Atomic Energy of Canada Limited Prepares for Nuclear Forensic Analyses

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Abstract. The Analytical Chemistry Branch (ACB) of Atomic Energy of Canada Limited (AECL) has focused on the following areas of improvement to prepare for nuclear forensics analysis: accreditation to ISO/IEC 17025:2005, modernization of the sample logging database to a Laboratory Information Management System (LIMS), and qualification under the IAEA's Network of Analytical Laboratories (NWAL) for Nuclear Material Analysis. The ACB obtained ISO/IEC 17025:2005 accreditation covering the Quality Assurance Plan and seven specific procedures, including thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS), and radiochemical analysis. Modernization of the sample logging database has been undertaken by installation of a Perkin Elmer LABWORKS LIMS. Configuration of the LIMS is nearing completion and the testing phase has begun. The qualification procedure to join NWAL includes testing shipment logistics and analysis of test samples. This was achieved through participation in the IAEA 2013 Nuclear Material Round Robin. Forty-five unknown uranium and plutonium nitrate salts were measured for isotopic ratios by TIMS. Lessons learned from these endeavours will be discussed in this paper.

1. Introduction

AECL has focused on developing peaceful and innovative applications from nuclear technology for over 60 years through its expertise in science and technology (S&T) and its more than 50 unique facilities and laboratories, including fuel development, hot cells, gloveboxes, x-ray diffraction, neutron beam, surface science and analytical chemistry laboratories. AECL is leading a national collaboration with other federal government laboratories to establish a Canadian nuclear forensics laboratory network. In preparation for AECL becoming part of this lab network, the Analytical Chemistry Branch identified three opportunities for improvement to enhance the credibility of analytical results presented as evidence in a court of law. These were accreditation to ISO/IEC 17025:2005 (International Organization for Standardization/International Electrotechnical Commission), procurement of a modern Laboratory Information Management System, and qualification as part of the International Atomic Energy Agency (IAEA) network of analytical laboratories for nuclear materials. While accreditation and a LIMS system are not strictly required by the partners in the Canadian National Nuclear Forensics Capability Project, they are strongly supported by Canadian law enforcement.

Accreditation to ISO/IEC 17025:2005 started with a gap analysis between the existing quality management system and the requirements of the standard. The ACB Quality Assurance Plan was restructured to align with the requirements of the standard, and several procedures covering a range of analyses were selected for the initial accreditation. An internal audit provided an opportunity to refine our documentation and records management prior to an accreditation assessment from the Canadian Association for Laboratory Accreditation (CALA), leading to successful accreditation to ISO/IEC 17025:2005. The on-going internal and CALA assessments to maintain accreditation will provide continual opportunities for improvement.

The ACB currently uses a quality assurance database developed in-house, using Windows Access 2000, to track samples, records, and equipment. Many features of this system became difficult to use as the database grew, necessitating a reassessment. A decision was made to utilize a commercially available LIMS, thus capitalizing on industry expertise in this area. Based on the client requirements document, a commercial LIMS was procured from Perkin Elmer. Configuration of the Perkin Elmer LABWORKS LIMS is underway, and experience gained is shared below.

As the third component of AECL's laboratory capability improvement initiative, becoming qualified as part of the IAEA's NWAL for Destructive Analysis of Nuclear Materials represents the advantage of AECL maintaining relevant equipment, procedures, and expertise. This is not only of direct value to the IAEA program on non-proliferation and safeguards, but also of strategic importance to maintain the capability in a ready state in the event it is required to respond to a nuclear forensics incident. As part of the qualification process, AECL participated in a round robin exercise and subsequent technical meeting for isotopic determination of U and Pu. Highlights from the exercise, including major lessons learned, are discussed below.

2. ISO/IEC 17025:2005 Accreditation

Quality improvement has become a key national and international business strategy, and can raise the national reputation and image of the ACB laboratories. Accreditation as an ISO/IEC 17025:2005 laboratory certifies that our laboratories have demonstrated the ability to produce technically valid results and have displayed excellence in technical and laboratory management competence. This accreditation assures continued technical competence and maintains a known standard of quality management in the areas of personnel qualification and training, calibration and maintenance of equipment, quality control and quality assurance procedures, testing and inspection procedures, accurate recording and reporting of data, and appropriate test environments.

To move to accreditation, a gap analysis was performed between the existing quality management system and the requirements of the standard. Advice was provided by AECL's Whiteshell Laboratories (Manitoba) as their analytical laboratory has held ISO/IEC 17025:2005 accreditation for a number of years. Due to the detail and work involved in accreditation, it was recommended to move progressively towards full accreditation. The initial scope included our Quality Assurance Plan (QAP) (an overall governing document covering how analyses are performed across the ACB) and selected procedures from the TIMS, ICP-MS, inductively coupled plasma atomic emission spectroscopy (ICP-AES), radioanalytical and water analysis laboratories. This selection represented a cross-section of the various laboratories within the ACB, providing an opportunity for all laboratory leaders to participate in implementation of the ISO/IEC 17025:2005 standard, learn from the exercise, distribute the work across a number of people, and ultimately ensure consistent application across the organization.

The ACB Quality Assurance Plan (previously structured according to the ISO 9001 standard) was restructured to align with the requirements of ISO/IEC 17025:2005. An internal audit against the standard was then conducted, followed by further refinement of the QAP, as well as the selected procedures. Areas addressed included inclusion of method validation proof, and a statement that the procedure was fit for use. Performance testing was also evaluated.

Participation in performance testing and/or interlaboratory comparisons is important in assuring the quality of test and is a requirement for maintaining accreditation. Most laboratories in the ACB had a strong track record in participating in voluntary performance testing with a history of 10 years. Though some laboratories did not subscribe to regular performance testing in the past, they had already participated in round robin testing competitions, or cross-technique comparisons.

Performance testing can be a costly process. Materials, transport, reporting of results, and analyst time all must be considered in this process. It can also be challenging to find suitable performance test providers for some analyses/sample types on a yearly basis. When considering that performance testing must occur regularly for accreditation and compliance, this cost must be recognized along with the cost paid to the accrediting body. The latter is typically an annual fee comprised of a base price plus an additional amount per procedure per matrix.

Following the refinement of ACB documentation and procedures, an external assessment was performed for accreditation by a third party. In the case of ACB, the third party was the Canadian Association for Laboratory Accreditation (CALA). CALA assesses in accordance with the ISO/IEC 17011 standard and assessments are conducted by highly trained volunteer assessors selected for their strong analytical backgrounds. Issues recognized by the assessor were addressed by ACB to expedite obtaining the ISO/IEC 17025:2005 accreditation.

Another challenge for analysis, particularly under the rigour of accreditation, is maintaining the laboratory environment. The ACB is located in buildings built in the early 1970s and maintaining steady temperature and humidity is difficult. Data loggers can be used to collect data for these parameters, thus providing the documented proof of the actual conditions. Requirements have been identified for air handling improvements for the buildings and this work is planned for the coming summer. The laboratory ensures that the environmental conditions do not invalidate the results or adversely affect the required quality of measurement despite the challenges of having to stop work during adverse environmental conditions. Environment conditions that can affect the results of tests are documented in the procedures and in some cases, it has been possible to test the impact of a wider range of environmental conditions on the data quality and expand the acceptable operating conditions.

Following the internal audit, document and procedural refinement, and external assessment by CALA, formal ISO/IEC 17025:2005 accreditation was received from CALA on July 29, 2013. Currently we are preparing for our first CALA assessment following accreditation.

3. Procurement of a Laboratory Information Management System

The Analytical Chemistry Branch developed an in-house database based on Microsoft Access 2000, which was used to log samples, quality control results, equipment information, and routine calibration verification of pipettes and mass balances. As the database grew with use, the system became difficult to use and maintain, some features did not get fully implemented, and functionality became limited to only one user at a time. In addition, Access 2000 is not supported in Windows 7, thus as AECL moved away from Windows XP, it became clear that a new database was required in order to meet the laboratory information needs of the branch. An internal decision was made to purchase a commercially available LIMS, thus capitalizing on the expertise from an experienced provider.

In order to plan for the implementation of a LIMS system, ACB met with other potential users at AECL Chalk River Laboratories (CRL) to establish required features of a LIMS to facilitate streamlined sample transfer between branches. A client requirements document (CRD) was developed and sent out to the appropriate vendors which allowed AECL and ACB to evaluate which vendor could meet all, or at least most, of our needs. From the vendor response, the Perkin Elmer (PE) LABWORKS LIMS was chosen as the most appropriate system and vendor. Following this choice, configuration work was initiated to align the features of the LABWORKS LIMS system with the operational needs of the ACB.

As we are nearing the end of this phase and moving to testing and production, we can now reflect on the pros, cons, challenges and lessons learned from the process. For this paper we have chosen to highlight some of the configuration work done to develop a functional LIMS for our purposes, specifically those which are useful for a nuclear lab and not offered in a typical or base level LIMS.

3.1 Highlighted LIMS Configuration Development Work

The basic LABWORKS LIMS provides modules to define what is to be analyzed, by whom, in what timeframe, with what equipment and quality control materials, the resultant data, and provides the audit trail for future evidence. The Analytical Chemistry Branch also wanted to streamline data upload, and ensure tracking of sample aliquots and equipment calibration/verification evidence. As well, we wanted to use the LIMS to track and easily generate reports for radioisotope and fissile material inventories for individual laboratories.

ACB chose not to interface the LIMS directly with analysis equipment. Samples are logged into the LIMS, required analyses specified, and a batch built to specify required quality control samples. The samples are then tracked with the unique LIMS sample identification number (also as a barcode), analyzed as per the required lab procedure, and then data is manipulated in Microsoft EXCEL calculation spreadsheets. To input the data into the LIMS, a macro-enabled spreadsheet was configured by PE. The analyst is able to link data from their calculations into this sheet and easily upload the sample and quality control (QC) results into the LIMS. User name entry is required for upload, thus tracking the user that performed the analysis and upload. A requirement of ISO/IEC 17025:2005 is to trend QC results and this is accomplished using the base functions of the LIMS.

The EXCEL sheet is attached to the LIMS for record retention, and is available for independent verification, including access to original data and calculations. The validation of data is tracked in the LIMS and must be performed before an analysis report is generated from the LIMS. To meet requirements of ISO/IEC 17025:2005 for maintaining the integrity of data, ACB utilizes locked cells or tracked verification of manual entries in the EXCEL calculation spreadsheets. When attached to the LIMS, record retention and audit trail requirements are met. This strategy for implementation of the LIMS has provided ACB with the required flexibility to easily adapt to changing analysis requirements.

An audit trail is an important part of daily operations in an ISO/IEC 17025:2005 accredited facility. The LIMS provides an audit trail on all operations performed within the database. During configuration, it is possible to specify actions that require user comments, a user's password, or stipulate actions that will be tracked in silent mode. The latter means that any time an analyst makes changes to a sample or batch, the LIMS will capture their user name and the date without prompting them. The LIMS was configured such that those changes

deemed significant changes (to a sample or batch) require a comment from the analyst, which is then captured and tagged to a sample.

Tracking of samples is an integral part of a LIMS. When portions of the sample are distributed to different labs (sub-sampled), the LIMS must be able to track this as well. The LIMS was configured to provide a unique identifier for the sub-sample, along with a new batch number. These are used by the lab receiving the sub-sample. The original batch is linked to the sub-sample batch within the LIMS. It is possible to generate an analysis report for all original and sub-sample tests together, or separately. Some care was taken to ensure comments associated with the overall sample are distinct from comments pertaining to specific analyses.

In addition to tracking samples, the ACB wanted to use the LIMS to track radioisotope and fissile material inventories for individual labs. ACB staff worked with PE developers to utilize *Special Information Sheets* to input this information into the LIMS, as well as retrieve this information from the LIMS by generating summary reports with totals for specific categories of information. The radioisotope inventories are used to ensure compliance with the AECL Radiation Protection Program, while the fissile material inventory ensures compliance with the AECL Nuclear Materials and Safeguards Management Program at a lab level. Development of the LIMS included a means of tracking these *Special Information* details between labs when sub-samples are moved to a different lab for analyses.

3.2 Challenges and Lessons Learned

The LIMS procurement and configuration project generated many lessons learned for ACB. These lessons fall into the categories: time, cost, and communication.

A considerable amount of effort was required to provide PE with more detailed descriptions of customer requirements. This was initially underestimated. A Client Requirement Document was used as a basis for the procurement process. In addition, a detailed design document should have been developed prior to configuration. It was necessary to have regular meetings between key AECL staff and PE developers to review progress on the configuration, demonstrate aspects of the LIMS, discuss application details, provide examples of information to become part of the LIMS (for example equipment details and code names, analyses performed, QC performed, units of measure, work flow requirements, sample data and reporting requirements), and to brainstorm resolutions to challenges between customer requirements and what is actually possible in the LIMS. This time commitment is critical in the configuration phase to ensure that the features implemented in the LIMS are exact and meet the client requirements. A detailed design document would also assist in the testing phase.

When discussing a LIMS system with a vendor, requirements must be defined very specifically. In particular, the type of data and how it is input into the LIMS, as well as trending and output are very important and specific to the customer. These items can be configured, but this requires that the vendor has a proper understanding of the details of the customer, and the customer must know the limitations of the basic LIMS. It is recommended that a facility become very familiar with a LIMS system before looking at individual configurations.

Installation of a LIMS system requires both capital and staff resource commitment. Configuration of a commercial LIMS to meet the needs of a laboratory requires a

considerable commitment of staff time to define the exact requirements, ensure the system functions in a meaningful way for the lab, and to test the system. The cost of the LIMS software must also be considered, as well as the cost to have the vendor configure the LIMS to specific requirements. Ongoing costs include the service agreement, which covers customer support to fix issues arising while in use, as well as software updates.The decision to utilize a commercial LIMS eliminated the need for internal program or database development expertise, but does increase the initial cost. The cost of configuration was minimized by limiting the scope of the configuration to two analysis groups within ACB (TIMS and multi-element). During training, a small group of users was trained in more detail to allow them to expand the LIMS to additional groups within the Analytical Chemistry Branch following implementation.

At this time, configuration for the two initial groups is almost complete and the testing phase has begun. There may be additional lessons learned as we complete this work and put the LIMS into production in the selected labs in ACB later this year.

4. Qualification for the IAEA's Network of Analytical Laboratories for Destructive Analysis of Nuclear Materials

In September 2012, an agreement was reached between the Canadian Nuclear Safety Commission (CNSC) and the IAEA that stated that, with the support of the Canadian Safeguards Support Programme, AECL Chalk River Laboratories (CRL) would proceed with qualification as a laboratory for the IAEA's Network of Analytical Laboratories (NWAL) for Destructive Analysis of Nuclear Materials. A qualification procedure was provided [1] describing the prerequisites and required steps. Staff from the IAEA visited CRL in April 2013 as part of the planning phase covering topics of laboratory capacity, capabilities and limits, sample analysis, quality system, shipping logistics and qualification logistics.

A significant step in the procedure is shipment and analysis of test samples, as well as review of quality documentation. The first aspect was addressed by participation in the IAEA 2013 Nuclear Material Round Robin [2]. Participating labs received 45 samples of U or Pu either as loaded filaments for TIMS or microgram amounts of material as dried nitrate salts in Savillex containers. AECL chose the latter as our filament loading procedure did not match that of the IAEA. These test samples were derived from standards and comprised of 7 U materials and 4 Pu materials. Shipment from the IAEA Safeguards Analytical Laboratories, Seibersdorf to Chalk River, Ontario took 9 days, and was without issue.

Preparations for the round robin included assessing the uncertainty of our TIMS measurements relative to the 2010 international target values (ITVs) for measurement uncertainties [3], and a more thorough implementation of GUM (the Guide to the expression of Uncertainty in Measurement) [4] utilizing the recommendations by Bürger et al.[5].

In brief, the round robin samples were analyzed by dissolving the nitrate salts in nitric acid, further refluxing the Pu samples with ferrous sulfamate and sodium nitrite, and adsorbing the analytes onto small Acropor anion exchange discs. The Acropor anion exchange discs were then sintered onto zone refined Re filaments and loaded in a double filament geometry in a MAT 262 TIMS. Operating parameters were optimized to maximize the use of the faraday detectors for simultaneous isotope measurements, with minor peaks being measured by peak hopping utilizing the retarding potential quadrupole (RPQ) ion counter. Blanks and isotopic standards were prepared and analyzed along with these samples.

The data verification step was incomplete at the deadline for submission of data. Unfortunately, an error was made in reporting of two materials [2], even though the analyses had been correct. The results presented here contain the corrected data (thus reflecting our normal procedure).

Figure 1 shows the results for U-235/U-238 ratio measurements, comparing the measured systematic (s) uncertainty, random (r) uncertainty and combined (u_c) uncertainty relative to the international target values. Although all 45 samples were sent as individual materials, they were in fact 3 or 6 replicates of 11 different materials. The replicates have been pooled for this evaluation. The ITVs differ for the different materials from depleted U (DU), natural U (NU), low enriched U (LEU) and high enriched U (HEU), as given in FIG. 1. HEU #4 was a mixture of reference materials such that each U isotope present was approximately a 1 to 1 ratio to the reference U-238 isotope. Figure 2 shows results for all three isotope ratios for HEU #4.

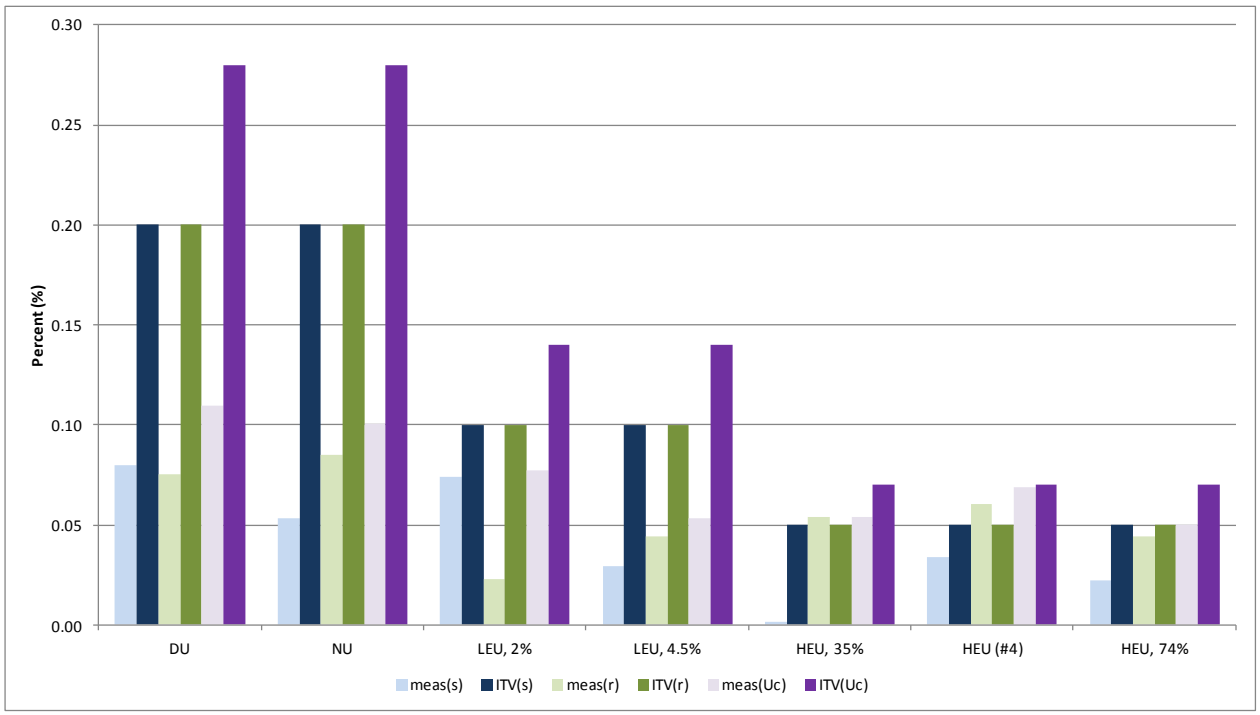

FIG. 1. AECL Measured U-235/U-238 Uncertainty vs. International Target Values (2010) Uranium Samples, 2013 IAEA Round Robin

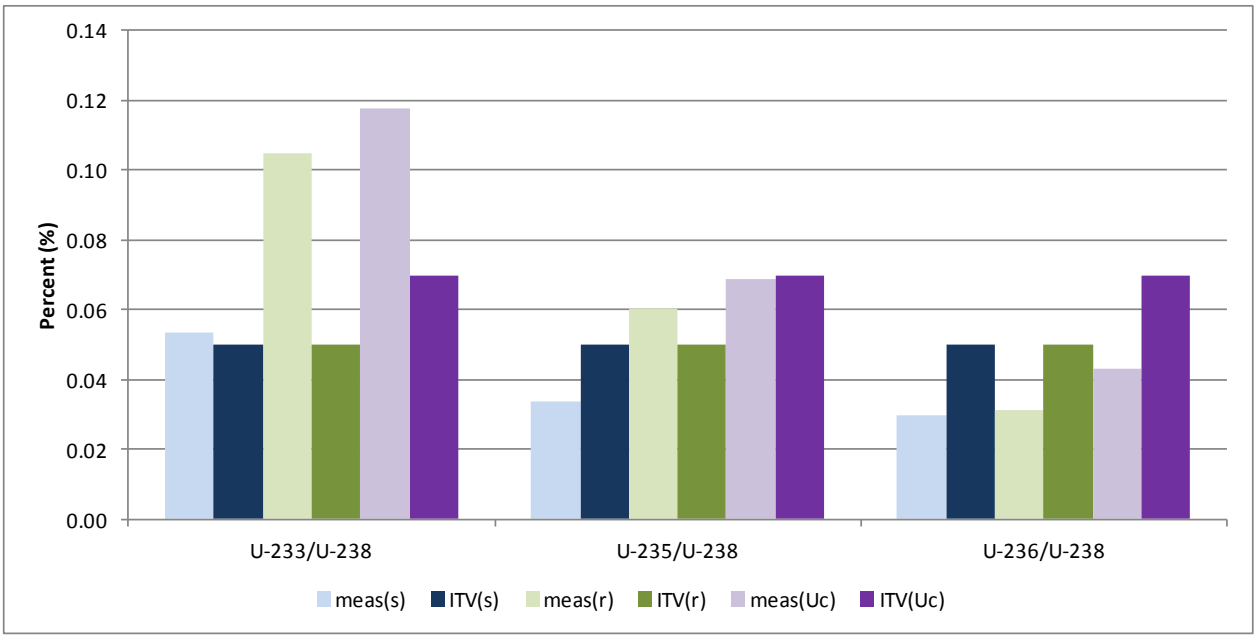

FIG. 2. Uncertainties for Simulated U Isotope Dilution (ratio ~1) HEU #4, 2013 IAEA Round Robin

Overall, the U-235/U-238 results show acceptable results relative to the target values, with the exception of the random uncertainty for HEU #4. The random error in the U-233/U-238 measurement for the same material was also outside the target value. U-233 is a common spike isotope in the lab and while our results showed we achieved results within our normal reported uncertainty, this was identified as an opportunity for improvement and investigation focused on minimizing contamination.

Figures 3 and 4 illustrate similar data for the Pu materials measured.

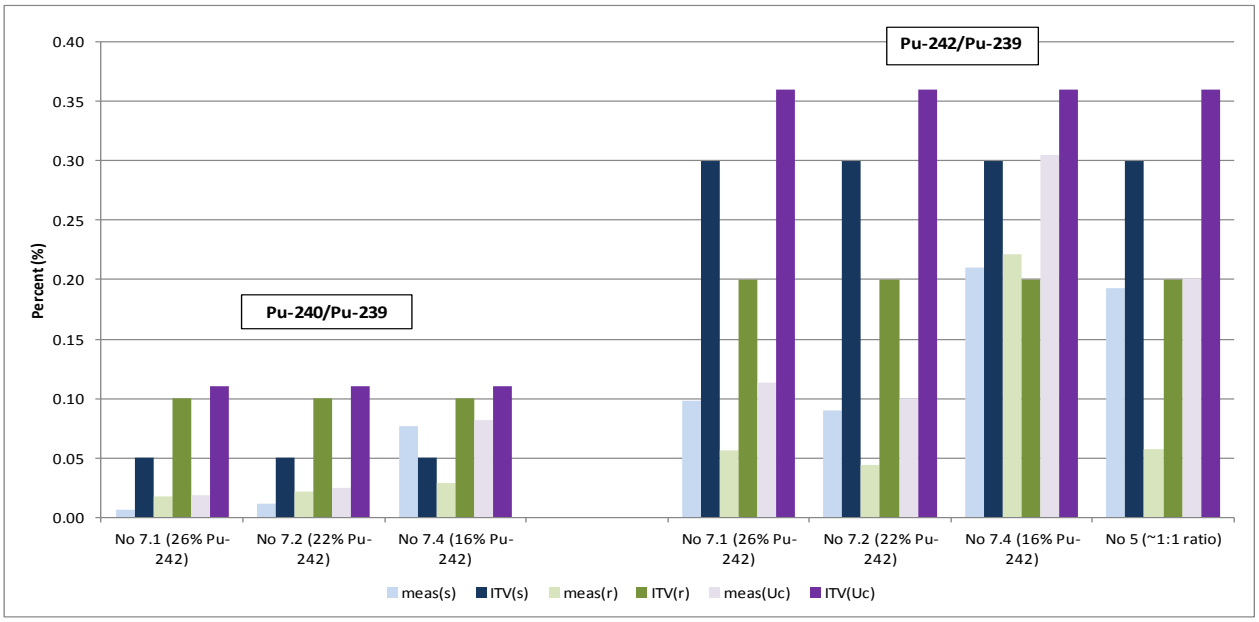

FIG. 3. AECL Measured Uncertainty vs. International Target Values (2010) Plutonium Samples, 2013 IAEA Round Robin

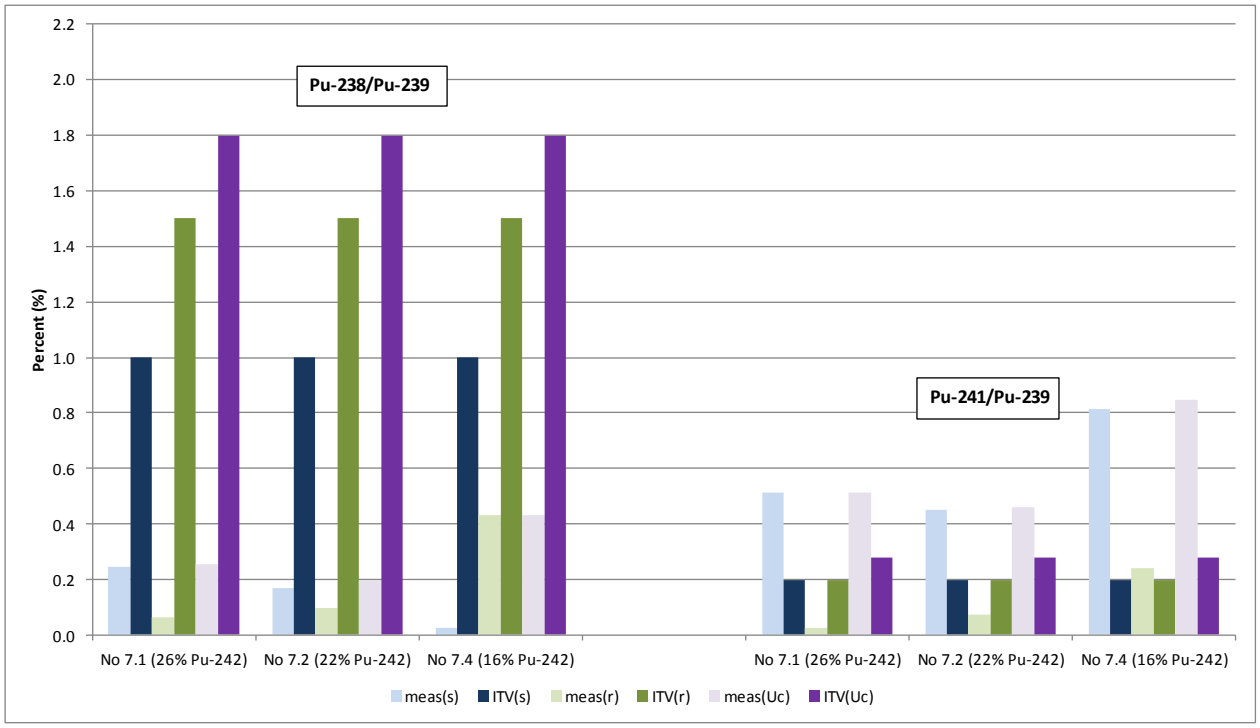

FIG. 4. AECL Measured Uncertainty vs. International Target Values (2010) Plutonium Samples, 2013 IAEA Round Robin

The Pu data shows that the majority of the target values were achieved, with the notable exception of the systematic error in the Pu-241/Pu-239 measurement. Note that the systematic error can be either positive or negative, and is plotted in Figure 4 as an absolute value for easy graphic comparison to the ITV. In the case of Pu-241, it was a consistent negative bias that is under investigation.

Based on some of the challenges and lessons learned from this exercise, the ACB has implemented some changes. To improve the throughput of analyses, additional staff are being trained in TIMS for both sample analysis and data verification. In preparation for the round robin, additional measurements were made to characterize contributors to the overall uncertainty and the Guide to the Uncertainty of Measurement was applied manually. The GUM workbench for uncertainty determinations has been purchased to facilitate the propagation of uncertainty and determine the uncertainty budget. A recommendation [2] from the Technical Meeting was for laboratories to use QC materials such as (certified) reference materials and blank samples to monitor and control the performance of the analytical procedure and for the estimation of the associated measurement uncertainties. The frequency of these QC measurements has been increased, as well as expanding the use of control charts for immediate feedback and trending purposes. In response to another recommendation of the round robin, an assessment is underway on moving to the total evaporation technique for TIMS. AECL plans to participate in the next round robin exercise planned for 2015 which is aimed at moving towards higher masses of material and analysis of mixtures of U and Pu.

5. Conclusion

The steps taken thus far in all three areas have improved AECL's ability to provide nuclear forensic support to the government of Canada through the provision of timely and defensible analyses. Striving for excellence in analysis via these improvement processes is a cornerstone of a nuclear forensics program.

REFERENCES

[1] Qualification Procedure for the Network of Analytical Laboratories for Nuclear Material Analysis, SG-SGAS-9017, IAEA Department of Safeguards, 2012 May 22.

[2] 2013 Nuclear Material Round Robin – Technical Meeting Summary, SG-RP-12319, IAEA Department of Safeguards, 2013 July 18.

[3] International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials, STR-368, Vienna, 2010 November.

[4] Joint Committee for Guides in Metrology, Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement, JCGM 100:2008.

[5] S. Bürger, R.M. Essex, K.J. Mathew, S. Richter, R.B. Thomas, Implementation of Guide to the expression of Uncertainty in Measurement (GUM) to multi-collector TIMS uranium isotope ratio metrology, Int. J. Mass Spectrom. 294 (2010) 65-76.