- Attempt to bridge old and new technologies
  - Currently 3 sites collaborating: NBL, ANL, Y-12
  - Independent measurements for as many characteristics as possible
- Provide new COA
  - Higher confidence in certified values
  - ISO GUM-Derived Uncertainties

CRM 17B Independent Methods

Isotopic Content	• **Y-12:** Pyrohydrolysis and TIMS (4, 5, 6, 8) • **NBL/ANL:** Fluorination and UF6 Mass Spectrometry
Uranium Content g-U/g*	• **Y-12:** Pyrohydrolysis and Gravimetry • **NBL/ANL:** Pyrohydrolysis and Titration
UO2 Content	• **Y-12:** Oxalate Extraction • **NBL/ANL:** Oxalate Extraction
UO2F2 Content*	• **Y-12:** Water Extraction Gravimetry • **NBL/ANL:** Methanol Extraction Gravimetry
Metal Impurities	• 69-Element ICP-OES and ICPMS • **NBL/ANL:** 40+ ICPMS Elements

*** Discussing these two methods here**

Gravimetric Determination of UO2F2

- Procedure Y/P65-3001 (Tom Goodpasture)
  - Essentially unchanged since the 1960's
  - Continued use of the CRM 17B as internal control sample for Y-12 – even in absence of certified value
- Uses differences in solubility of UO2F2 and UF4 in ambient aqueous solutions
  - UO2F2 – Soluble
  - UF4 – Sparingly Soluble
  - Multiple washes/extraction allow for correction for dissolution of UF4

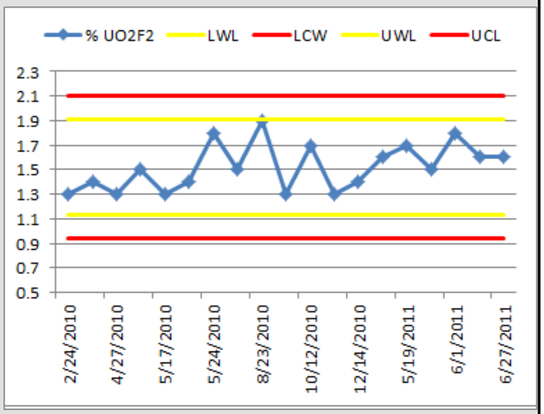
Gravimetric UO2F2

Step	Details
1. Prepare and Weigh UF4	• Homogenized and Blended in Ball Mill/Mixer • ~5g Weighed to nearest 0.1 mg
2. Extract Water Soluble Fraction	• Stirred in RT deionized/demineralized water • Solid filtered and dried at 110 C for 2 hours
3. Measure Weight Loss	• Solid cooled to RT and weighed
4. Repeat Extraction and Measurement	• 2. and 3. repeated to obtain weight loss from UF4 dissolution
5. Calculate UO2F2 Content	$R = 100 - \left(100 \times \left(\frac{2B1 - D - B2}{W}\right)\right)$

W: weight of UF4
B1: gross weight 1st wash
D: weight of Buchner funnel
B2: gross weight 2nd wash

CRM-17B Quality Control Data (%-UO2F2)

- Over 36 Months and ~70 duplicate measurements and 5 different bottles of CRM 17B
  - Mean: 1.63% UO2F2
  - S.D.: 0.30%
- Over past ~18 months using same bottle
  - Mean: 1.52% UO2F2
  - S.D: 0.193%



g-U/g by 'Direct Ignition'

- Procedure: Y/P65-3023 (Tom Goodpasture)
  - Has changed slightly since the 1960's
    - Direct flame ignition was followed by pydrohydrolysis to produce U3O8 in 1960
    - Now – Just grinding/mixing and Pyrohydrolysis for 2 hours (~1980)
- Still a gravimetric calculation to derive U-content
  - Includes corrections to the weight loss (from theoretically pure UF4) due to:
    - Isotopic content measured by TIMS
    - Metal Impurities (0.05-0.1%) measured by a combination of ICP-OES and ICP-MS
      - Revising procedure now to better capture metal impurities

Gravimetric UO2F2

1. Prepare and Weigh UF4
- Homogenized and Blended in Ball Mill/Mixer
- ~5g Weighed to nearest 0.1 mg

2. Pyrohydrolysis
- Muffle/tube furnace at 850 C for 2 hours

3. Measure Weight Loss
- Solid cooled to RT and weighed
- Aliquots taken for isotopic and metal impurities

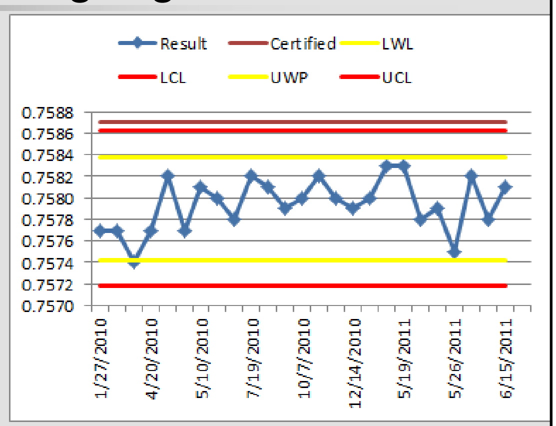
4. Measure Isotopic Content and Impurities
- Analyze oxide by TIMS as normal
- Analyze 69 elements by ICP-OES & ICP-MS

5. Calculate Uranium Content
- Correct for measured isotopic content
- Correct for concentration of metal impurities

Very convoluted calculation - ~15 steps to fully account for isotope ratios and the form of metal impurities in the starting UF4 material

CRM 17B QC Data: g-U/g

- Since 2008
  - Mean: 0.75789 g-U/g
  - S.D.: 0.00031 g-U/g
  - Bias: -0.00080 g-U/g
- Last 30 Points
  - Mean: 0.75794 g-U/g
  - S.D.: 0.00024 g-U/g
  - Bias: -0.00076



Summary

- Proposed recertification of CRM 17B will provide a much needed standard for the central UF4 compound in uranium processing schemes
  - g-U/g, UO2, UO2F2, metal impurities
  - Attempting to use independent analytical techniques for each of the certified values
  - Modern and historical techniques to both prove in technologies and bridge certification data
  - Modern (ISO-GUM) uncertainties with certified values

- Ongoing Y-12 control measurements
  - %-UO2F2 Measured by Y-12 on CRM 17B is consistent with the *missing* mass from 1961 certified values
    - Y-12 %-UO2F2 mean: 1.6% +/- 0.3
    - Unaccounted for mass: 1.9%
  - g-U/g has continued to be a very consistent value with relatively low *standard deviation*
    - (0.75789 +/- 0.00031) g/U/g
    - Study will also verify the small bias (-0.00080 gU/g) we measure

Questions

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An Independent Analysis Protocol for Thermal Ionization Mass Spectrometric Measurement of Low-Enrichment Uranium in Blend-Down Process Solutions

Maureen A. Bernard and Michael K. Holland

Savannah River Nuclear Solutions, LLC

July 16, 2011

Measurement Evaluation Program Annual Meeting

Palm Desert, CA USA

SRNS-N3100-2011-00037 RSM: 10674 Retention 5 years

AGENDA

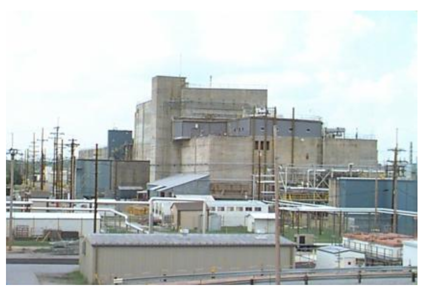
- Summary of LEU Blend-down Process
- Laboratory Method of Analysis
- Results Summary from 2003 – 2011

Disclaimer

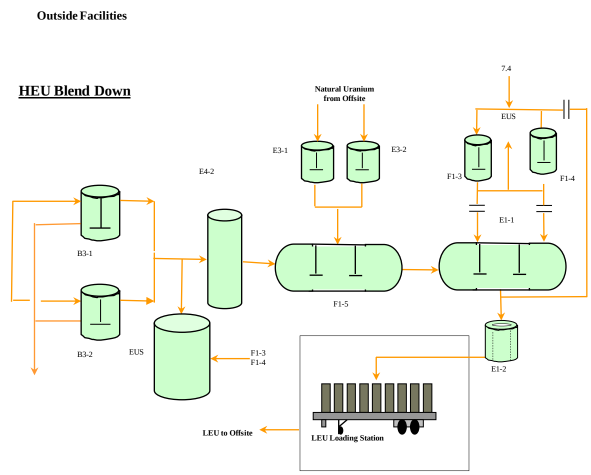
- The findings and conclusions in this presentation are those of the authors, and do not necessarily represent the views of SRNS or the U.S. Department of Energy (DOE).
- Mention of commercial products or companies in this presentation does not imply endorsement or criticism of those products or companies.
- The speaker is an employee of a DOE contractor, and is not a spokesperson for DOE itself.

H-Canyon Dissolution Campaigns: U-Mo, HEU, Pu Scrap

- **Material Dissolved**
- **Solids Removed**
- **Uranium separated in 1st U Cycle**
- **Uranium further decontaminated in 2nd U Cycle**
- **Low Activity Waste**
- **High Activity Waste**
- **Solvent Recovery**



Outside Facilities – HEU Blend Down Process



H Outside Facilities Blend-down

- **Reliable blending depends on:**
  - Representative sampling
  - Accurate uranium conc. measurements (UDG/IDMS)
  - Reliable uranium isotopic abundance measurement
  - Reliable measurement of key impurities
  - Properly calibrated tank volume instrumentation
  - Effective bulk solution delivery capabilities and operating procedures

LEU Product

- **Excellent Isotopic Abundance Agreement between SRS and AREVA for shipper-receiver agreement (SRA)**
- **DOE-NBL: Official referee laboratory, SRA issue resolution**
  - **Limited but Effective, Helpful and Appreciated**
  - **DOE/NBL Staff visits to SRS**
  - **SRNS AL staff visit to NBL on UDG titration measurements**

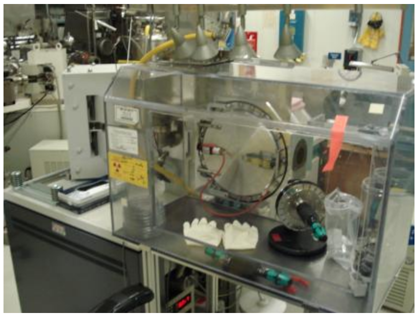
LEU Blend-down

- **Product Solution**
  - Blended Product solution is homogenized
  - Representative samples pulled.
  - Validated by the Laboratory visual analysis and density measurement, then full analytical characterization.
  - LEU solution characterized for uranium concentration, isotopic abundance, impurities (metals and non-metals) and radionuclides including actinides.
  - Samples are also sent to AREVA, in Richland, Washington, for confirmation of the uranium concentration and isotopic abundance.

Thermal Ionization Mass Spectrometer (TIMS) for Isotopic Abundance

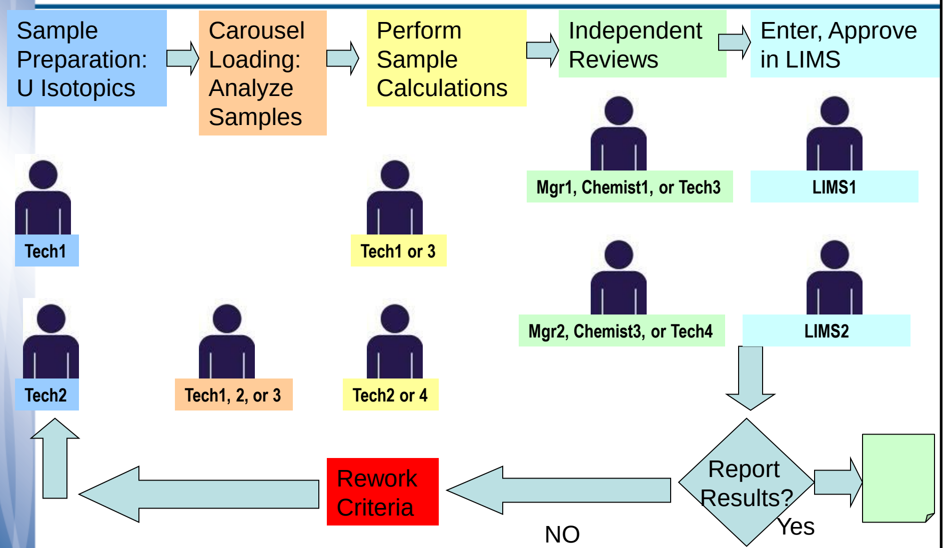
- Thermo Fisher Triton®
- Multi-sample turret (capacity: 21 samples)
- Operates with an acceleration ion energy of 10 KEV
- Automated operation which enables consistency between samples
- Multicollector platform, with one fixed Faraday cup and 8 moveable computer controlled Faraday cups
- Zoom optics for enhanced multi-dynamic measurements

Uranium Isotopics by Mass Spectrometry, TIMS analysis Independent Analysis Protocol



- Segregated IAP Sample preparation
- Carousel Loading, Analysis Sequence
- Quality Control Criteria
- Sample Calculations
- Independent Review
- Rework Criteria

Schematic of Independent Analysis Protocol



Uranium Isotopics by Mass Spectrometry Independent Analysis Protocol, continued

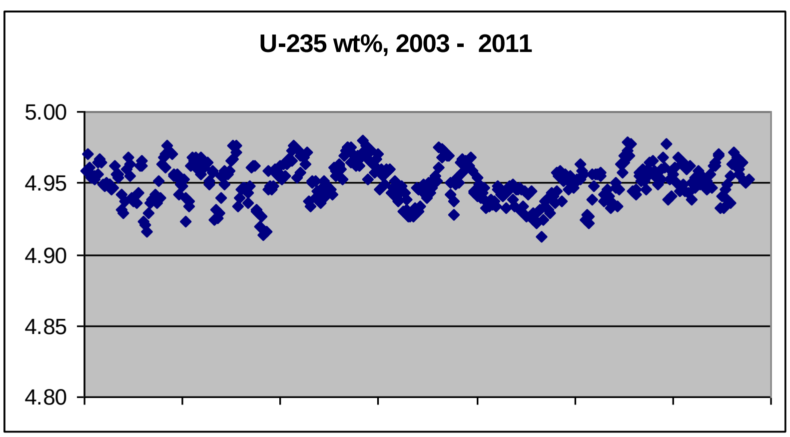
- **Reporting Criteria**
- **QC Wt% U-235 Limits**
  - U010 @ 0.9911 ± 0.0162 wt% Range [0.9749 - 1.0073 wt%]
  - U050 @ 4.9490 ± 0.0208 wt% Range [4.9282– 4.9698 wt%]
  - U100 @ 10.0750 ± 0.0423 wt% Range [10.0327 –10.1173 wt%]
- **Sample Result Limits**
  - U-235 wt% Relative Difference WITHIN each sample < 0.40 %
  - U-235 wt% Relative Difference BETWEEN samples < 0.30 %

Uranium Isotopics by Mass Spectrometry Independent Analysis Protocol, continued

- **Sample Reporting**
  – LIMS data entry and Approval

- **Rework Criteria**
  – Performed by Technician 1 or 2 or other qualified technicians
  – For any criteria failure, 2 technicians prepare entire set of QC standards and samples for analysis
  – For 2nd failure, customer contacted for resample

Chart of U-235 wt% Results, 2003 - 2011



IAP Data Summary for U-235 wt%, 2003 - 2011

	Std Deviation Within Sample	Std Deviation Between Samples
Count, N	226	113
Mean	0.0047	0.0027
Median	0.0038	0.0021
Min	0.0001	0.0000
Max	0.0137	0.0105
RSD, 1 sigma	0.10%	0.05%
Acceptance Criteria, RD%	0.40%	0.30%

Uranium Isotopic Abundance Performance Summary

Performance Requirement	Performance Specification	Comments or Explanation
Maximum throughput	16 determinations/day	Includes sample preparation, Carousel segregated for IAP samples only
Routine Precision (RSD, 2 – sigma)	± 0.2% ± 10%	Major isotope ratios (10-100 wt%) Minor isotope ratio (0.001 wt%)
Limit of Detection	0.001wt%	With 1 ug material plated on filament
Other		Participate in DOE complex-wide U and Pu performance comparison studies

Sources of uncertainty

- TIMS measurement of U-235 wt%
- Technician – to – technician differences in sample preparation
- Sampling and sample – to – sample differences

Measurement Control Goal

- Set acceptance criteria at 4-times the expected standard deviation for sample results.
- The "within sample" standard deviation was ¼ of the acceptance criteria.
- The "between sample" standard deviation was 1/6 of the acceptance criteria.
- For the average of four (4) determinations, the uncertainty in the mean is improved by the ($\sqrt{4}$).
- GUM analysis using GUM Workbench™ supports the conclusions that the total uncertainty would be 4.95 wt% U-235 ±0.02 wt% U-235 (with coverage factor 2.00, 0.4% relative).

Acknowledgements

- Kenneth E. Cheeks, SRNS
- Sherold R. Johnson, SRNS

Current TIMS Technicians

- Jacob M. Gue, SRNS
- James C. Pearre, Jr., SRNS
- Nancy H. Norris, SRNS
- Samuel A. Bagby, Jr., SRNS