Safeguards Measurement Evaluation Program

Annual Report – CY2010 Results

An Evaluation of Uranium Measurement Capabilities and Comparison to State-of-the-Practice Target Values, including an Examination of Historical Performance

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NBL 2011 MEASUREMENT EVALUATION ANNUAL REPORT

DISCLAIMER

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1. NBL 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-theart 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 areas include:

- 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.

2. Statement from Acting Laboratory Director
Dr. Usha Narayanan

Dear Colleagues,

I am happy to present the 2011 New Brunswick Laboratory Measurement Evaluation Program Annual Report, covering measurements performed during the 2010 calendar year. 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.

Peter 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.

As many of you know, 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'. We expect to fully resume all uranium operations through the end of 2011, and plan to gradually implement plutonium operations through 2012. Please look for the resumption of plutonium in the SME program in the near future!

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

Best wishes for a successful meeting.

Usha Narayanan, Acting Laboratory Director

3. NBL Contact Information

Information	Web Address
Website	www.nbl.doe.gov
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4. Abbreviations and Acronyms

ABACC	Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials
ANL	Argonne National Laboratory
ARN	Autoridad Regulatoria Nuclear, Argentina
CALEX	Calorimetry Exchange Program
CNEA	Comisión Nacional De Energía Atómica
CONUAR	Combustibles Nucleares Argentinos
CY	Calendar year, January to December
DA	Destructive Analysis
D&G	Davies and Gray Titration
DOE	(United States) Department of Energy
DU	Depleted Uranium ($^{235}U < 0.3$ wt %)
GUM	Guide to the Expression of Uncertainty in Measurement
GSMS	Gas Source Mass Spectrometry
HEU	High-enriched uranium ($^{235}U \geq 20$ wt %)
IAEA	International Atomic Energy Agency
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
INMM	Institute of Nuclear Materials Management
ISO	International Organization for Standardization
ITV	International Target Value
LEU	Low-enriched uranium (1wt % < ^{235}U < 20 wt %)
ME	Measurement Evaluation
NBL	New Brunswick Laboratory
NMCC	Nuclear Material Control Center
Q	Quarter (e.g., 1Q is first quarter of the year)
RD	Relative deviation (expressed in percent); also written as % RD
SC	Office of Science
SD	Standard deviation (expressed in percent)
SME	Safeguards Measurement Evaluation
SMES	Safeguards Measurement Evaluation System
TIMS	Thermal Ionization Mass Spectrometry
U	Uranium (0.3 wt % < ^{235}U < 1 wt %)
UF_6	Uranium hexafluoride
UNH	Uranyl nitrate hydrate (solution)
UO_2	Uranium dioxide

UO_3	Uranium trioxide
U_3O_8	Uranium (mixed) oxide
u(r)	Random component of uncertainty (indicative of precision) of ITV
u(s)	Systematic component of uncertainty (indicative of bias) of ITV
XRF	X-Ray Fluorescence

5. A Letter from the SME Program Coordinator

The New Brunswick Laboratory's Safeguards Measurement Evaluation Program (SME), established in 1986, continues NBL's long history of interlaboratory comparison programs dating back to the 1950's. These efforts included the General Analytical Evaluation campaigns, the Safeguards Analytical Laboratory Evaluation program, and a number of projects to produce reference materials to settle specific, vexing analytical questions. These programs are a vital part of NBL's mission, which is to enhance the United State's ability to accurately measure special nuclear materials.

The accurate measurement of nuclear materials is vital to national and international safeguards and nonproliferation efforts, enhances U.S. competitiveness in a number of industrial and research areas, and ensures the U.S. continues to be the world-leader in nuclear material measurement and measurement quality control and assurance.

The scope and purpose of the SME program has evolved gradually over the years along with changes in the U.S. goals for national and international safeguards. At the commencement of the program, the SME program was exclusively reserved for Department of Energy laboratories that perform nuclear accountability measurements, and was designed to specifically establish an external measurement Quality Assurance system for those laboratories. As QC/QA systems have been implemented and refined at the DOE Laboratories, and as additional needs for measurement quality assurance have arisen within the U.S. and internationally (driven by U.S. program goals) the SME Program has expanded to include non-DOE domestic labs, commercial and university facilities, and numerous foreign facilities. The types of data evaluation have changed also with differing standards for performance and program goals have changed. The U.S. continues to benefit from the activity associated with the program, as evidenced by its continued growth and the number of different U.S. programs (including many non-DOE Federal programs) that sponsor or participate.

Traditionally, the SME Program encompasses both destructive analytical techniques (DA – mass spectrometry, titration, etc) and non-destructive methods (NDA – gamma spectrometry, neutron counting, etc). However, over the past several years the NDA part of the program has nearly disappeared. This is due to several reasons, including the US effort to consolidate its nuclear materials into fewer sites and the cost of producing test materials. As the new SME program coordinator, I made a big mistake in not raising the issue of NDA analyses at the NBL SME Annual Meeting on July 16th, 2011. This oversight was partially due to my own technical background (and therefore bias), but will not be made again. In the coming year, NBL will make a concerted effort to begin re-establishing an interlaboratory comparison program for NDA analysis, and we welcome any input from interested facilities or individuals on how best to accomplish that.

The SME Annual Report is generated each year, and contains summaries of the performance of each laboratory for the previous Calendar Year. Although NBL has an extensive data validation and verification system in place, occasionally errors do occur. Any such error is the fault of NBL and does not reflect on the performance of any laboratory. Should an error be noticed, please contact Peter Mason, SME Program

Coordinator, at peter.mason@ch.doe.gov. A correction will be made and electronic copies of the corrected report will be distributed. Any questions, comments or suggestions are also welcome and the reader may address them to Mr. Mason or to any of the staff listed above in the "NBL Contacts" table.

All of us at NBL thank our program sponsors for their support and in understanding the importance of our work, particularly as a Federal function. We also thank the participating laboratories, their managers and analytical staff, for their participation both in the program and in the annual meeting, and we look forward to a significant growth in the program in the coming years.

Best regards,

Peter Mason
SME Program Coordinator
New Brunswick Laboratory

peter.mason@ch.doe.gov
630-252-2458

6. 2010 Safeguards Measurement Evaluation Assay Samples

Samples offered for uranium content (assay) in 2010 included a number of uranyl nitrate solutions in sealed glass ampoules, a fuel pellet (UO_2), the "yellow oxide" UO_3 powder commonly found as an intermediate product in uranium production processes, a suite of UF6 samples in P-10 tubes, and "black oxide" U_3O_8 powders.

The UF_6 samples offered were not certified for uranium content, and so submitted results were compared against a calculated uranium content value which was based upon the theoretical stoichiometry. Since these materials are generally of high purity, the reported assay values showed good agreement with the theoretical value. These samples are stored in plastic P-10 tubes, which do show some degradation (and therefore loss of UF_6) over time. Future UF_6 samples will either be drawn from larger steel 1S or 2S cylinders certified for assay and filled shortly before distribution or a new container type will be implemented to replace the P-10 tube to extend the shelf-life of the packaging. NBL has begun examining storage/shipment options for this valuable material type.

The UO_3 material was packaged in a dry box some years ago and has been utilized regularly without sign of degradation. However, last year one customer reported results consistent with possible moisture pick-up. Since the powder is particularly hygroscopic, NBL has begun an effort to evaluate the existing inventory of the material. NBL is also working with the customer to determine if there is a sample handling issue on the customer end, as no other user has indicated a problem. Should there be signs that the material no longer meets the requirements of the program, it will be removed and eventually replaced.

The use of U_3O_8 as an assay standard this year did lead to one problem, due to the fact that NBL did not clearly state that the material needed to be fired to 800^{o}C for one hour and then cooled in a sealed desiccator in order to validate the uranium content value. It is well known that U_3O_8 is a non-stoichiometric material, is somewhat hygroscopic, and the stoichiometry varies depending upon firing temperature. For those labs that did not fire the material prior to measurement, a correction factor was applied to the reference value to accommodate the changed stoichiometry.

The fuel pellet has been in use for a number of years for both uranium assay and isotopic analysis. Recently, a customer has noticed a regular slight trend in the U-235 content to be just above the Certified value. While still within the uncertainty of the material, the trend is consistent for several different laboratories within the customer's country. NBL will verify that the isotopic composition as certified is correct, and will issue a report of analysis with the results.

The UNH solutions are supplied in flame-sealed glass ampoules, and as such are shelf-stable for decades. Previously, the Safeguards Analytical Laboratory Evaluation program clearly showed that even highly qualified labs were having some trouble in consistently performing uranium assay measurements. The theory is that handling soluitions may lead to evaporation, while handling powders and solids is more straightforward. This possibility was investigated and will be discussed later in this

report:

As is clear from the short paragraphs above, NBL takes all of its materials seriously, and continually verifies and tests both its Certified Reference Materials and also those materials used in the SME program. Beginning this year, all new SME materials will be produced by NBL utilizing the procedures and data verification/validation methods employed when certifying our reference materials. Each new material will have an associated report of analysis, certified values and GUM-compliant uncertainty associated with those values. These reports will be made available to those customers requesting them, with the values themselves hidden to protect the utility of the sample as an "unknown" for the user as much as possible.

7. 2010 Safeguards Measurement Evaluation Isotopic Samples

The same suite of UF_6 materials described above are available for testing isotopic measurement techniques. There are six different enrichments, from slightly depleted to nearly 5% enriched available, and they are available in "pairs", in which the U-235 content between pairs only differs slightly. There is a short discussion later in this report comparing 2010 UF_6 (and other material) isotopic measurements to those performed in an NBL mid-1970's measurement campaign, illustrating the improvement in measurement technology and the addition of UF_6 calibration standards since the 1970's.

The fuel pellet and the UO_3 materials are also certified for U-234 content. Additionally, they are certified for the other main isotopes of uranium (U-234, U-236 and U-238). While traditionally the NBL SME program focused solely on U-235 measurement proficiency, in the future more focus will be paid to minor ratio determinations, perhaps even including other isotopes. Additionally, at least two new sets of fuel pellet standards are expected to be added to the SME material inventory in the coming months.

A wide variety of UNH solutions and U_3O_8 powders, ranging from highly depleted to highly enriched, are available in mg quantities for isotopic measurement testing. NBL hopes to continue to expand the suite of isotopic materials to environmental levels, and also add additional materials useful to the environmental characterization, clean-up, mining, and waste disposal industries.

8. Plutonium Safeguards Measurement Evaluation Samples

Plutonium samples are not yet ready for distribution yet. NBL believes a limited set of samples will be available in 2012. As NBL ramps up its plutonium facility capabilities throughout CY2012, materials will be added to the SME program.

9. Evaluation of Submitted Data

Since it's inception in the mid-1980's, the SME program has been structured to serve as an external QC program, and was implemented to ensure that the participating laboratories (at the origin only a few DOE labs were invited to participate) were performing enough QC samples during the course of the year to adequately determine their measurement performance. Since some labs did not routinely perform all measurements on a variety of sample types, the program was designed so that each lab performed numerous analyses of each material type, on different days and utilizing different staff, on a quarterly basis. This allowed NBL to perform a statistical analysis on the relatively large data set generated each quarter and to determine precision and bias values in addition to looking for other sources of variance such as day-to-day or analyst-to-analyst variation utilizing ANOVA techniques.

This is still the basis of the data evaluation, however NBL recognizes that not all laboratories need or are capable of performing many analyses over different days and analysts in order to generate the level of statistical analysis that was previously required. Thus, each laboratory is now asked to choose how many samples/replicates/days they wish to perform, including how often throughout the year. Therefore, there are two possible evaluation reports generated for each set of submitted data:

- Those labs submitting sufficient replicate data for ANOVA analysis will receive the usual statistical evaluation report.
- Those labs reporting a value and associated GUM-compliant uncertainty will receive a simplified report comparing their result to the certified value and uncertainty

The statistical evaluation typically performed is described in the evaluation reports and previous annual reports. To summarize, an outlier test is performed on the submitted date, the average percent relative deviation from the true value is calculated to reflect the overall accuracy of the result, and the simple standard deviation of the result is calculated to reflect the overall precision of the analyses. These results are compared to the International Atomic Energy Agency's 2010 International Target Values (where available) to serve as guidance to the labs as to acceptable performance. Additionally, an 'uncertainty' is calculated using the standard deviation, the number of analyses, a coverage factor based on the Student's t-table, and if present contributions from day-to-day and analyst-to-analyst variations. This "uncertainty" should not be confused with a "Guide to the Expression of Uncertainty in Measurement" (GUM) uncertainty.

In the future, it is likely that the SME program will move towards a data evaluation that is based more on demonstrating agreement with a certified value and uncertainty for the samples, and laboratories are encouraged to report their results with a value and GUM-compliant uncertainty. Laboratory results will be compared to the certified value and also to the ITV-2010 associated GUM uncertainty to serve as guidance to the laboratory as to acceptable performance.

10. Uranium Content (Assay) Measurements

The table below illustrates the laboratories, materials and methods performed for uranium content evaluation in the CY2010 program.

Lab Code	UNH	U_3O_8	UO_2 PELLET	UF_6	UO_3
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				

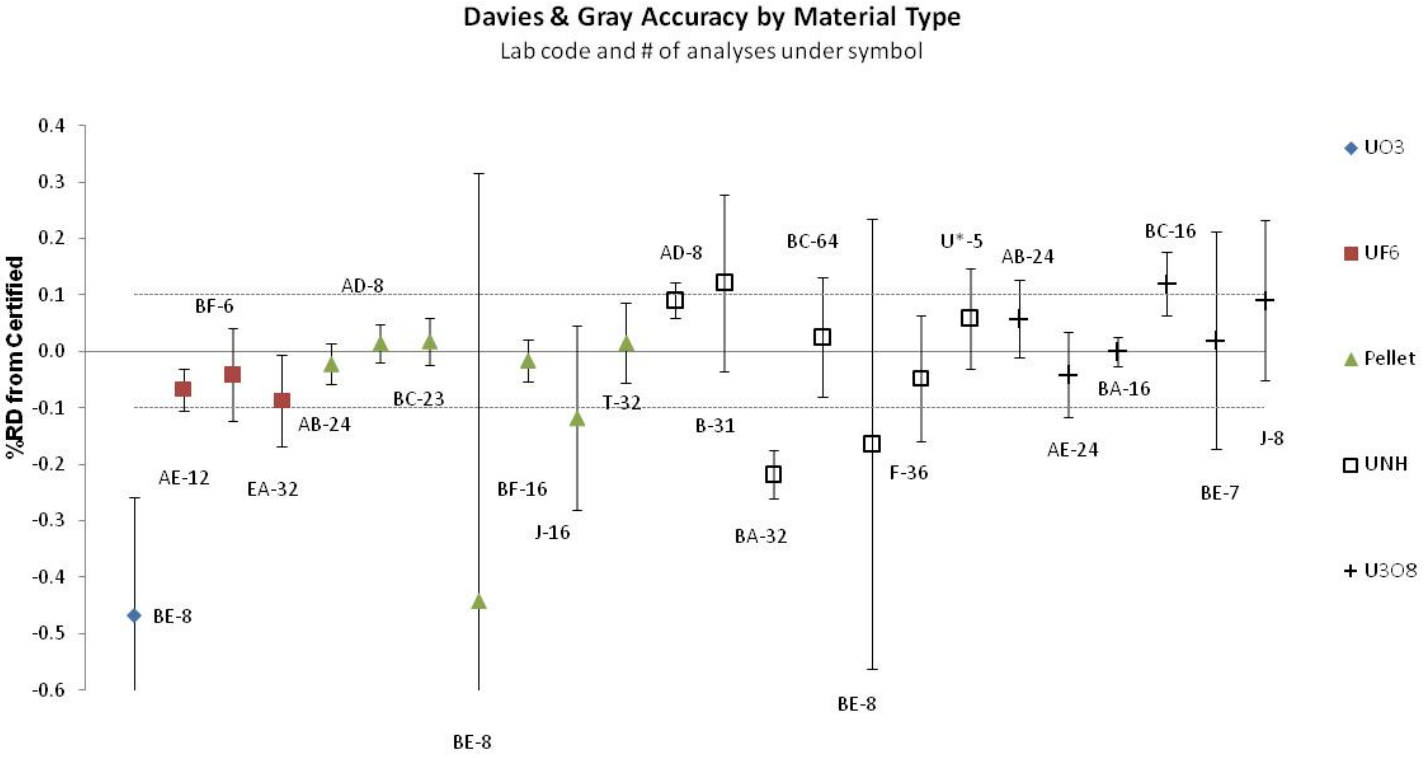
There were a total of 19 laboratories participating in the program for uranium content determination, and in CY2010 a total of 611 individual uranium content determinations were performed. The vast majority of the laboratories and measurements were utilizing variations on the Davies and Gray titrimetric method. This is a very robust technique, suitable for nearly all forms of uranium and impervious to many interferences. Four laboratories performed the gravimetric method, only three labs reported Isotope Dilution Mass Spectrometry results, and two labs performed X-Ray fluorescence.

Because of the dominance of the D&G titrimetric technique utilization, both in terms of overall measurements (456) and in a variety of material types there is sufficient data to

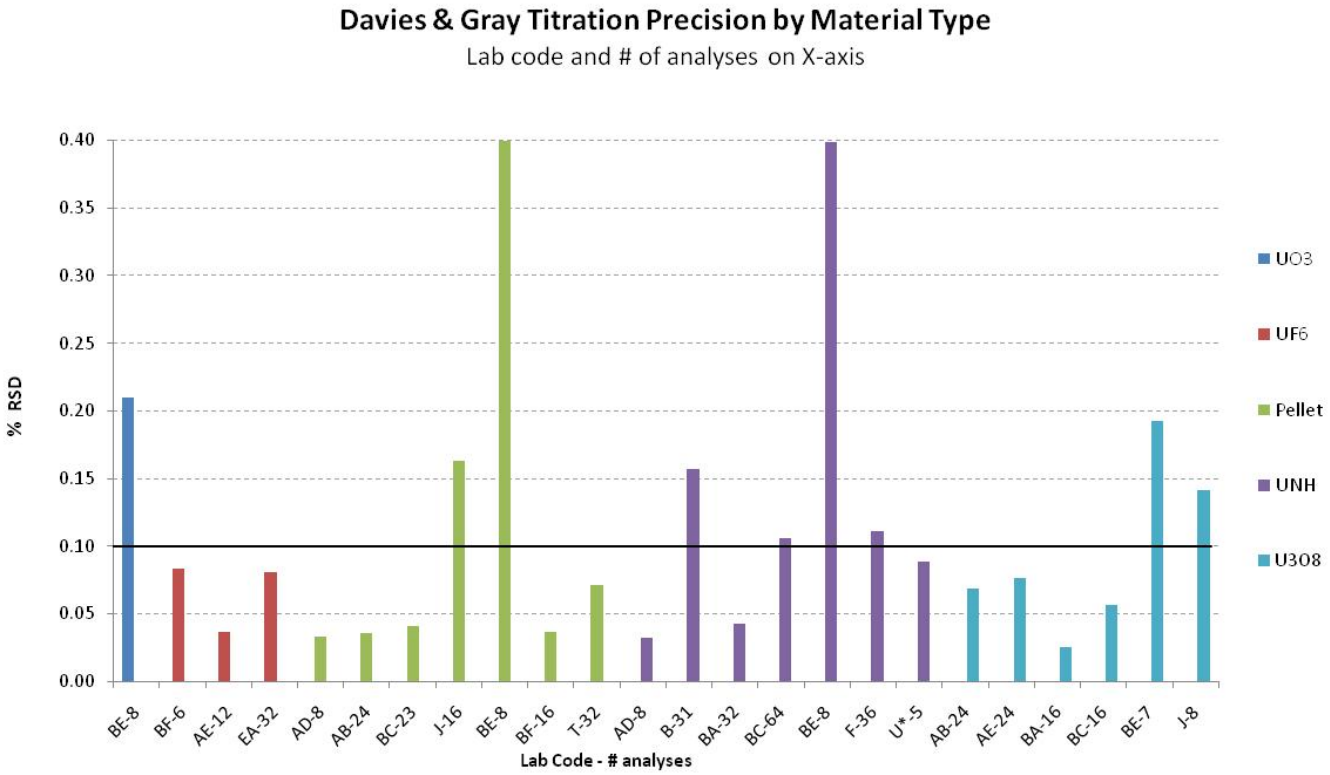
examine performance more closely, and compare to previous efforts. In CY2010, D&G titrations were performed on the following material types, in the following numbers:

UF_6:	50 measurements
Fuel pellets:	127 measurements
UNH Solutions:	184 measurements
U_3O_8 :	95 measurements

The accuracy of the individual laboratories Davies & Gray titrimetric results are plotted below by comparing average percent relative deviations from the certified value for each laboratory and each material type. The error bars in the chart are simple standard deviations calculated from the replicate results. The dashed lines represent the ITV-2010 target values for accuracy.



Of the 24 laboratories participating, seven fell outside of the ITV-2010 target value for accuracy, and only three of the seven were the same lab using different materials, indicating that the laboratory needs to improve its method via changes to the procedure and/or additional staff training. An examination of the laboratories performance in terms of precision yields similar results, as illustrated in the bar chart below:



Again, seven laboratories significantly exceeded the ITV-2010 target value for precision of the technique and these were the same labs having difficulty with accuracy also.

Due to the relatively large number of measurements done on each of the different material types, we were able to compare performance of the labs using current, CY2010 data, with a large data set collected between 1982 and 1984 from the predecessor to the SME Program, the Safeguards Analytical Laboratory Evaluation (SALE) program.

Between 1982 and 1984, the SALE program distributed UNH solutions and UO2 powders to on average abut 33 laboratory's each year. One result from that program was that the laboratories demonstrated more accurate uranium content measurements for the powder over the UNH solution. The table below shows the results for each year, and indicates the percent of laboratories reporting results to within 0.05% and 0.10% of the true value for each year and material:

Material	n	1982 % within 0.05%	0.10%	n	1983 % within 0.05%	0.10%	n	1984 % within 0.05%	0.10%
UNH Sol'n:	34	**53%**	79%	30	**57%**	83%	31	**58%**	74
UO_2 powder:	45	**71%**	84%	35	**86%**	97%	41	**73%**	90

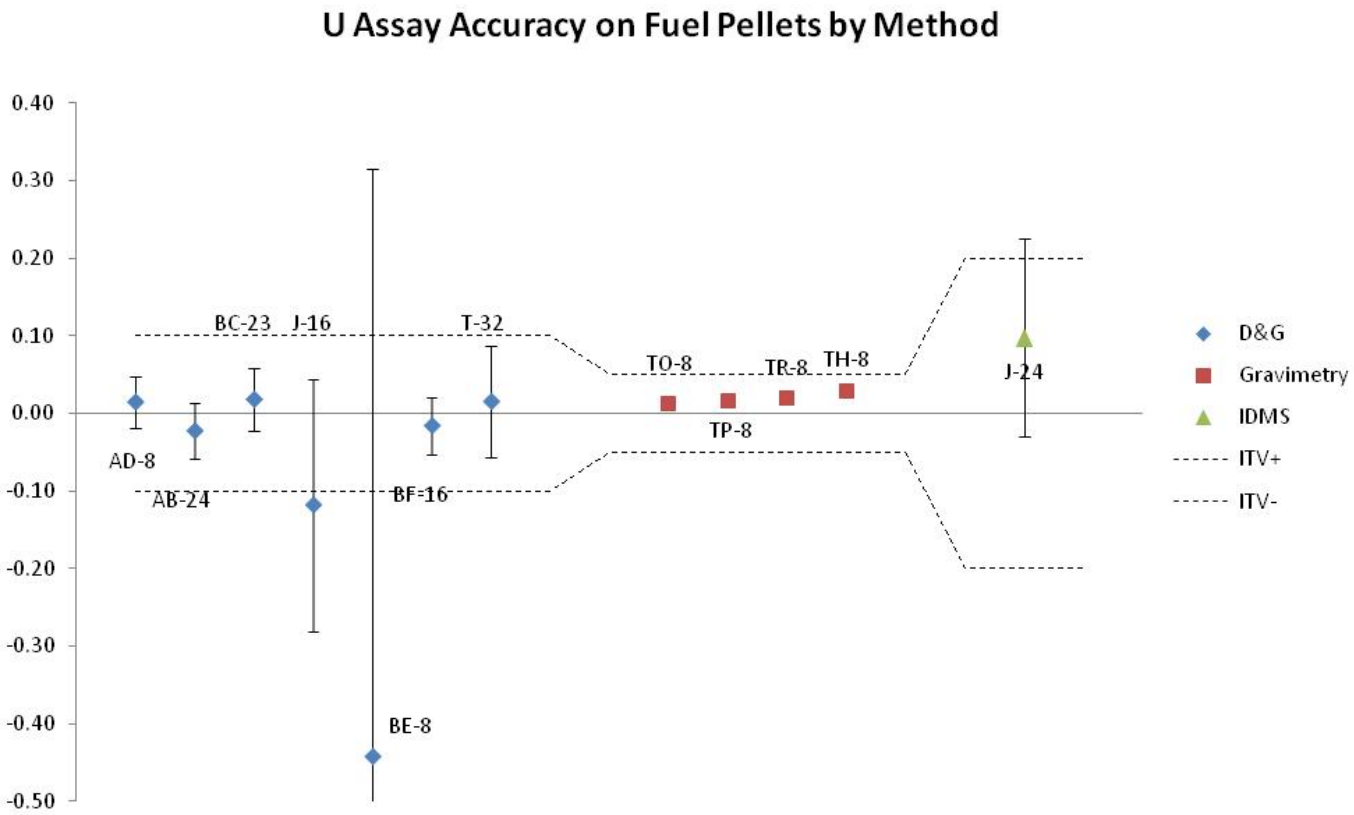
The 1982-1984 table shows (in bold red font) that typically only a little over 55% of the laboratories on average were able to determine UNH solution assays to within 0.05% of the true value. Meanwhile, many of the same laboratories were able to measure the UO_2 powder assay to better than 0.05% more than 75% of the time.

The table below shows the same results for the CY2010 data, while including UF_6 and U_3O_8 in the same material row as UO_3:

2010 SME Data	N (means)	% within 0.05%	0.10%
UNH Sol'n	9	**22%**	57%
UO_2, UF_6, U_30_8	22	**59%**	82%

In the case of the 2010 data, a similar trend is seen, where only about 20% of labs are able to accurately determine U assay on a solution sample, while nearly 60% of labs could do so on other material types. The 2010 data set is small, but it does indicate that facilities still face some difficulty in handling liquid samples, and some effort may be usewhile to train staff on the care and handling of liquids. It's also possible that many facilities do not handle liquids as a primary analytical material, and thus do not have procedures in place to prevent significant evaporation or splashing of materials. While that may seem to relieve a laboratory of the need for those procedures, nearly every analytical laboratory processes materials, samples and standards into a liquid form at least some time, and knowledge of good handling practices should be encouraged.

In addition to the large amount of Davies & Gray analyses, there was a significant data set associated with the fuel pellet material type, utilizing three different, significant uranium assay techniques. The graph below plots the performance of a number of laboratories in determining the uranium content of fuel pellets by either Davies & Gray, he gravimetric method, or by Isotope Dilution Mass Spectrometry:



In this case, the dashed lines represent the ITV-2010 values for accuracy, and the average for each lab is plotted along with standard deviation error bars. We note that one lab was significantly outside the ITV value, with most laboratories performing well within the limits. Also, the precision of the analyses was excellent; particularly for the gravimetric method (error bars are too small to be visible). There is a lack of data for the Isotope Dilution Mass Spectrometric (IDMS) method, which is unfortunate as it's a method that is important and will likely be further developed and implemented in coming years due to its small required sample size and very small waste stream. The NBL hopes to enroll a few more laboratories in coming campaigns that utilize the technique in order to develop a data-set able to firmly establish performance values. Additionally, it is expected that the gravimetric technique will be employed more often in the future as it is a preferred method of analysis for nuclear fuel producers.

The results for all of the uranium content measurements performed are given in the tables below, sorted by material and method. The data for the Davies & Gray technique is collected into a single table and sorted by material type to yield a more easily visualized comparison of results.

DATA TABLES FOR URANIUM ASSAY

D&G-by Material

Lab	Material	Avg %RD	ITV	Std Dev	ITV	N
BE	UO_3	**-0.47**	0.1	**0.21**	0.1	8
AE	UF_6	-0.067	0.1	0.037	0.1	12
BF	UF_6	-0.041	0.1	0.083	0.1	6
EA	UF_6	-0.087	0.1	0.081	0.1	32
AB	Pellet	-0.023	0.1	0.036	0.1	24
AD	Pellet	0.014	0.1	0.033	0.1	8
BC	Pellet	0.018	0.1	0.041	0.1	23
BE	Pellet	**-0.44**	0.1	**0.76**	0.1	8
BF	Pellet	-0.016	0.1	0.037	0.1	16
J	Pellet	**-0.12**	0.1	**0.16**	0.1	16
T	Pellet	0.015	0.1	0.072	0.1	32
AD	UNH	0.090	0.1	0.032	0.1	8
B	UNH	**0.12**	0.1	**0.16**	0.1	31
BA	UNH	**-0.22**	0.1	0.043	0.1	32
BC	UNH	0.026	0.1	0.10	0.1	64
BE	UNH	**-0.16**	0.1	**0.40**	0.1	8
F	UNH	-0.048	0.1	0.11	0.1	36
U*	UNH	0.059	0.1	0.089	0.1	5
AB	U3O8	0.058	0.1	0.069	0.1	24
AE	U3O8	-0.041	0.1	0.076	0.1	24
BA	U3O8	0.000	0.1	0.025	0.1	16
BC	U3O8	**0.12**	0.1	0.057	0.1	16
BE	U3O8	0.020	0.1	**0.19**	0.1	7
J	U3O8	0.090	0.1	**0.14**	0.1	8

Pellet - Gravimetry

Lab	Avg %RD	ITV	Std Dev	ITV	N
TO	0.012	0.05	0.000	0.05	8
TP	0.016	0.05	0.001	0.05	8
TR	0.020	0.05	0.005	0.05	8
TH	0.030	0.05	0.006	0.05	8

Pellet - IDMS

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

UNH - IDMS

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

UNH - X-Ray

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

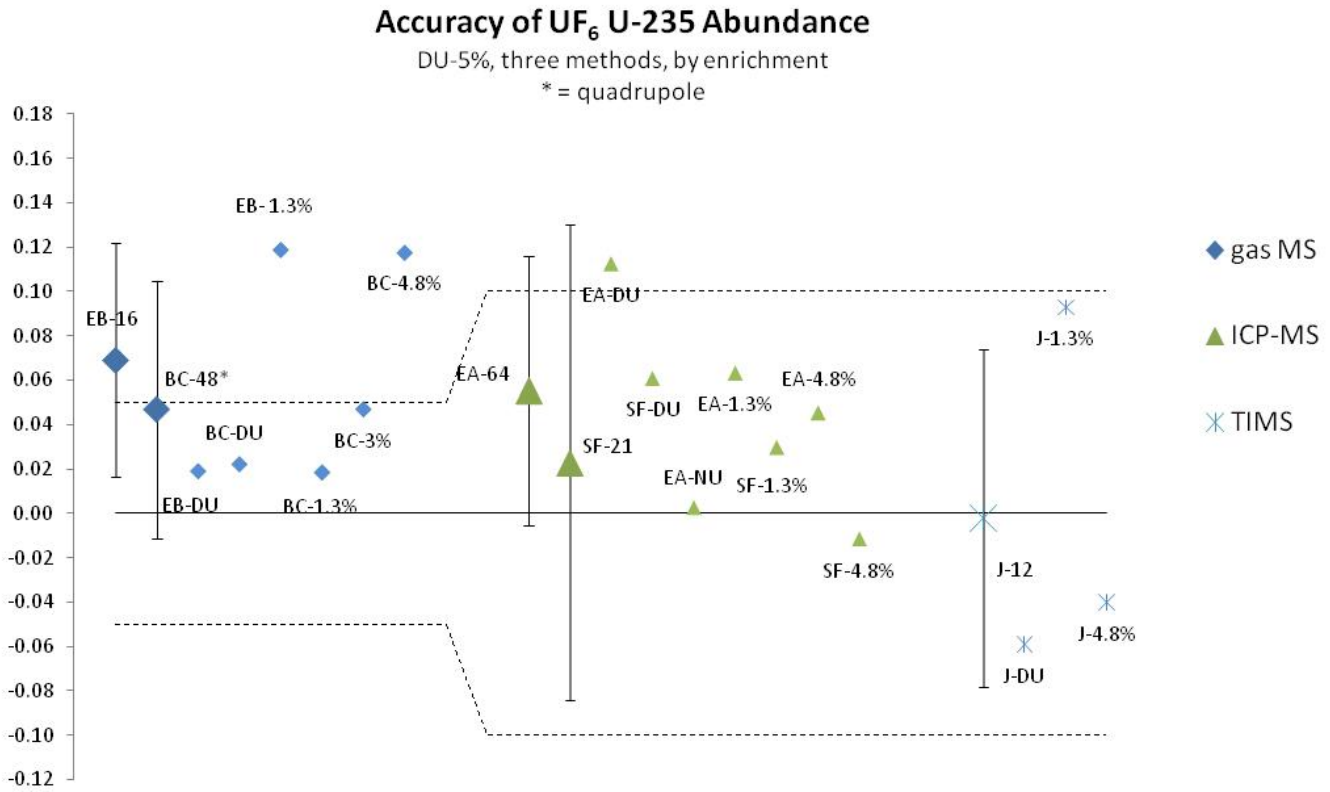
11. Uranium Enrichment Measurement Evaluation

For uranium enrichment measurements, a total of 17 laboratories participated in CY2010, and performed a total of 615 individual U-235 determinations. The table below details the labs, methods and materials performed:

Lab	UNH	U_3O_8	Pellet	UF_6	UO_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		

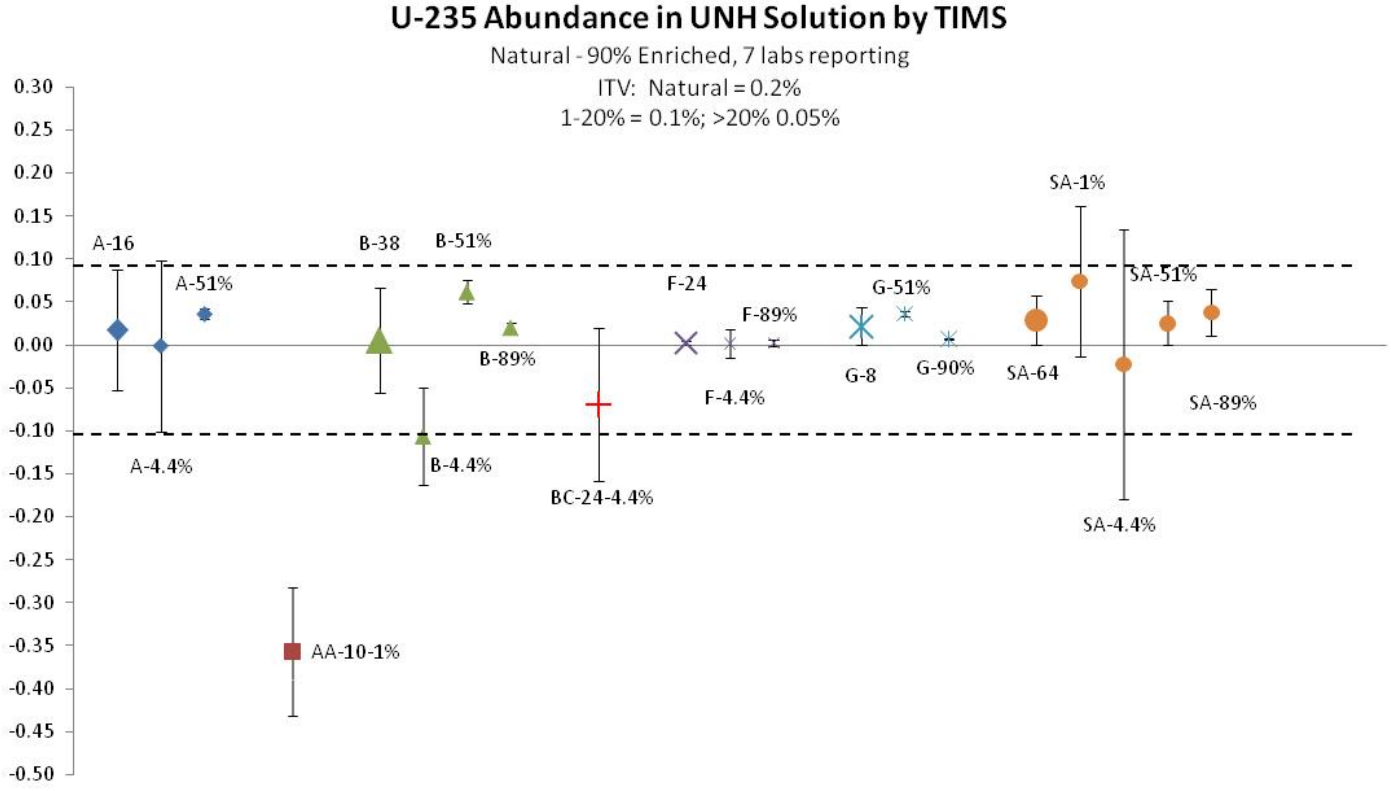
Of the 17 labs and 615 measurements, 13 laboratories utilized the Thermal Ionization Mass Spectrometric technique (TIMS) to determine 352 uranium enrichment samples. The other techniques included one quadrupole ICP-MS, one gas-source mass spectrometer for UF6 measurements, and two multi-collector magnetic sector ICP-MS. The two multi-collector magnetic sector ICP-MS instruments are state-of-the-art instruments whose precision and accuracy rivals that of the traditionally chosen TIMS technique.

Five laboratories performed U-235 abundance measurements of UF6 materials ranging from depleted to nearly 5% enriched. The chart below plots the overall average relative deviation from the certified value for each lab, along with individual average results for each enrichment:



The results varied depending on laboratory and enrichment. There was only one laboratory participating which performed enrichment measurements on UF6 by TIMS, so a comparison of the MC-ICP-MS and TIMS methods for this material type is not possible with this limited data set.

There was a relatively large number of laboratories measuring U-235 enrichment by TIMS in UNH solutions. The chart below indicates the labs overall averages and individual results by enrichment, which ranged from natural up to 90% enriched:



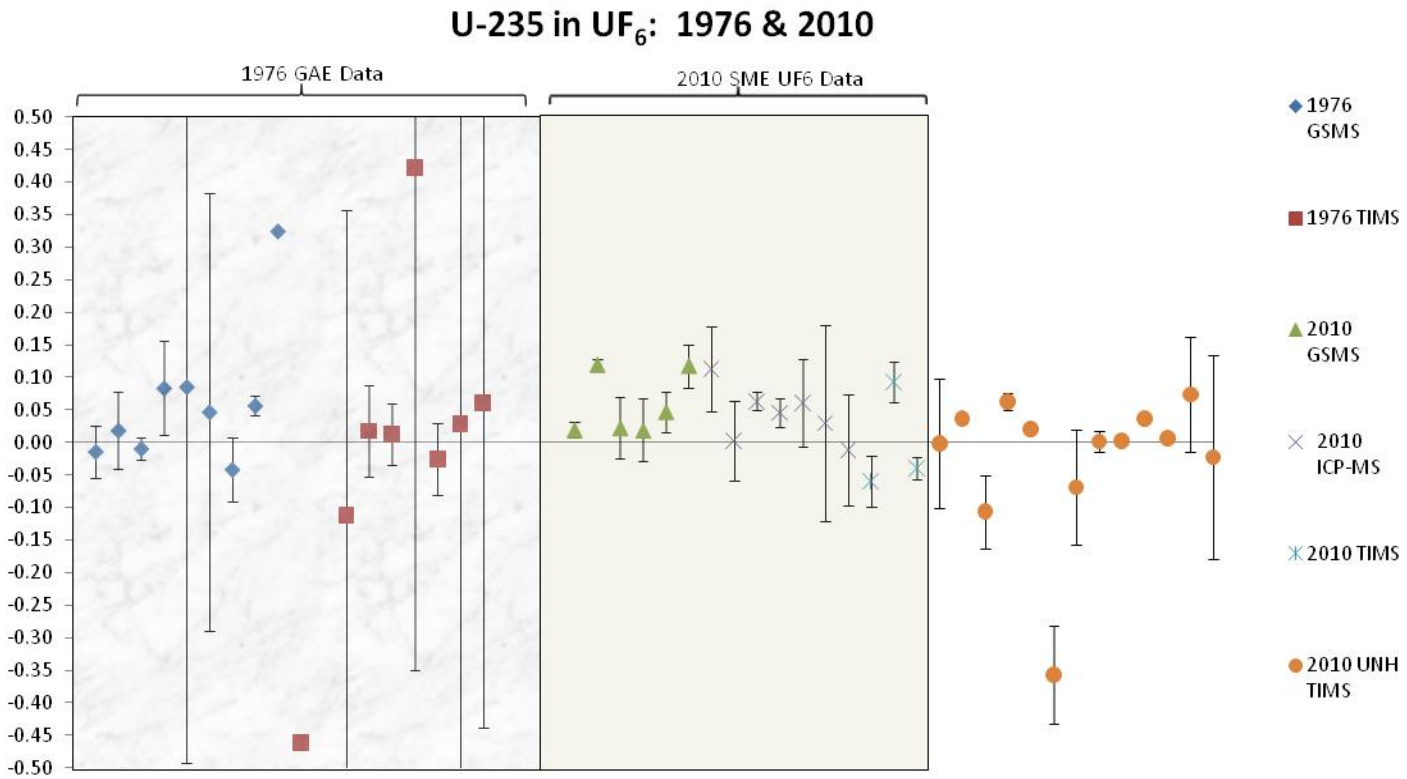
Most laboratories had no problems meeting the accuracy limits suggested by the ITV-2010 document, indicating the use of the TIMS method is a mature method that laboratories have developed and have achieved routine good capability.

12. Examination of UF6 Enrichment Measurement Capability: 1976 vs. 2010

In 1976 as part of NBL's General Analytical Evaluation (GAE) program, a set of 4 UF6 isotopic standards were produced and distributed to a set of labs which were believed to be capable of the best U-235 determinations. These were labs that routinely handled the material type and had previously demonstrated proficiency in enrichment measurements. The study utilized two pairs of samples, with each pair differing slightly in enrichment. One pair was a near-natural enrichment, and the other pair was enriched to 1.7%.

A total of 18 labs participated, with nine using direct UF_6 analysis via gas-source mass spectrometers and the other nine utilizing TIMS instruments with hydrolysis of the material prior to analysis. Results of the intercomparison indicated that only 10 of the 18 labs involved could differentiate between the materials of similar isotopic composition, and 4 of the 18 exhibited a significant bias. Part of the problem was due to a lack of UF_6 Certified Reference Materials to calibrate, although there were primary isotopic reference materials of other forms available, particularly for the TIMS instruments.

Below is a chart which compares the 1976 GAE data with data compiled from the CY2010 NBL SME database.



The left block shows the 1976 data with percent relative deviations from the true value and standard uncertainty error bars plotted for both GS-MS and TIMS data. The middle block shows the same plots but for CY2010 data. Clearly, there has been a significant improvement in enrichment measurement precision for the UF_6 material, and overall accuracy appears to be improved also. For comparison purposes, the rightmost data points (orange circles) are TIMS enrichment results from a number of labs analyzing solutions (UNH), showing similar precisions and accuracies as the 2010 UF_6 data.

The results for all of the uranium enrichment measurements performed are given in the tables below, sorted by material and method. Individual lab results are further broken down by enrichment in each table.

DATA TABLES FOR ALL ENRICHMENT MEASUREMENTS

UF6 - GAS-SOURCE MS

Lab	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	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	**0.15**	0.10	7
SF-4.8%	-0.011	0.10	0.085	0.10	8

UF6 TIMS

Lab	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

U3O8 TIMS

Lab	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	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

UNH TIMS

Lab	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

13. Conclusion

For uranium content determinations:

- the Davies and Gray technique is the preferred means, although it does generate relatively large volumes of mixed (hazardous plus radioactive) waste
- In the past few years, IDMS and XRF have been used by fewer facilities, although the use of IDMS is expected to increase.
- Some of the XRF users have developed very precise methods of determining uranium amount contents.
- Powders seem to be more easily handled than solutions
- Most labs are in conformity with the IAEA's ITV-2010 'state-of-the-practice' limits.
- NBL is requesting labs report results with GUM-compliant uncertainties in the future.

For the isotopic enrichment determinations:

- The TIMS instrumentation and methodology is widely used around the world,
- >90% of participating labs are making measurements in conformity with the ITV-2010 document
- There is evidence of an increase in the use of MC-ICP-MS instruments due to higher throughput
- Most labs are in conformity with the IAEA's ITV-2010 document.

NBL, as part of its mission and an integral part of the SME program, plans to continue to offer hands-on training in:

- Chemical handling for high accuracy (weighing, solution handling, aliquanting, dissolution, etc)
- D&G Titration
- High precision titration
- TIMS techniques

NBL will also continue to offer measurement uncertainty workshops (GUM workshops) and work to promulgate GUM principles throughout industry and government. An expansion of the SME program is underway, and new materials and participants are expected to be added in the coming year, including the addition of two new materials: new fuel pellets and we hope to run a unique campaign.

14. A Brief History of U.S. Measurement Evaluation Programs

P. Mason

A. Overview of NBL

The New Brunswick Laboratory was founded in 1949 and staffed with chemists from the Manhattan Project with the goal of improving on the measurement science of uranium. There are several samples in NBL's archive dating from the mid-1940's and on that are labeled as 'characterized samples' – the predecessors of today's NBL Certified Reference Materials.

While developing methods and advancing analytical chemistry techniques, NBL contributed to the certification of most of the nation's uranium and then plutonium reference materials by assisting in experimental design, providing analytical data, providing guidance on the production and processing of base materials, and by conducting and participating in interlaboratory comparison exercises. During the late 1970's and early 1980's, U.S. interest in nuclear power severely reduced, and the expense of maintaining nuclear facilities began to climb. In 1981, the National Bureau of Standards (NBS) could no longer afford to maintain the nuclear Standard Reference Material program on-site, and many of the materials were shipped to NBL. NBL then began serving as a shipping site, and over the next six years more materials and functions were passed on from NBS to NBL. Eventually, in 1987 NBL took over the reference materials program from the National Bureau of Standards, purchased the remaining inventory from NBS, and re-named all of the Standard Reference Materials as Certified Reference Materials.

Several of the measurement evaluation programs or campaigns that NBL has conducted over the years are briefly summarized here. Details are contained in published NBL reports. The reader is cautioned that the definitive source of information regarding these campaigns is found in the reports, and not necessarily in this document.

B. General Analytical Evaluation

One of the earliest intercomparison programs run by NBL was called the General Analytical Evaluation (GAE) program. It ran successfully (and periodically) between 1952 and 1984. It consisted of primarily U.S. participants, with some notable exceptions for major campaigns which required international support. Typically, a campaign would range from six to more than 30 laboratory participants, all analyzing the same material.

The example referenced in this report was from a major UF_6 GAE campaign which was conducted between 1974 and 1977. The goal of the campaign (actually multiple campaigns) was to determine the state-of-the-art capability for uranium assay and isotopic composition in uranium hexafluoride. As such, only those labs deemed by NBL to be experienced and capable in these measurements were selected to participate. Fifteen different organizations were identified, with 22 laboratories operating that met the criteria of experience and quality. The laboratories were located throughout the world, including the U.S., France, Germany, the Netherlands, Italy and Belgium. The labs chosen to participate are listed in the table below, first by organization with the individual locations identified.

Facility	Location	Facility	Location
British Nuclear Fuels	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		

The UF_6 program was conducted in three phases. The first phase tested the labs abilities to measure uranium purity (assay) and enrichment, Phase 2 would test lab sampling ability with participating laboratories sampling from 1s containers, and phase 3 tested measuring impurities in uranium hexafluoride.

The plans for Phase 1 consisted of six samples (3 assay/3 isotopic) to shipped monthly for 12 consecutive months to the participating U.S. and European labs. Two sets of samples were made and measured at NBL for phase 1: four 'purity' samples in P-10 tubes, and four isotopic samples in PE 'pigtails. The reference values for the materials are given in the table:

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		

The enrichment materials were grouped into two pairs: a pair of near-normal enrichment but measurably different, and a pair of nominally 1.7% enriched, also measurably different.

The labs performed uranium purity measurements by Gravimetry, Davies & Gray titration and coulometry. Enrichment measurements were performed by Gas Source Mass Spectrometry (9 labs) and by Thermal Ionization Mass Spectrometry (9 labs). Details of the phase 1 results and the overall program can be found in multiple NBL reports. The conclusions from the phase 1 report state:

- *Most labs consistently measure to within 0.1% of the assay reference value*, and
- *Only 10 of 18 laboratories could differentiate materials of similar isotopic composition, and four of them exhibited significant bias.*

In this annual report, the results from the isotopic measurements compiled in 1976 are compared with a smaller set of measurements performed in 2010.

C. Grand Junction Interlaboratory Exercise (circa 1982)

The Atomic Energy Commission ran an office out of Grand Junction, Colorodo, one of who's responsibilities was to estimate domestic uranium reserves. The U.S. government convened a program, the National Uranium Resources Evaluation (NURE) as part of its efforts to encourage uranium mining, development and resource discovery. As part of the NURE program, the AEC identified the need for an interlaboratory exercise in order to:

- *provide a reference database for comparison of various methods used on ores,*
- *verify reference values for synthetic ores that NBL had produced and certified and establish consensus values for them if necessary,* and
- *document the traceability of NURE measurements to the national measurement base*

Two sets of reference materials were employed in the campaign, a uranium set and a thorium set. The uranium materials were CRM's 101A-105A certified for uranium and radium assay measurements. These reference materials were blends of a characterized pitchblende ore and highly pure silica to yield between 0.001% U to 1% U by weight. The thorium materials were CRM's 106A-110A certified for thorium. These were made by blending a characterized monazite sand with pure silica to yield 0.001%

Th to 1% Th by weight.

Participating laboratories included Bendix, EG&G Idaho, Eldorado Nuclear, Los Alamos National Laboratory, Texas A&M, Union Carbide Oak Ridge, and the Radiological and Environmental Sciences Laboratory (RESL). Methods used included fluorometry, colorimetry, XRF, ICP-OES, alpha spec, neutron activation, delayed neutron and passive gamma using both GeLi and NaI detectors. Most of the uranium results verified the reference values, but many thorium results did not as there was particularly poor precision on thorium methods, and there was a significant lack of NDA reference materials.

D. Safeguards Analytical Laboratory Evaluation (SALE)

NBL's largest contribution to the database of measurements was the SALE program, which ran from 1970 to 1984. A total of over 26,000 uranium and plutonium measurements were conducted on behalf of the program, using many different material types and analytical techniques. The goal of the program was to continuously monitor the ability of DOE, the nuclear industry, and the international nuclear community to determine the quantities of nuclear materials being stored, handled, processed or transported.

The program involved many laboratories from around the world, and had as many as 70 participants in some years. Both uranium and plutonium materials were utilized, and generally analyses were performed on a bi-monthly basis. We will examine the final there years of the program here, taking place between 1982 and 1984.

Five materials were certified by NBL for this campaign. The materials, quantities, packaging, characterized values and methods used to establish those values are given below:

Material	Quantity	Container	Atmosphere	Measurement	Characterization Methods
UNH solution	5-20 mL	Flame-sealed ampule	air	U conc U-235 abundance	D&G titration 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

The production of these materials was a major effort, especially since many of them are

moisture sensitive and/or sensitive to normal atmospheric constituents. Details of the production and certification of each material is contained in a number of NBL reports.

Once material production was completed, over 50 facilities chose to participate in the measurement campaign. Over 6,000 assay and isotopic measurements were performed on these materials utilizing 22 different analytical methods. Each analysis period and year, tests of lab-to-lab , method-to-method and day-to-day variations were conducted. Additionally, test of laboratory and method compatibility were conducted.

The table below summarizes the SALE results for the three-year period between 1982 and 1984 for each material and measured value, and lists the percentages of labs that reported results within 0.05% and 0.1% of the reference values, respectively, for each year.

Measurement	**n**	**1982 % within 0.05%**	**0.10%**	**n**	**1983 % within 0.05%**	**0.10%**	**n**	**1984 % within 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	-

The conclusions from the three-year study are summarized here, and can be found in the summary report for the SALE program, which is notable as 1984 was the final year of the program as DOE headquarters no longer felt the program was justified.

SALE 1982-1984 Study Conclusions

Uranium:

- *There were favorable measurement trends compared to the 1970's for UNH and UO_2*
- *Gravimetry w/ impurities and NBL-modified D&G: all labs had good results and therefore these two should be 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 were better than UNH solutions: sampling ease of*

solids over liquids? Evaporation/storage problems?

- *U-235 in UNH more accurate than in $U0_2$ partially due to inhomogeneity in $U0_2$*
- *U conc in Pu,U oxides difficult, perhaps due to 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 (amperometric and 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 versus the results from the 1970's*

And perhaps most important of all the conclusions:

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"

- *The number 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*

These two improvements – more laboratories agreeing with one another and all laboratories improving their measurement precisions, meant that ***"apparent shipper-receiver differences due to analytical variation had become less likely during this period".***

E. The Importance of Interlaboratory Measurement Evaluations

The improvement in performance among and between laboratories also meant that detecting an anomaly in nuclear materials inventories became easier. And this improvement and consequent increase in nuclear security came about primarily because the participating laboratories exercised their abilities in a blind measurement campaign that forces all participants to perform under identical and unknown conditions. This, combined with the support that NBL and other laboratories provide in terms of technical assistance, has directly lead to the U.S. increasing its measurement abilities. Lacking programs like this, measurement capability is likely to maintain at current levels or even to deteriorate as experienced staff retire and measurement systems are used less often.

It was because of a perceived lack of need for these programs that the SALE program was terminated, and when its replacement (the current SME program) was instituted participation was limited to a very small group of laboratories. With the re-birth of the nuclear power industry in the U.S., its explosive growth in the rest of the world, and most importantly the greatly increased worry of proliferation and terrorism, the SME program and programs like it have begun to expand and grow. Unfortunately, DOE is

experiencing a ‘brain-drain’ and due to the high costs of operating nuclear facilities, there are fewer and fewer laboratories with the experience and capability to perform even relatively simple and safe uranium and plutonium analyses. This trend has been identified, and steps are being taken to ease the problem.

At the start of the SME program in 1986, only six laboratories participated. Currently, participation varies between 20 and 30 labs, about equally distributed between domestic and foreign, and there are urgent requests to expand. The need for new material types, measurements, and techniques is increasing each year, and NBL is working to position itself to be able to effectively respond to the United States government nonproliferation, nuclear safeguards, nuclear energy, environmental and commercial/industrial needs for the coming years. This will help to maintain the U.S. as the world’s leader in nuclear security and maintain U.S. economic competitiveness in the nuclear arena.