Challenges in Bulk Nuclear Forensics Sample Analysis

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Abstract. Analytical chemistry operations at Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL) support technical nuclear forensics by providing chemical and physical measurements of bulk special nuclear material for a consortium of key United States (US) government agencies. Capabilities to support the nuclear forensic mission continue to evolve from the basic analytical method set developed half a century ago to support reactor operations and US defense programs. Evolution of analytical chemistry capabilities includes new certified reference materials (CRMs) for quality assurance and quality control to maintain historical measurement surety but with improved fidelity and defensibility. A lack of traceable, matrix-matched standards, with certified uncertainties representative of modern analytical techniques has been recognized as affecting confidence in the measurement results on important nuclear materials. Drawing guidance from the National Institutes of Standards and Technology (NIST) and New Brunswick Laboratory (NBL), the US nuclear forensic community is working to define and develop the well-characterized reference materials necessary to ensure the integrity of critical forensic measurements. In this paper, discussions will deal with a case for using available pedigreed materials that are commonly used to provide quality assurance on relevant nuclear materials for nuclear forensic CRMs. A discussion of challenges associated with transitioning from a production-oriented, analytical laboratory to an ISO 17025 accredited laboratory will also be presented.

1. Introduction

Analytical chemistry operations at Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL) provide chemical and physical measurements of special nuclear material (SNM) for a consortium of United States (US) government agencies. The discussion herein will focus exclusively on LANL capabilities. Analyses range from assay of the major components down to trace analysis of impurities – a concentration span of over seven orders of magnitude – and consist of both non-destructive and destructive analyses. LANL has the necessary facilities, glove boxes, hoods, analytical instrumentation, and technical expertise for handling and analyzing microgram to kilogram quantities of special nuclear material safely [1, 2]. These capabilities evolved from a classical analytical method set developed at the onset of actinide research that have been refined over the last half a century to support reactor fuel development and US defense programs. The depth and quality of characterization capabilities have improved with advances in computing, analytical instrumentation, actinide separation science, and material structure and composition imaging at the microscopic level [1, 2, 3, 4].

Today, the results from nuclear material analysis is further evolving to support international engagements (State Department, Department of Energy), emergency response, nuclear forensics (criminal law enforcement, environmental law enforcement), national and international regulations (safeguards and safety), as well as support the more historical defense and energy programs. Because of ongoing actinide product certification work at LANL, analytical chemistry capabilities already operate under comprehensive quality assurance (QA) and quality control (QC) guidelines. However, the transitioning of analytical chemistry capabilities to support new programs requires a corresponding improvement in operational QA to meet courtroom admissibility standards [5]. For example, nuclear forensic work requires much more stringent application for chain-of-custody of sample materials than standard requirements for international accountability and safeguards. In addition, application of new analytical methods to material analysis is often required. Pcynometry, scanning electron microscopy, and x-ray diffraction are methods traditionally used in areas of research and development rather than in routine characterization of SNM materials. These new methods require development of standards and appropriate controls if they are to be useful to all programs [2].

The majority of the existing certified reference materials (CRMs) for bulk SNM analysis were produced in support of international safeguards, but are also relevant to nuclear power and defense programs, amongst others. In the nuclear forensic analysis community, the ability to prove or trace sample measurement data back to a traceable, established metrological standardization scheme is critical to defensibility. Availability of a limited number of traceable, matrix-matched standards with certified values and uncertainties representative of modern analytical techniques has been recognized as affecting confidence in the measurement results on important nuclear materials [2]. In addition, available matrix-matched, traceable standards are (1) limited in material type (U, Pu…) and compositions; (2) provide certified values for a limited analyte set focused on past nuclear program needs; (3) carry measurement uncertainties determined using old and less precise methods; (4) are packaged in amounts too large for easy shipping or site handling; or (5) are often not available at all for important characteristic measurements. Extensive discussions of these shortcomings are published in the Inn et. al. 2008 [6] and 2013 paper [7].

Drawing guidance from the National Institute of Standards and Technology (NIST) and New Brunswick Laboratory (NBL), the US nuclear forensic community is working to define and develop the reference materials necessary to ensure the integrity of critical forensic measurements. From this work, various federal agencies have developed a plan to produce CRMs and working reference materials (WRMs) for trace actinides, trace metal elements, and chronometers in uranium (U) and plutonium (Pu) matrices [6, 7]. Separately there is an ongoing effort at the international level through the various metrology labs from across the globe (including NIST, NBL, Commission d'ÉTAblissement des Méthodesd'Analyse: Analytical Methods Committee [CETAMA], and the Institute for Reference Materials and Measurements [IRMM]) to provide support for nuclear forensics and the International Atomic Energy Agency (IAEA) [8, 9]. In this paper, work LANL has performed towards the overall goal of providing well-characterized, homogeneous, stable, pedigreed materials for QA and traceability on nuclear forensic materials is discussed.

In the absence of relevant reference materials, well established QA programs with appropriate QC materials, inter-laboratory comparison programs, application of independent methods based on different principles, and method implementation by different operators are often used to verify and validate analytical methods and techniques [9, 10, 11]. It was anticipated that adding the ISO 17025 program could build on the existing quality program to ensure legal defensibility of data for forensic programs, especially when limited RM is available. In 2012 the first 6 methods were accredited with another 7 methods accredited in 2013. Acquiring ISO 17025 accreditation has further strengthened LANL's reputation as a leader within the international nuclear community for its technical depth and ability to produce accurate and precise analytical data. A discussion of challenges associated with transitioning from a non-accredited to an ISO 17025 accredited analytical laboratory will be discussed.

2. Use and support of traceable pedigreed materials.

Analytical chemistry at LANL has addressed traceability in a multi-faceted effort. Initially, as part of the broader community working with nuclear materials, expert personnel participated in discussions over the last six decades to identify existing and emerging needs of the analytical laboratory communities [7, 9, 12]. From recent discussions, LANL has collaboratively acted on 3 approaches to making pedigreed materials more available: repackaging, recertifying, and producing new reference materials. LANL is a logical and effective partner for these activity as it possessed (1) the facilities to handle both the high activity and quantity of material; (2) trained personnel; (3) a 60 year, demonstrated history with providing measurements for certification and production of Pu reference materials in conjunction with NBL and NIST; (4) demonstrated excellence in providing high quality measurements; and (5) a robust QA program.

2.1. Repackaging

The activity of many Pu CRMs have significantly increased due to ^{241}Am in-growth from ^{241}Pu decay over the decades following certification., In many instances, the increased activity of Pu CRMs had increased to the point that it became difficult to ship these materials to sites with very limited abilities to handle more than milligram quantities of SNM. These sites could not receive the RMs as originally packaged. Thus, repackaging into smaller amounts became an effective and relatively quick solutions to make currently certified materials more widely available without the expensive and time-consuming option of having to completely refabricate and re-certify these materials.

In 2008, LANL analytical chemistry repackaged CRM 136, 137, and 138 into smaller quantities. These standards are most commonly used as isotopic QCs or calibration standards. The plutonium sulfate tetrahydrate ($Pu(SO_4)_2$-$4H_2O$), isotopic CRMs had been originally packaged in 1970 by NIST, then called the National Bureau of Standards, as SRMs 946, 947, and 948. In 1982, the ownership of these materials transferred to NBL and their identification changed to CRM 136, 137, and 138 with new certificates of analysis issued. Each original SRM vial held 0.25g of material. Upon receipt and un-packaging of this material, LANL identified several issues with the degradation of the old, original packaging (see Figure 1).

Figure 1: Photos showing original packaging of these materials as received. Material was verified in good condition, and the outer bag intact. Forty years of aging effects seen in the inner packaging. A) Original colorless glass vials now opaque with brittle caps, B) inner containment bag completely disintegrated.

These SRMs were successfully repackaged into 10 mg and 50 mg quantities. To verify that handling during the repackaging process did not contaminate the materials, blanks modeling the entire process were performed prior to the introduction of the RMs to the workspaces. This process was proceeded by preparing the area with extensive clean up and introduction of new materials and supplies used for processing. Blanks in this case returned values at the picogram levels for Pu. In addition, process blanks were created and handled through the entire process of repackaging alongside the RMs. Pu isotopic analyses of the re-packaged materials were carried out via thermal ionization mass spectrometry on randomly selected vials. All verification measurements performed at LANL are traceable to CRM 126a. (See Table 1 for comparison of the analyzed and certified values.) The measurements carried out to support this work are within the uncertainties associated with the original certified values, and the data verified that the material was not contaminated during handling [13].

Table 1: Example of verification data. Ten replicate analyses across multiple vials provided the data below.

CRM 137	**Pu Isotope Weight % (2/10/09)**				
	238	**239**	**240**	**241**	**242**
LANL Average	0.230	78.705	19.039	0.7846	1.242
LANL uncertainties	*0.001*	*0.008*	*0.008*	*0.0008*	*0.002*
Certified Value, (decay corrected)	0.228	78.703	19.040	0.786	1.244
Certificate uncertainties, 95% confidence interval	*0.007*	*0.015*	*0.015*	*0.005*	*0.003*
Absolute Difference	0.002	0.002	-0.001	-0.001	-0.002

The repackaged material became available through NBL in mid-2009. Figure 2 shows the materials as they are currently packaged.

Figure 2: Newly re-packaged standards in A) first tape sealed, zip lock bag, B) second, heat-sealed, Mylar bag, and C) final container ready for shipping.

2.2. Recertification

Another more involved approach is to recertify existing stocks of CRMs with more modern analytical methods and technologies while applying principles from the Guide to the Expression of Uncertainty in Measurement (GUM), also known as ISO/IEC Guide 98-3. In 2011, LANL worked with NBL to analyze CRM 125a for U assay values using a modified Davies-Gray analysis. The original U125a assay values are from the 1997 certificate determined using the high accuracy and precision NBL titration method that was traceable to NBL's CRM 99 Potassium dichromate standard.The LANL modified Davies-Gray method was traceable to NBL CRM 112a U metal standard. LANL assay values (Table 2) showed no statistically significant difference from the original certified value within the uncertainty of the measurements, and supported an NBL decision to continue using the original certified assay values produced by the high accuracy and precision titration method.

Table 2: Example of verification data provided to NBL for CRM 125a. Each analyst had n = 5 and performed his or her work on different days.

CRM 125a	U Assay (wt. %)	Expanded uncertainty, k = 2 (wt. %)
Certified value 1997	88.129	0.014
LANL, analyst 1, avg.	88.112	0.062
LANL, analyst 2, avg.	88.117	0.065
Absolute difference, analyst 1	-0.017	N/A
Absolute difference, analyst 2	-0.012	N/A

In 2013, NBL reissued the certificate of analysis including expanded information with many orders of magnitude improvement in the certified isotopic accuracy and associated uncertainties. Also included on the reissued certificate is a model purification date. This revised latter information is extremely important for nuclear forensics applications since for the first time it provides a U chronometry RM [8]. The great improvement in accuracy and uncertainty information, as well as the certified purification date, allow this standard to be used in many more applications and provide the traceability that many new forensic methods require.

2.3. Production

Finally, the most difficult and costly approach is to produce new RMs. The analytical chemistry group and the wider Los Alamos assets have been involved in the production and independent characterization of Pu-based RMs – for example, the Pu metal CRM126a (an isotopic and assay standard) was produced and certified in 2004. More recently, LANL produced, packaged, and characterized two Pu oxide reference materials. These will be certified for the trace actinides in Pu along with Pu assay and isotopic compositions.

The first proposed RM material started as doubly electro-refined (very high purity) Pu metal. This material was converted to oxide by exposure to air. The second proposed RM material was prepared from kilogram quantities of oxide that went through extensive cleanup for actinides and trace element including dissolution and ion exchange followed by oxalate precipitation and oxide conversion. In both cases, the entire processing history of the material is known including the dates of chemical separation. Both RMs were stabilized by calcining with slow ramp heating and then holding the final temperature for two hours at 750 ^{o}C and 650 ^{o}C respectively. For relatively pure PuO_2 RMs, these temperatures ensure the materials are stable as determined by loss-on-ignition measurement. Higher calcination temperatures could have been used, but this can result in a material that is much more difficult to dissolve with standard acid dissolution protocols utilized globally. These temperatures are high enough to ensure the RMs remain stable over time in the current storage/packaging environment.

These new RMs were portioned in labeled, sealed containers. Each container held between 160 to 200 mg of Pu oxide with 150 units total prepared. Characterization measurements were performed using analysis protocols developed with NBL that ensured high quality results with traceability to existing certified standards. These methods have been validated through participation in inter-laboratory comparison programs where these attributes have been tested annually for the last decade. Measurements performed included (1) Pu assay by controlled potential coulometry; (2) U assay by isotopic dilution mass spectrometry; (3) Pu/U isotopic analysis by thermal ionization mass spectrometry; (4) Am by gamma spectrometry; and (5) Np by total alpha counting and alpha spectrometry and inductively coupled plasma mass spectrometry. Measurements were performed on multiple vials, in duplicate for each sample for all measurements. A final report on these materials was submitted to NBL to initiate the formal certification process in October 2013.

3. ISO 17025 Transition Challenges

LANL analytical chemistry has always maintained a robust QA program due to the consistent work for nuclear energy (NQA-1 *Quality Assurance Requirements for Nuclear Facility Applications* requirements) and defense programs (QC-1, *Weapon Quality Policy* requirements). Analytical methods and associated procedures have defined QC measures to assure validity of a method's precision, accuracy, and sensitivity. Quality control measures may include, but are not limited to, method blanks, laboratory control samples, laboratory surrogates, internal standards, matrix spikes and matrix spike duplicates, interference check samples, serial dilution, and environmental contamination controls. The acceptance criteria for each QC measure are identified and tracked via control charts. Thus, the additional requirement to become ISO 17025 accredited requested by some external customers did require a philosophical change to the way the QC program was implemented. To start the process, a review of our existing programs against ISO 17025 requirements was conducted for the group by independent QA specialists. This section will focus on the analytical quality activities that required most effort.

3.1. Validation of ongoing methods

All QA programs at LANL require that a method be validated and tested for performance based on accepted, peer reviewed, scientific principles. However, ISO 17025 requires that the validation of bias, accuracy, and uncertainty have to be formally documented. Most of the methods used by the analytical chemistry at LANL have formal validation reports for operations support documented over the last several decades. These validation reports were modified as new technologies and instruments were implemented within the method. However, during preparation for the ISO 17025 audit it was discovered that no formal validation documentation existed for a few historical/classical methods. Furthermore, these methods had been modified slightly due to the evolution in both environmental law and health/safety rules and regulations since the time the originating peer reviewed papers were published.

Due to the inadequate documentation, analysts reviewed 25 years of records and data to establish that the modifications made to the original methods did not affect the quality of results being provided. For example, analytical chemistry at LANL has been using a version of the Davies-Gray titrimetric analysis modified to use ceric sulfate as the titrant with CRM 112a for calibration since 1992. The record review found that two separate LANL technicians had run identical samples using the original dichromate standard titrant method and the modified ceric sulfate titrant method prior to implementation of the changes. These records included comments regarding modified method's performance. In addition, the modified method LANL currently uses was published in a peer report by NBL [14]. This report was a rigorous statistical comparison of the original and modified methods, finding that the two methods produced identical data on appropriately matrix-matched materials. Finally, the method had continuous participation in an ongoing inter-laboratory comparison program evaluating against International Target Values. As a result, memos and yearly reports from an independent evaluator proved the modified method was yielding continuous, unbiased, and accurate results with uncertainties that met international standards. With these facts in hand, a validation memo formally documenting the history, the statistical accuracy, and uncertainty of the method, as well as the ongoing excellent performance, was issued.

3.2. Procedural issues and potential impacts

Once a method is validated, and after proving long-term statistical control, the next challenge is to keep the method validated by exercising the measurement system on a regular basis. It is also important to maintain traceability through use of appropriate calibration and QC materials. Nuclear forensic samples can sometimes provide unique challenges by being greatly different than production samples [7, 15, 16, 17]. To address this, the program must be designed in a manner that allows for variability found in material types so that the results are admissible in court or pass scientific peer review. Therefore, when updating methods with new information, care must be taken to ensure that additions to or deletions from the procedure do not change the overall validation status of the method.

The validation process should evaluate a sufficient variety of material types to verify and retain method flexibility and conditional boundaries needed to produce defensible result in terms of accuracy, precision, and uncertainty. For instance, Table 3 gives examples of wording that can potentially lead to issues that preclude admissibility in court. However, if more flexible phrasing is used with options for unusual materials or situations, the analyst can produce results that are court admissible. Therefore, the initial method and associated validation approved by the customer and performed by the analyst has to be designed in a careful, thoughtful manner. Years of experience at LANL in the support of various national and international programs have resulted in procedures already containing some flexible wording needed to address the variability sometimes encountered. However, as part of the ISO17025 accreditation, this aspect was especially scrutinized. In some cases, it was found that an updated validation was required to include some additional aspect or additional flexibility in a method.

Table 3: Inflexible procedural wording compared to flexible procedural wording

Example	Inflexible	Flexible
Minimum number of sample replicates	Run three replicates of every sample.	Three replicates of each sample are typically run unless the amount of available sample is limited.
		The supervisor will consult with the customer to see if an analysis using less than three replicates is acceptable or if the customer wants the analysis cancelled.
Acceptance criteria	Sample analyzed "x" value exceeding the calibration range cannot be used.	If a sample analyzed "x" value exceeds the calibration point by · For calibrations ≤ 1000 ppm, >250 ppm, · For calibrations above >1000 ppm, >25%
		1) Analyze a check standard that has a certified value as close as possible to the reported sample value.
		2) If the check standard results are within 3-sigma from the standard's certified value, then the returned result for the sample may be reported.
		3) If the check standard results are not within 3-sigma from the standard's certified value, the sample must not be reported. Instead, obtain recuts and recalibrate the system using the higher value standard or reanalyze the sample using a smaller sample size.

3.3. Performance assessment protocols

In order to assure a customer that the results provided are accurate and meet expected uncertainties, ISO 17025 requires that all certified/accredited methods be evaluated by performance testing. The minimum testing specified is two techniques per year with all certified techniques tested once within a four-year window. Since analytical programs are only recently ISO-17025 compliant, LANL has conservatively chosen to exceed this requirement by testing every method at least once every year for both Pu and U matrices Assurance can be accomplished by participating in performance tests, inter-laboratory comparison programs, or by monitoring QC data for matrix-matched, traceable standards. The challenge for LANL – and all laboratories that do bulk special nuclear material nuclear forensic work – is that there are currently very few certified (ISO 17043) performance test programs available to participants in the US. This means round-robins or QC data from traceable RMs must be used.

Fortunately, US Department of Energy (DOE) has required US laboratories providing Materials Control and Accountability analyses to participate in inter-laboratory control programs in order to provide independent verification of analytical QC [18] and have long funded the NBL SME program for U materials. Other agencies within the US government and international agencies (such as the IRMM, CETAMA, IAEA and individual countries such as Japan) are beginning to implement regular national and/or international performance test and benchmarking studies to study key attributes.

US DOE has also funded a LANL-based, Pu materials exchange program over the decades. These programs assess our validated methods using matrix-matched RMs or traceable, well-characterized matrix-matched materials and compare multiple independent methods amongst independent laboratories [11]. Most of the criterion covered under ISO 17043 (such as materials testing and stability) is incorporated in these two DOE exchange-robin programs. The LANL program requests analysis of almost the entire periodic table and up to six peer labs have participated. NBL's program has focused on safeguard measurements with over 20 labs and multiple countries participating. Table 3 shows an example of LANL data from the Pu exchange assessing the trends for ^{237}Np analysis. Though not a key attribute for past programs, these analyses have become critical in age-dating nuclear forensic samples.

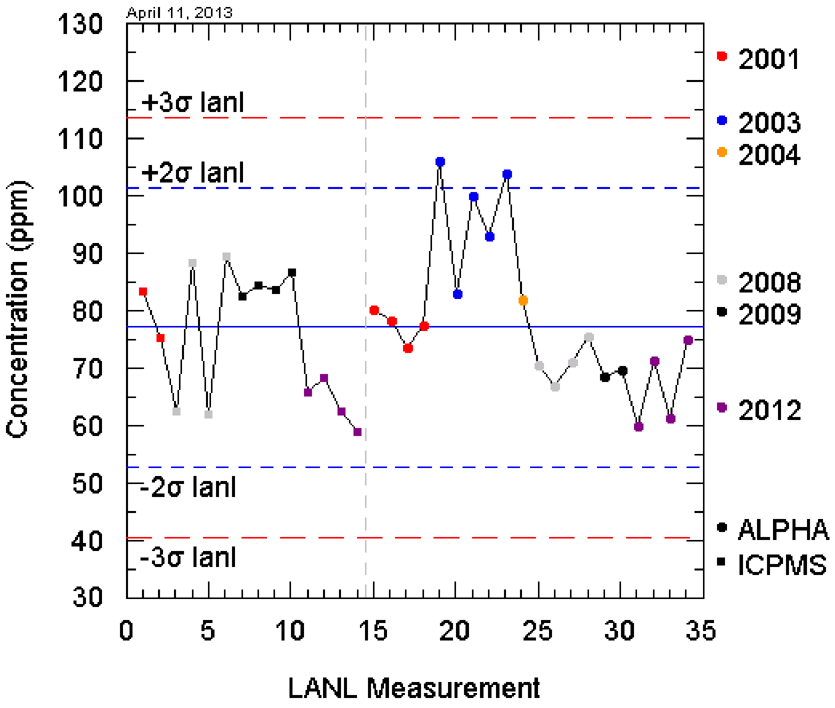

Figure 3: Trend plot for ^{237}Np measurements on a particular Pu Exchange metal by LANL ICP-MS and alpha spectrometry. All data decay corrected to the same date. Individual data points, 10% expanded uncertainty.

Unfortunately, escalating health, safety, and security challenges can cause previously functioning facilities or programs to shut down or change their manner of operations interrupting the historical supplies of round-robin or performance test materials. These challenges also impact shipping rules and regulations – especially when shipping materials internationally where customs, export rules and regulations, and international safeguards agreements can have a profound impact in a country's or a laboratory's ability to participate in these programs. Per the ISO 17025 requirements and dictated by good analytical laboratory practices, when test materials are unavailable, analysts submit their QC control charts at the end of the year for review by an independent analyst and the QA team. The review includes comparing QC data to the acceptance criteria stated in written procedures to ensure that it is continuing to meet the specified performance conditions.

3.4. Law enforcement requirements

All forensic science must meet requirements of certainty such as maintaining a chain-of-custody, ensuring sample integrity, applying corroborating methods of analysis, and rigorously validating sensitivity and selectivity. Nuclear forensics often requires rapid analysis of unique samples with additional safety and security requirements. In the US, analytical reports must follow Rules 701 and 706 of the Federal Rules of Evidence [5]. To meet these requirements, the reasoning and methodology must be scientifically valid, properly applied, and have relatively widespread acceptance within the scientific community. In addition, the techniques used must be previously tested, have existing standards, and known error rates (uncertainties) [5].

The gap related to calculation of uncertainties proved to be the most challenging, not specifically for the implementation of ISO 17025 itself, but because of customer requirements. The customer required uncertainties be calculated using the GUM rather than reporting the simpler standard deviation from repeat measurements or historical method uncertainty that many programs typically request. The generation of these reports for forensic samples can be complex, labor intensive, and require additional experimentation to provide legal support for the data used in the uncertainty models. Once initially trained on GUM, analysts reviewed existing QC data to determine uncertainty factors for the models' variables. For variables that did not have historical QC data, experiments were designed to not only understand the measurement systems in greater detail, but to provide the required information for the GUM models in order to calculate both Type A and Type B uncertainties. Finally, independent peer review of the GUM models has resulted in greatly improved models that capture known sources uncertainties for the techniques being modeled.

In addition, participation in the nuclear forensic program necessitated the development of detailed data packages. Traditionally, data packages included relevant general information in support of the results. However, with the potential for legal review, a procedure for the development of a full casebook was written. The casebook procedure details the need to include, at the time of the report, all measuring and testing equipment and associated calibrations, information sufficient for traceability reconstruction, chain-of-custody documentation, raw data, associated correspondences, etc. Understandably, these data package requirements create a significant amount of additional work.

4. Conclusions

Drawing guidance from the NIST and NBL, the US nuclear forensic community is working to define and develop the well-characterized reference materials necessary to ensure the integrity of critical forensic measurements. LANL, has assisted the global community of nuclear forensic analysis by repackaging, providing measurements for re-certification, and producing these pedigreed materials to assure traceability and validation for measurements. In addition, the analytical chemistry resources at LANL have continued to validate historical methods, update protocols, and apply law enforcement requirements to forensic samples while achieving and maintaining ISO 17025 accreditation.

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Proof of Principle for the Preparation and Validation of an Uranium Age Dating Reference Material

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Abstract. The present paper discusses the outcome of a joint effort of expert nuclear forensic laboratories in the area of age dating of uranium. Completely separated uranium materials of known production date were distributed among the laboratories, and the samples were dated according to the routine laboratory procedures. The measurement results were in fairly good agreement with one another and also with the known production date, thus strongly underlining that the concept for preparing such age dating reference material is valid and a useful and appropriate certified reference material can be produced applying this methodology. The detailed knowledge of the laboratory procedures used for measuring the age of the sample allows to identify possible improvements in the current protocols and to develop the best practice for uranium age dating in the future. The availability of age dating reference materials as well as the evolvement of the age dating best-practice protocol will increase the relevance and applicability of age dating as part of the tool-kit available for nuclear forensic investigations.

1. Introduction

If nuclear materials are diverted and afterwards interdicted, detailed investigation is required to identify the possible origin, intended use and hazard related to the material. Such analysis, which is now commonly referred to as *nuclear forensics*, involve the comprehensive physical, chemical and isotopic measurements (*e.g.* physical dimensions, crystal structure, radioactive and stable chemical impurities, classical forensic analysis) as well as the interpretation of these measured parameters [1-3]. Based on this complex information, the assumed origin of the material can be verified or for an unknown material the provenance can be identified with high reliability.

Numerous characteristics (so-called *signatures*) of the material can be used for such purpose, such as the isotopic composition of U, Pb or Sr, elemental impurities, trace-level radionuclide content, crystal structure or anionic residues. Besides these parameters the elapsed time (commonly referred to as the "age" of the material) since the last chemical purification of the material can also be measured for radioactive (nuclear) materials. This unique possibility is based on exploiting the presence and decay of the long-lived radionuclide (usually uranium or plutonium as major component in case of nuclear materials): in the course of the production the radionuclide is chemically purified from the impurities, including also its radioactive decay products. After production, the radioactive progenies start to grow-in again in the material. Assuming that the parent-daughter separation was complete, the elapsed time since the last separation, thus the production date, can be calculated according to the decay equations after the measurement of the parent-daughter ratio in the sample. This age value enables either to identify the origin of the unknown sample or to verify the source of the feed material. In contrast to most other characteristics used in nuclear forensics, the production date of the material is a predictive signature, thus it does not require comparison samples for origin assessment. This feature makes the production date one of the most prominent signatures for attribution.

However, in order to put the obtained results on a more solid scientific or legally defensible foundation, dedicated reference materials are required. In consequence, an emerging need for such materials has been recently expressed by the community involved in national or international nuclear security programs.

Our major objective was the preparation and validation of a uranium-based reference material, which can be applied for the validation of age measurements based on the ^{230}Th/^{234}U chronometer. The material was prepared from high-purity uranium solutions with various uranium enrichments by completely separating the thorium decay product [4]. By this means, the production date is very precisely known (with an uncertainty of less than about 5 hours). In contrast to other methods of producing age dating reference materials , this approach does not require measuring the age of the final material and thus deriving a certified production date, because, if all conditions are fulfilled (completeness of separation, long-term stability, closed system), the ^{230}Th present in the material will solely depend on the radioactive decay laws. Therefore, the material prepared can be used as a primary standard for age dating of uranium materials.

The aim of the present collaboration is two-fold: firstly, to prove the applicability of this methodology for the preparation of a uranium age dating reference material by the independent measurement of expert laboratories. Since the validation requires the measurement of the ^{230}Th decay product at very low level from the freshly separated material, state-of-the-art instruments and well-established techniques are required. Secondly, this joint effort enables the identification of the best methodologies (best practices) for uranium age dating. The availability of age dating reference materials will help validate current and future age dating protocols, leading to a more robust source of nuclear forensic signatures and a legally defensible basis for the use of age dating results in nuclear forensics investigations. Validation of these methods will increase their relevance and applicability as part of the tool-kit available for nuclear forensics investigations.

2. Preparation of the materials

The material was prepared from uranium after complete separation of thorium decay products (zeroing the initial daughter nuclide concentration) at a well-known time and allowing the ingrowth of the daughter nuclides.

The preparation of the material is described in details elsewhere [4]. The materials used were high-purity uranium-oxide samples dissolved in nitric acid. Three uranium materials with different uranium enrichments were prepared: natural uranium (0.71% ^{235}U abundance), low-enriched uranium (LEU, approximately 4% ^{235}U abundance) and a highly-enriched uranium material (HEU, ^{235}U abundance is about 70%). The dissolved uranium samples were purified with three consecutive extraction chromatographic separations in order to completely remove the ^{230}Th decay product.

The final thorium purification of the material took place on 19 July 2011. The purified uranium solutions were aliquoted into screw-capped PFA vials right after the uranium purification and sample homogenization. Approximately 30 mg U was placed into each vial, and then they were evaporated to dryness right after its preparation to avoid loss of Th by adsorption.

The separation efficiency of Th was determined by gamma spectrometric measurement and by the addition of ^{232}Th to the starting material and its re-measurement following the chemical separations. A total separation factor of approximately 3×10^7 was achieved, which corresponds to a ^{230}Th/^{234}U ratio in the final reference material of $10^{-11} – 10^{-13}$ at the time of preparation. Therefore, the residual ^{230}Th is negligible compared to the ingrowth thereafter (corresponds to less than a few hours' expressed as time), and the amount of ^{230}Th in the material is then solely the function of the ^{234}U amount. The number of atoms of ^{230}Th can be derived from the decay equations:

$$N_{Th-230} = N_{U-234} \frac{\lambda_{U-234}}{\lambda_{Th-230} - \lambda_{U-234}} \left(e^{-\lambda_{U-234} t} - e^{-\lambda_{Th-230} t} \right) \qquad (1)$$

where N_{Th-230} and N_{U-234} are the number of atoms of ^{230}Th and ^{234}U in the sample, respectively, λ_{Th-230} and λ_{U-234} are the decay constants of ^{230}Th and ^{234}U, respectively, and t is the elapsed time since the separation of the material.

3. Reported results from the participating laboratories

Aliquots of the prepared samples were shipped to the participating expert nuclear forensic laboratories, where the production dates of the materials were determined according to their routine procedures. The participating laboratories in this study were Lawrence Livermore National Laboratory (USA), two laboratories from the Los Alamos National Laboratory (USA), DIF of CEA (France) and EC JRC Institute for Transuranium Elements (European Commission). It should be noted, though, that the analytical determination of the production date by measuring the parent/daughter ratio is fairly challenging because the time span between the preparation and the measurement (approximately 2.5 years) is very small compared to the half-life of the parent nuclide ^{234}U (245 000 years). In consequence, only minute quantities of daughter nuclide ^{230}Th will grow in and have to be separated and accurately quantified. The reported age results are shown in Figs 1-3.

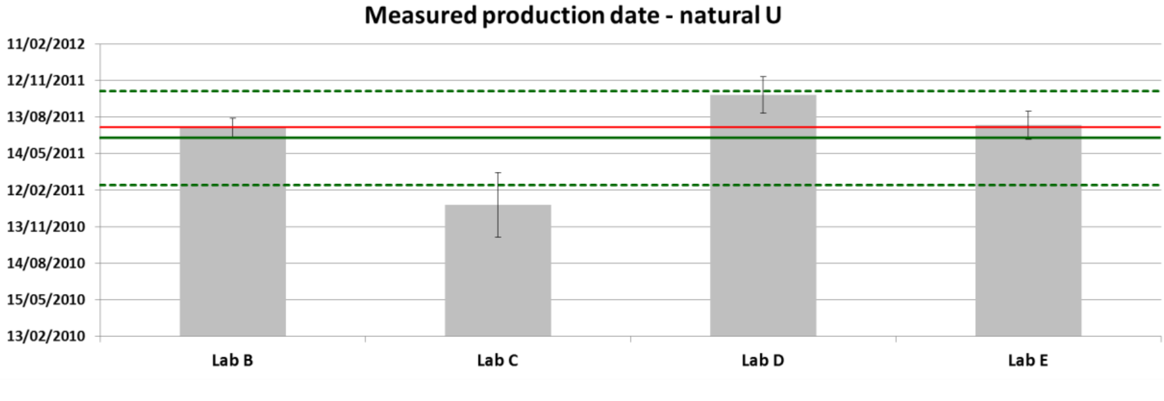

FIG. 1. Reported production dates for the natural uranium sample. Red line: known production date (19 July 2011); Green line: average of the reported dates with the confidence interval expressed as one standard deviation of the reported dates (dotted lines).

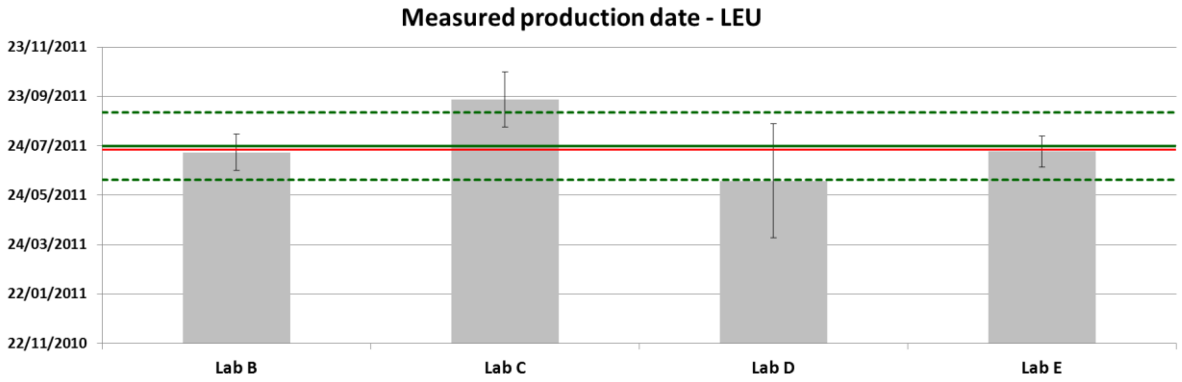

FIG. 2. Reported production dates for the low-enriched uranium sample. Red line: known production date (19 July 2011); Green line: average of the reported dates with the confidence interval expressed as one standard deviation of the reported dates (dotted lines).

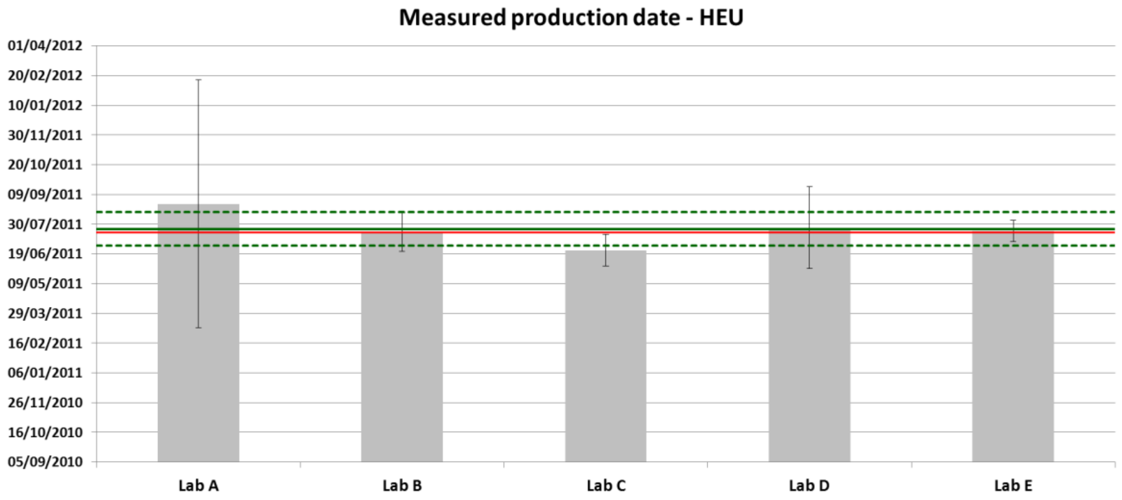

FIG. 3. Reported production dates for the highly-enriched uranium sample. Red line: known production date (19 July 2011); Green line: average of the reported dates with the confidence interval expressed as one standard deviation of the reported dates (dotted lines).

The reported average production dates for the natural, LEU and HEU samples are 21/06/2011 (with an uncertainty of 117 days at $k = 2$), 23/07/2014 (with an uncertainty of 42 days at $k = 2$) and 23/07/2011 (with an uncertainty of 23 days at $k = 2$), respectively. For all samples the reported averages are in good agreement with the known production date of 19/07/2014 within measurement uncertainty. The differences between the known production dates and the reported average production dates for the natural, LEU and HEU samples are 27.2 days, 4.7 days and 4.5 days, respectively. As no significant or systematic bias could be identified between the known and reported values of all three materials, the methodology for such uranium age dating reference material is expected to be applicable, which is an additional confirmation of the earlier study [4]. All the reported production dates of the individual laboratories overlap with the average results even at 1-sigma level.

However, if one compares the individual laboratory results, significant differences can be observed. While all reported individual HEU age results overlap with one another, in case of the LEU and natural uranium samples the reported individual results from the laboratories are significantly different (Figs 1-3). This difference is much higher for the natural uranium sample than for the LEU material, which is in correlation of the ^{234}U content (and therefore with the amount of ^{230}Th progeny). As the difference is possibly not related to the reference material properties (e.g. inhomogeneity between the items), it is assumed to the consequence of the difficulties in the measurement of the trace-level ^{230}Th.

In case of the natural uranium and LEU samples the corrections for the trace-level ^{230}Th measurement are more significant than for the HEU material, thus more detailed studies and investigations are necessary to develop more robust procedures in the participating laboratories. By sharing the details of the existing methodologies, the possible inappropriate steps in the procedures can be rectified (Table I and II). By this means the approaches can be harmonized and the best practices for age dating measurements can be developed.

Table I. Analytical measurement methodologies of the participating laboratories

	Lab A	Lab B	Lab C	Lab D	Lab E
Sample preparation					
Sample taking, subsampling or sample pre-treatment	Sample was dissolved and aliquots were taken for U/Pa and U/Th analysis	Sample dissolved in original sample vials and transferred with rinses into weighed vial	Sample was dissolved in original vial prior to splitting	Total sample was dissolved in the original Teflon vial without splitting.	Total sample was dissolved in the original PFA vial without splitting/transfer.
Dissolution conditions (e.g. type of acid, temperature, labware type)	HCl UP, heated to 90°C overnight	4 M HNO_3 + 0.05 M HF, into 30 mL PFA vial for primary solution, warmed on low temperature hotplate and ultrasonicated	Dissolved in heated acid (80-90 °C) for ~ 1 hour and allowed to equilibrate overnight prior to use.	24 hour closed vessel digestion on hotplate at 90˚C in 8M HNO_3 (Optima HNO3 + triple distilled H2O)	Subboiled *cc*HNO_3 (3 ml to 30 mg U), heated to 90 °C for 1 hour
Uranium analysis					
Measurement technique and instrument type	TIMS (Triton)	Static multi-collection on NuPlasma MC-ICPMS. U-isotopic composition measured first on un-spiked aliquots. U IDMS on separate spiked aliquot from secondary diluton	TE TIMS- VG Sector 54	Multi-collector TIMS U isotopic analysis	TIMS, MTE-TIMS (Triton) and ICP-MS (Element2)
^{234}U quantification method	Isotope dilution with ^{233}U	IDMS using ^{233}U spike.	Isotope Dilution	Isotope dilution on Element 2 ICP-MS + U isotopic composition by MC-TIMS	Isotope dilution
Sample amount used for U analysis	1.2 µg done in triplicate	0.4-0.6 µg U	3 mg	500 ng for U isotopic, 5 ng for U IDMS measurement	5 mg, done in duplicate
Thorium analysis					
Measurement technique and instrument type	ICP-MS (Element XR)	Peak jumping on secondary electron multiplier (229-230), NuPlasma MC-ICPMS	Ion Counting TIMS- Isotopx Isoprobe T	Isotope dilution on Element 2	ICP-MS (Element2)
Thorium chemical separation method	Ion chromatography (AG1X8), single step	Three step: anion exchange, TEVA extraction, anion exchange	Ion Chromatography (Lewatit MP5080)	Anion exchange x 3 (2 8M HNO3 columns then 1- 9M HCl column)	Extraction chromatography (TEVA), single step
^{230}Th quantification method	Isotope dilution	Isotope dilution	Isotope Dilution	Isotope dilution	Isotope dilution
Standards (calibrants) applied, manufacturer	^{229}Th (AEA Technology)	NBL U010 used for mass bias correction.	NBL ^{229}Th	NIST SRM 4342A ^{230}Th radioactivity solution	Custom-made natural ^{232}Th (certified as weight fraction (Spex Certiprep Inc.)
Sample amount used for Th separation	1.2 µg done in triplicate	2.25 to 4.52 milligram U.	27 mg	1-3 mg, three replicates of each sample except natural U sample.	1 mg, three replicates are done
Mass bias/mass fractionation factor for Th measurement (if applied)	Exponential law correction with IRMM183 (U standard) in bracketing	0.99309 (^{230}Th/^{229}Th) determined from U standards during analytical session.	None applied as not enough data to quantify	NBL CRM-U010 measured by ICP-MS	Using uranium with CRM U010
Detector efficiency/gain measurement for Th	None (single collector ICP-MS)	N/A – peak jumping on same detector.		None	None (single collector ICP-MS)
Abundance sensitivity measurement (if applied)	None measurement of ^{229}Th/^{230}Th; no significant amount of ^{232}Th	None.	Not applied. WARP used	Measured ^{236}U in NIST U-960 (natural U) as a monitor of peak tailing. No correction applied. Measured ^{232}Th signals < 1e6 cps for all samples, natural U samples with comparable ^{238}U signals exhibited negligible tailing.	Used on ^{230}Th/^{232}Th ratio with natural uranium with ^{236}U abundance less than 10^{-9}, linear correction
Typical absolute method blank	Below 1 fg	(4-5)×10^6 atoms ^{230}Th	85 fg of ^{230}Th	10-30 fg ^{230}Th	30 fg of ^{230}Th
Quality control sample used	IRMM-184 (U standard)	Table Mountain Latite, secular equilibrium standard for spike calibration check.	U-630 U and Th Fractions	IRMM-035	IRMM-035

Table II. Age dating calculation procedures of the participating laboratories

Age calculation					
^{234}U half-life used	245 250 ± 490 years (k=2) (Cheng *et al*.,2000 [5])	245250 ± 490 years (Cheng *et al*., 2000 [5])	245500 ± 545 (k=1), from IAEA Live Chart	245,250 ± 490 years at 2σ (Cheng *et al*., 2000 [5])	245500 ± 600 (k=1), from Decay Data Evaluation Project (DDEP) [6]
^{230}Th half-life used	75690 ± 230 years (k=2) (Cheng *et al*., 2000 [5])	75690 ± 230 years (Cheng *et al*., 2000 [5])	75400 ± 300 (k=1), from IAEA Live Chart	75690 ± 230 years at 2σ (Cheng *et al*., 2000 [5])	75380 ± 300 (k=1), from Decay Data Evaluation Project (DDEP) [6]
Quality control sample used	NBS100	None	U 630 from NBL	NBL CRM-125A and NBL CRM-U630	Self-prepared completely separated U with known production date
Software used for calculation	Excel spread sheet	Excel	GUM Workbench Pro	Excel based LANL developed software	GUM Workbench
Approach used for uncertainty calculation	Error propagation	BIPM Guide		Estimates of uncertainty are standard deviations on internal independent observations propagated in quadrature with a coverage factor of two	BIPM Guide
Major uncertainty components	^{229}Th concentration of the tracer and counting statistic of ^{229}Th and ^{230}Th.	1) ^{230}Th measurement (^{229}Th spike calibration – Th standard uncertainty) 2) ^{234}U measurement (^{233}U spike calibration) 3) ^{234}U half-life 4) Mass bias corrections	Measured ^{229}Th/^{230}Th ratio, ^{229}Th and ^{233}U concentration of the standard.	Measured ^{230}Th/^{229}Th ratio, ^{230}Th and ^{233}U concentration of isotope dilution standards, mass bias correction factors (NBL CRM U-010)	Measured ^{230}Th/^{230}Th ratio, ^{232}Th and ^{233}U concentration of the standards, mass bias correction factors

4. Conclusions

Based on the results we can conclude that the production methodology is a valid approach to obtain a measureable and fit-for-purpose uranium age dating reference material. The average reported production date results are in good agreement with the known production date. The reported individual laboratory values for the HEU sample (containing higher amounts of ^{230}Th) are in agreement with one another within measurement uncertainty. However, for the natural uranium and LEU samples more pronounced differences could be observed. This reflects the enormous challenges associated with age dating of such young material, particularly when the sample size is fairly small. Thus, further efforts are required to improve existing methodologies for the lowest enriched and/or most recently-produced materials.

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First Certified Uranium Reference Material for the Production Date in Nuclear Forensics

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Abstract. In order to support research in Nuclear Forensics, the European Commission - Joint Research Centre Institute for Reference Materials and Measurements in Geel (IRMM, Belgium) and the EC-JRC Institute for Transuranium Elements in Karlsruhe (ITU, Germany) joined efforts to produce the first ever uranium reference material certified for the production date. IRMM-1000 has been prepared from a low-enriched uranium solution after complete separation of thorium decay products at a well-known time. Such a CRM is indispensable to establish the accurate age of a nuclear material using validated mass spectrometric or radiometric methods. This paper describes the preparation of IRMM-1000 and first steps towards the certification of this reference material, as certified for the production date based on the ^{230}Th/^{234}U radiochronometer. The IRMM-1000 was produced in compliance with ISO Guide 34 and will be available beginning of 2015 in units of two sizes, 20 mg for mass spectrometric methods and 50 mg for radiometric methods.

1. Introduction

Nuclear forensics is a relatively young science, which develops and applies thorough, interpretative and comparative (radio-) analytical methodologies to investigate the origin and intended use of nuclear or other radioactive material intercepted from illicit trafficking. The parameters to be investigated are inherent to the material and range from isotopic composition, microstructure, chemical impurities to decay products [1-3].

Among these parameters, the elapsed time since the production of the material, commonly referred to as the "age" of the material, is measured for nuclear materials. Indeed, during its production, the nuclear material is chemically purified from impurities, which includes the removal of radioactive decay products or daughter nuclides (typically decay products from U and Pu for nuclear materials), thereby "zeroing" the initial amount of daughter nuclides in the nuclear material at the time of separation. Therefore, assuming that the parent–daughter separation was complete and allowing the ingrowth of the daughter nuclides in the sample, the elapsed time since the last separation (i.e. the age of the material) can be determined by measuring the parent-daughter ratio later in the sample, according to the equations of radioactive decay [4-5].

Unlike other characteristic parameters, this age of the material- i.e. the time elapsed since the last chemical separation of the daughter nuclides from the mother radionuclide - does not require comparison samples or reference data for interpretation. It is a self-explaining parameter and supports without ambiguity the identification of the origin of unknown material or helps to verify the source of intercepted nuclear material. However, up to now, no certified reference material exists for validation of measurement procedures to determine accurately the age or the production date of a nuclear material. "Age determination" has been based so far on historical data, archives and on the determination of the aforementioned combined parameters for the characterisation of nuclear material.

As a consequence, the European Commission - Joint Research Centre Institute for Reference Materials and Measurements, IRMM in Geel (Belgium) and the EC-JRC Institute for Transuranium Elements, ITU in Karlsruhe (Germany) joined efforts to produce the first ever uranium reference material certified for the production date (IRMM-1000) to answer the emerging need expressed by communities involved in national or international nuclear forensics, security and safeguards programmes for such a reference material [2-3]. Reference materials are a prerequisite for method validation. Such validated methods in combination with correct propagation of uncertainties are required when characterising intercepted nuclear material, establish its origin, and identify perpetrators and their network as well as providing evidence to bring them to justice [6].

Two parent/daughter pairs are generally used to determine the age of a highly enriched uranium material: ^{234}U/^{230}Th and ^{235}U/^{231}Pa [7-8]. However, the lack of a suitable isotopic tracer and the challenging processing currently prevent a broader application of the ^{235}U/^{231}Pa isotope ratio as an efficient chronometer for U-age dating. Another constraint on the use of these radiochronometers is the low concentration of daughter products, and therefore it requires a very sensitive measurement technique such as Thermal Ionisation Mass Spectrometry (TIMS) or High-Resolution Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [7-8].

In this paper, we describe first the production of this reference material from low-enriched uranium after the complete separation of the ^{230}Th decay product from its mother nuclide ^{234}U, thereby using the ^{234}U/^{230}Th as radiochronometer for the determination of the production date. Then, we present the characterisation and homogeneity study carried out according to ISO Guide 34 and ISO 17025 to establish the reference value (i.e. the production date) and its uncertainty (according to ISO/IEC Guide 98-3) towards final certification and distribution as IRMM-1000.

2. Principle of uranium age-dating

The age of a uranium material can be calculated from the ratio of the measured ^{230}Th and ^{234}U amount contents. Consequently, for the confirmation and homogeneity studies carried out in the context of the certification of the IRMM-1000, as presented in the next sections, the 'target value' was the age of the material estimated from the measurements of the thorium and uranium amount contents in the uranium reference material at a certain time.

The method used to determine the two concentrations is based on Isotope Dilution Mass Spectrometry (IDMS). In IDMS, a known amount of an isotope (ideally not present in the sample) of the element of interest, called spike or tracer, is introduced in the sample and the ratio of the blend is then measured [9]. Therefore, for the ^{230}Th determination a ^{232}Th spike was used and for ^{234}U, a ^{233}U spike was added to the uranium fractions.

The simplified IDMS equation used to calculate the amount content of the analyte in the sample is then expressed as follows:

$$C(Analyte, sample, X) = \frac{(R_Y - R_B)}{(R_B - R_X)} \times \frac{m_Y}{m_X} \times R_X \times C(Spike, Y)$$

Equation 1

Where R_X is the amount ratio in the unknown sample, R_Y the amount ratio in the spike, R_B the amount ratio in the blend (spiked sample), m_X and m_Y are respectively the masses (in g) of unknown sample and of spike used for the measurement and C (Spike, Y) is the amount content of the spike.

That, for instance, gives the following equation for the ^{230}Th determination, with R_X, R_Y, R_B equal to the amount ratio $n(^{230}\mathrm{Th})/n(^{232}\mathrm{Th})$ in the sample, spike and blend respectively:

$$\left(C^{230}Th\right)_X = \frac{\left(R_Y - R_B\right)}{\left(R_B - R_X\right)} \times \frac{m_Y}{m_X} \times R_X \times \left(C^{232}Th\right)_Y$$ **Equation 2**

Note that to determine the production date/time of last purification of the daughter radionuclide from the parent nuclide, the following assumptions are made: firstly, that there is disequilibrium between the two radionuclides, secondly that the daughter nuclides have been completely removed after the last separation (as assessed by the separation factor) and thirdly, a closed system is assumed with a constant content of the parent nuclide (i.e. no variation in the ^{234}U content in the time frame of the analysis). Therefore, based on these assumptions the equations of the radioactive decay can be simplified and the age can be then determined using the measured amount ratio of $n(^{230}\mathrm{Th})/n(^{234}\mathrm{U})$ in the sample and the following equation [8, 10]:

$$t = \frac{1}{\lambda^{234}U - \lambda^{230}Th} \times \ln\left(1 - \frac{n(^{230}Th)}{n(^{234}U)} \times \frac{\lambda^{230}Th - \lambda^{234}U}{\lambda^{234}U}\right)$$ **Equation 3**

where t is the age of the uranium sample (in years), λ^{234}U and λ^{230}Th are the respective decay constants of ^{234}U and ^{230}Th based on their half-lives ($T_{1/2}$= 245.5 (1.2)·10^3 a and $T_{1/2}$= 75.38 (0.3) ·10^3 a, k = 2, respectively [11]) with $\lambda = \ln 2/T_{1/2}$.

The amount contents of Th and U and the final age are traceable to the SI and their combined standard uncertainties were determined by identifying and quantifying the sources of uncertainties for IDMS according to the ISO/BIPM Guide to the Expression of Uncertainty in Measurement (GUM).

3. Selection of material, preparation and characterisation

The uranium age dating reference material IRMM-1000 was prepared from a mixture of low-enriched uranium dioxide pellets of three different origin: one natural uranium (from Sweden) and two slightly enriched uranium (at ~ 6% from Kazakhstan and at ~ 3% from Germany), resulting in a relative mass fraction $m(^{235}\mathrm{U})/m(\mathrm{U})$ of 3.6% in the base material. The mother solution used for the separation contained about 20 g of uranium in 3 M HNO_3, from which an aliquot containing about 6 gram of uranium was used to produce the reference material.

Most of the instrumental methods and analytical procedures for the preparation and purification of a uranium reference material (using TEVA resin) and associated γ- and ICP-MS measurements have been fully described in [8] for a (highly enriched) uranium-based radiochronometry reference material. Therefore, the methodology is only briefly described here and the preparation steps and measurements are highlighted when different from the method used in [8], hence relevant for the production of the IRMM-1000.

Note that one chemical separation of the uranium material requires a full day of laboratory work from the evaporation of the sample, subsequent dissolution and weighing, the chromatography to separate Th from U with intermediate γ-spectrometric measurements of the recovered fractions, and finally evaporation of the sample [8].

The separation of the thorium from the slightly enriched uranium bulk matrix was done by extraction chromatographic separation applying TEVA resin, in a "sandwiched-column" containing silica-gel, thereby allowing as well the protactinium separation from the uranium material. However, the certified production date of IRMM-1000 has been established after complete separation of thorium decay products, there is no guaranteed complete separation from the Pa daughter. This means that when using the Pa/U chronometer, the certified reference value of IRMM-1000 can be used as indicative value.

The separation was carried out in four consecutive separation steps, and for each step the solution was divided into 16 aliquots and loaded on 16 separate extraction chromatography columns (**Fig.1**).

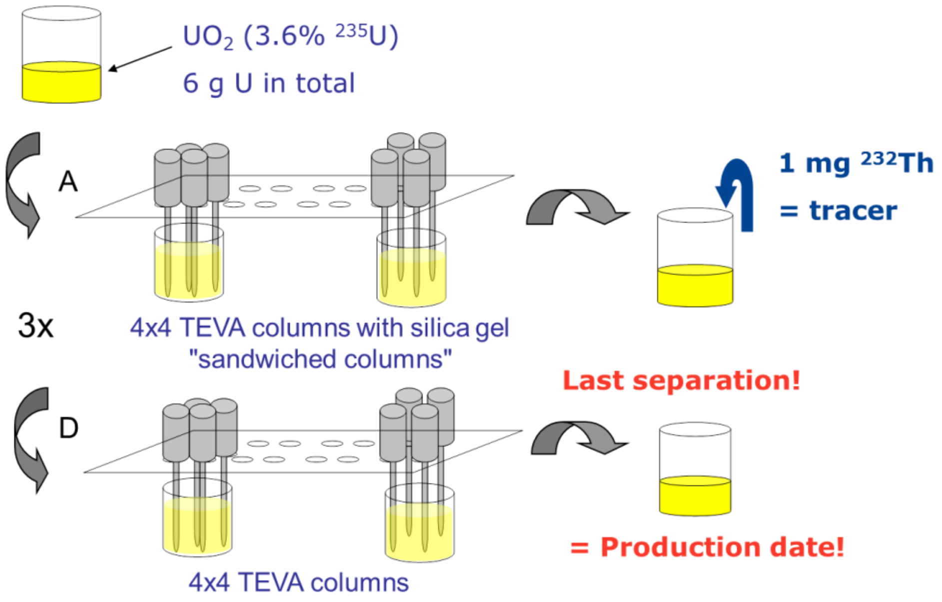

Figure 1 Four-step chemical separation using TEVA resin of the thorium from the uranium base material to ensure efficient Th removal from the uranium matrix (U/Th separation factor > 10^7).

In order to ensure homogeneity of the sample throughout the whole process, the uranium eluates from the sixteen columns were combined after each separation step, measured by γ-spectrometry and evaporated overnight.

As the final separation factor and uranium recovery are very important to determine the thorium/uranium separation efficiency (i.e. the completeness of the U/Th separation) and quantify the effective recovery of uranium, measurements of the recovered U fractions (four batches A, B, C and D) were performed using γ-spectrometry between each of the chemical separation using the well-resolved γ-peaks of the short-lived ^{234}Th ($T_{1/2}$= 24.1 days) and the ^{235}U (at 185.7 keV) respectively [7].

Moreover, a natural ^{232}Th tracer (1 mg of a Custom Claritas Standard with a total Th concentration of 1000 ± 5µg/g, k=2) was added to the solution before the second chemical separation in order to determine later on by ICP-MS the residual thorium in the reference material after the last chemical separation **(Fig.1**). Then, the procedure of chromatography, weighing and γ–spectrometry was repeated as described above.

The fourth and last chemical separation corresponding to the "production date", i.e. the reference value of the material, was carefully recorded as dd/mm/yyyy and time. After this separation, the final purified solution was aliquoted into cleaned PFA vials: altogether 108 units containing about 20 mg of uranium and 53 units containing about 50 mg of uranium were prepared. The aliquots were evaporated and kept in solid form in the capped and sealed vials.

Table 1 summarises the results obtained from the different γ-measurements (between each separation and after the final separation) for the uranium recoveries using the ^{235}U and separation factors using the ^{234}Th. These results (**Table 1**) proved that the 'target value' was reached, with an overall U recovery of 83.7% ± 0.3% (relative standard uncertainty) and a cumulative U/Th separation factor (i.e resulting from the four successive separations) better than $2.77 \times 10^7 \pm 0.93 \times 10^7$ (standard uncertainty) attesting of the effective/quantitative recovery of uranium in the final reference material and of the efficiency of the separation of Th from the uranium material.

The completeness of the removal of thorium from the initial uranium material was further confirmed by the measurements of the Th amount content and isotope ratio by mass spectrometry using ICP-MS and the ^{232}Th tracer that had been added to the uranium sample after the first separation. Based on this measurement, the final (cumulative) U/Th separation factor was found to be higher than 1.81×10^7, but still fulfilling the 'target value' with thorium in the purified solution being less than 0.01 µg/g uranium.

Note that other impurities in the final U material were measured as well by the ITU Analytical Services but were identified to be insignificant for the determination of the age.

Table 1 Summary of the uranium recoveries (based on γ-peak of ^{235}U) and separation factors based on γ-peak of ^{234}Th and on ICP-MS measurements of the total Th (traced with ^{232}Th) for each of the four chemical separations and total separation factors (cumulative, i.e. from steps 1 to 4). Reported uncertainties are standard uncertainties.

Separation steps	U recoveries (^{235}U)	SF from Th/U	SF from total Th
1	95.0 ± 0.4 %	714 ± 126	714 ± 126[a]
2	94.9 ± 0.4 %	22 ± 4	*25366*
3	96.2 ± 0.5 %	24 ± 4	
4	94.4 ± 0.4 %	75 ± 12	
Cumulative	**83.7 ± 0.3 %**	**$2.8 \times 10^7 \pm 0.9 \times 10^7$**	**1.8×10^7**

[a] Note that for the first step no separation factor can be calculated based on ^{232}Th since it is only introduced in the sample after the first step. It is therefore assumed to be equal to the separation factor based on the γ-determination of the U/Th ratio.

Based on the cumulative U/Th separation factor (**Table 1**) and the known initial $n(^{230}\text{Th})/n(^{234}\text{U})$ amount ratio in the uranium base material, any residual amount of ^{230}Th present after the last chemical separation can be estimated. This can be done from measurements by ICP-MS of the $n(^{230}\text{Th})/n(^{234}\text{U})$ amount ratio in the purified uranium material directly after the last separation, but the amount of ^{230}Th is often too close to the detection limit to be accurately measured. Therefore, by applying **Eq. 3**, the residual ^{230}Th in the reference material can be expressed as a time and was found to be less than 1.3 hours in IRMM-1000.

Finally, the uncertainty on the production date of our uranium age-dating reference material includes the uncertainty on the date of the last chemical separation (i.e. the time interval bracketing the exact time of the last elution of Th from the U material) and the uncertainty coming from the residual thorium measured in the final purified uranium material. The elution of thorium lasting about 3 hours, the uncertainty on the last elution time of the Th from the U material was estimated to be 1.5 hours in order to account for the whole thorium elution time. Finally, the combined standard uncertainty inherent to the production of the reference material was estimated to be 0.08 days (k=1).

4. Confirmation measurements of the certified reference value

After ingrowth of Th in the U reference material confirmation measurements were carried out following ISO Guide 34 to assess if the measured age corresponded to the known production date. This confirmation step consisted of the analysis of 6 randomly selected 20 mg out of the 161 IRMM-1000 units. The 6 randomly selected 20 mg units (referred as A, B, C, D, E, F) were first dissolved. The expected U concentration in these samples was ~ 10 mg/ml of total U and should correspond to an amount of ~ 1 pg of ^{230}Th per sample 7 months after the production of IRMM-1000. Subsequently, aliquots were prepared gravimetrically and by dilutions from the 2 ml dissolved samples in order to measure the U isotopic composition using TIMS, the U concentrations by ICP-MS (and the thorium isotope ratios and concentrations with ICP-MS. For the isotope dilution measurements, a ^{233}U spike was used to determine the uranium amount content, whereas two different natural Th spikes (^{232}Th) were used to determine the thorium amount content [8]. With each of the 6 units, a procedural blank (using 2 ml concentrated HNO_3) and an unspiked sample were prepared as well. Procedural blanks were measured before each measurement series and amount contents in the samples were corrected for the respective bracketing blanks. The unspiked samples were measured with each corresponding measurement series in order to establish $R_{X,}$ in the IDMS equation (**Eq. 2**).

After evaporation, the thorium and uranium fractions were recovered in 4% HNO_3 to be measured with the double-focusing magnetic sector ICP-MS, Element 2. The detailed mass spectrometric parameters and corrections applied for the measurements of the $n(^{230}Th)/n(^{232}Th)$ and $n(^{234}U)/n(^{233}U)$ amount ratios are described in [8].

Based on the ^{230}Th and ^{234}U amount contents determined by IDMS applying **Eq. 1-3**, the ages from the six selected units and their associated expanded uncertainties (k=2) were calculated according to ISO/BIPM using the GUM Workbench Software [12]. The calculated age values reported in **Fig.2** were then compared with the known elapsed time between the production of the reference material and the last chemical separation carried out for this study. The date of the separation of the first batch A was taken as the reference date hereafter referred to as the "known age". Since the reference value, i.e. the exact production date of IRMM-1000, cannot be revealed yet, the age values, calculated in days, are presented in this study normalised to the known age (**Fig.2**).

A good agreement of the calculated ages per single units, the average age and the known age was established (**Fig.2**); successfully confirming the completeness of the separation of the thorium from the uranium during the production of the uranium reference material. Note that the associated uncertainty of the known age (**Fig.2**) combines the uncertainty on the production date as given in the previous section, i.e. 0.08 days (k=1), and the uncertainty of the reference time of the Th/U separation for this study and is therefore of 0.21 days (k=2). Finally, the uncertainties on the calculated ages take into account the performed replicate measurements (standard deviation), thereby resulting in an expanded uncertainty of 4.6 days (k=2) on the calculated average age.

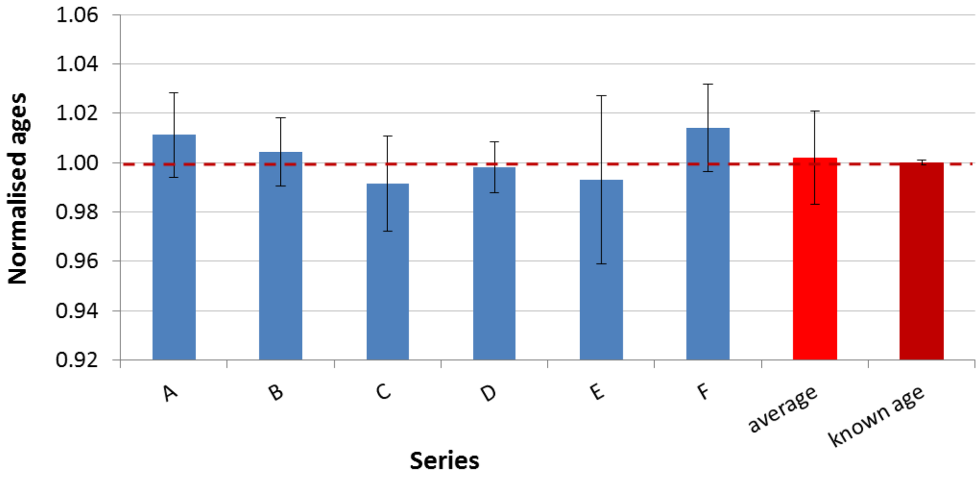

Figure 2 Final ages obtained for the 6 units selected for the characterisation study (blue), their average (red) and the known age based on the reference value (burgundy) with their expanded uncertainties (k=2).The age values are here normalised to the known age.

5. Homogeneity study

The homogeneity study took place about 14 months after the production of the reference material. For the homogeneity test, 10 units (5 of 20 mg and 5 of 50 mg uranium units) were randomly selected among the whole batch of IRMM-1000. The 20 mg uranium samples were referenced from A to E and the 50 mg uranium samples from F to H.

The randomly selected units of 20 mg and 50 mg uranium, in dry form, were first dissolved and subsequently the same measurement procedures were applied as for the confirmation measurements described in the previous section. All together 10 units/series of 3 replicates were prepared together with an unspiked sample with each series and 8 procedural blanks, resulting in a total number of 48 samples to be measured for the homogeneity study.

The chemical separations were performed for each aliquot at consecutive dates. Therefore, the separation for the first series of samples is considered as the reference date for the comparison of the final results. The thorium fractions were measured with HR-ICP-MS in a randomised order as follows: I, D, B, J, C, H, F, G, A, E.

Applying **Eq 1-3** on the determined ^{230}Th and ^{234}U amount contents, the 30 ages for the selected units and their associated expanded uncertainties (k=2) were calculated according to ISO/BIPM using the GUM Workbench Software [12]. The results from the homogeneity study for the calculated ages per selected unit (10 values) are presented in **Fig. 3** in the chronological order of the ICP-MS measurements. The overlap of the average age value with the known age, as well as with all the individual age values confirmed the homogeneity of the complete IRMM-1000 batch.

The final evaluation of the homogeneity was carried out using an ANOVA Single Factor analysis (analysis of variance) on the 30 age values (3 Th replicates x 10 units). No trend was observed in the results related to the chronological order of the analysis and measurements (**Fig.3**).

The ANOVA analysis allows the separation of the method variation (s_{wb}) from the experimental averages over the replicates measured in one unit to obtain an estimation for the real variation between units (s_{bb}). The relative standard uncertainty for method repeatability (s_{wb}) was 0.43%. The absolute expanded uncertainty resulting from the homogeneity study was 7.8 days (k=2). This uncertainty will be the major component of the expanded uncertainty of the reference value of IRMM-1000.

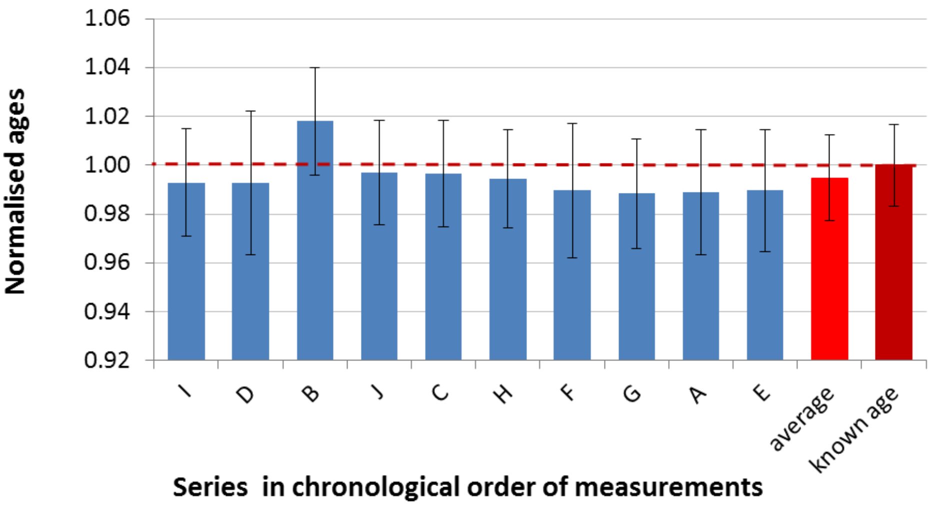

Figure 3 Calculated ages obtained for the 10 units selected for the homogeneity study (blue), their average (red) and the known age based on the reference value (burgundy) with their expanded uncertainties (k=2). The age values are here normalised to the known age.

6. Conclusion

Combining the complementary capabilities of two JRC institutes enables the conception, preparation and certification of the first ever uranium reference material certified for its production date. The release of this new reference material, IRMM-1000 responds to a demand expressed by the Nuclear Forensics International Technical Working Group (ITWG) and laboratories in the field. The results from the verification and homogeneity studies both confirmed the completeness of the chemical separation of thorium from uranium in IRMM-1000, and were fully consistent with the date of last chemical separation. Moreover, these two studies demonstrated the accurate characterisation of this material and the reference value as it will be given on the reference material certificate in dd/mm/yyyy ± days (k=2).

This new reference material is certified for the production date in uranium age-dating and can be used in applications such as nuclear forensics, security and safeguards using the ^{234}U/^{230}Th parent/daughter pair. Prior to the release of IRMM-1000, first the long-term stability study needs to be finalised during summer 2014 and secondly the result reporting for the Regular European Inter-laboratory Measurement Evaluation Programme (REIMEP-22) called "U Age Dating - Determination of the production date of a uranium certified test sample" and based on this material needs to be closed [13]. The certified reference material IRMM-1000 should be available in 2015.

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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 **Error! Reference source not found.**] 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 [1]. 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 [2], and a more thorough implementation of GUM (the Guide to the expression of Uncertainty in Measurement) [3] utilizing the recommendations by Bürger et al.[4].

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 [1], 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.

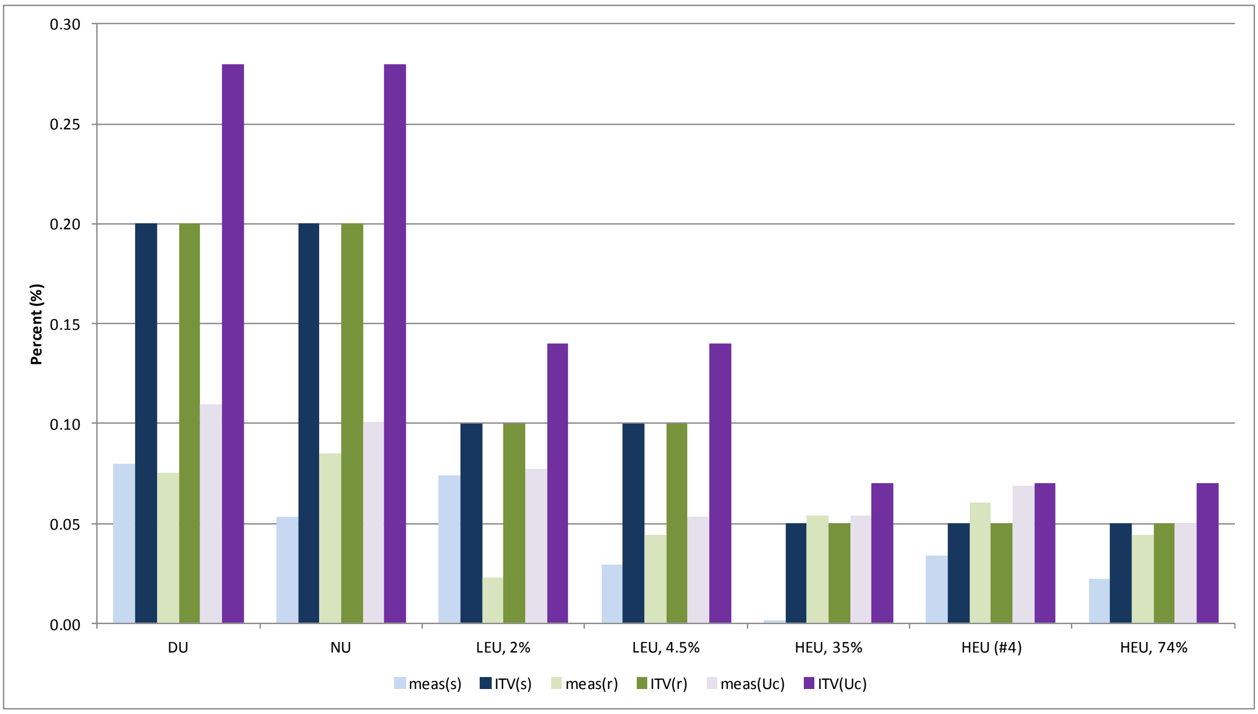

FIG. 1. AECL Measured U-235/U-238 Uncertainty vs. International Target Values (2010) Uranium Samples, 2013 IAEA Round Robin

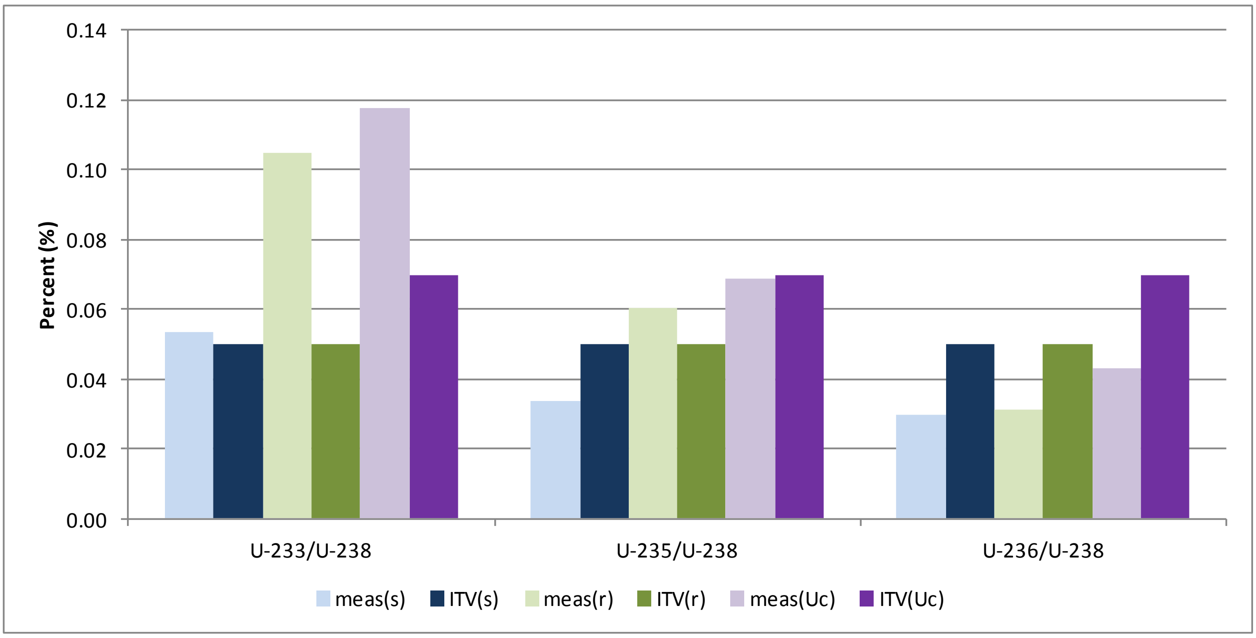

FIG. 2. Uncertainties for Simulated U Isotope Dilution (ratio ~1) HEU #4, 2013 IAEA Round Robin

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.

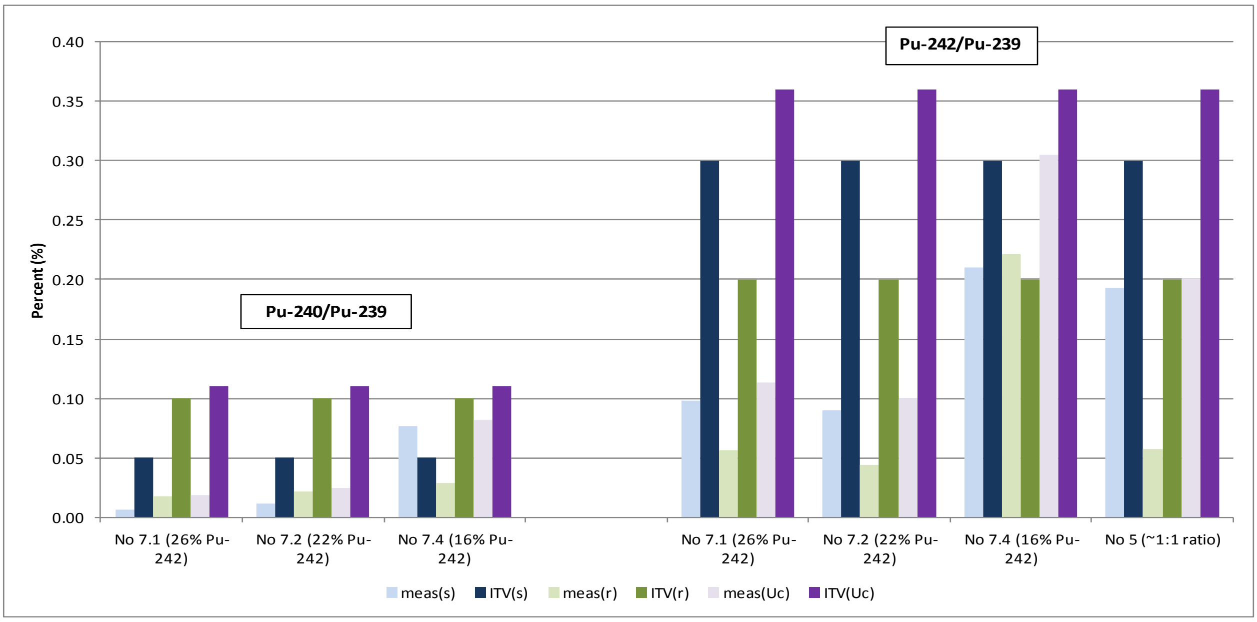

FIG. 3. AECL Measured Uncertainty vs. International Target Values (2010) Plutonium Samples, 2013 IAEA Round Robin

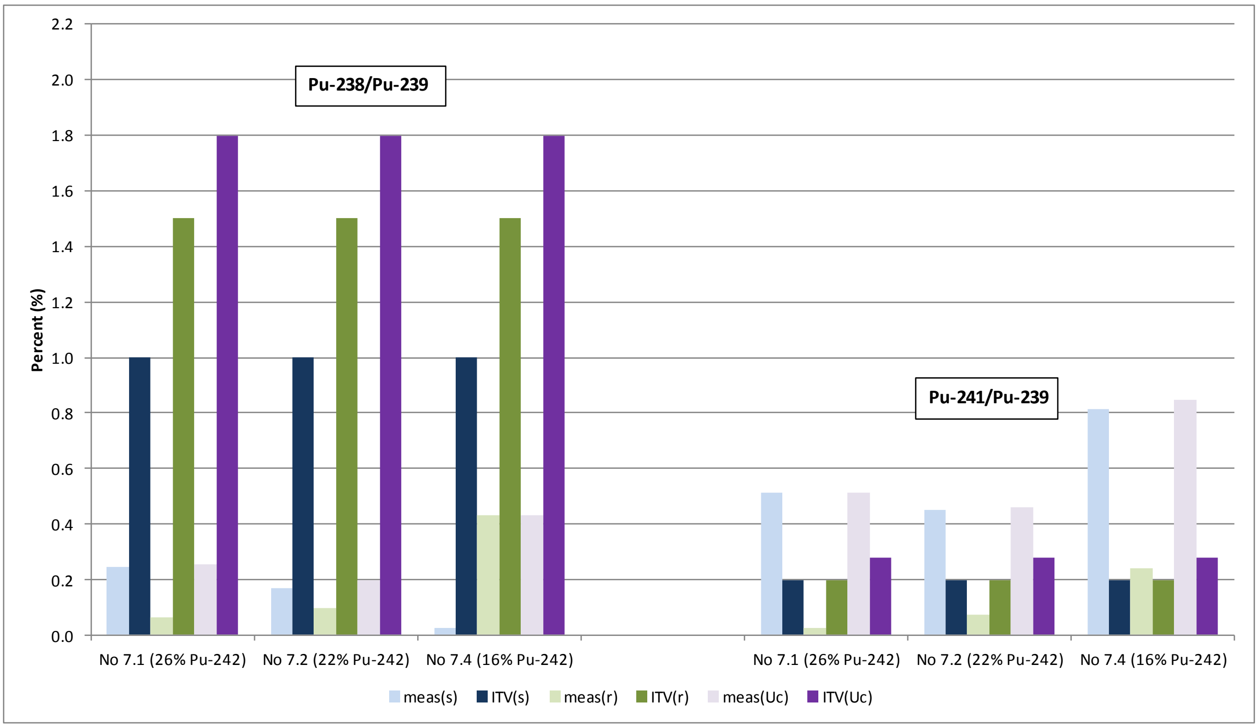

FIG. 4. AECL Measured Uncertainty vs. International Target Values (2010) Plutonium Samples, 2013 IAEA Round Robin

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 [1] 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.

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