

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. Pycnometry, 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 Méthodes d'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

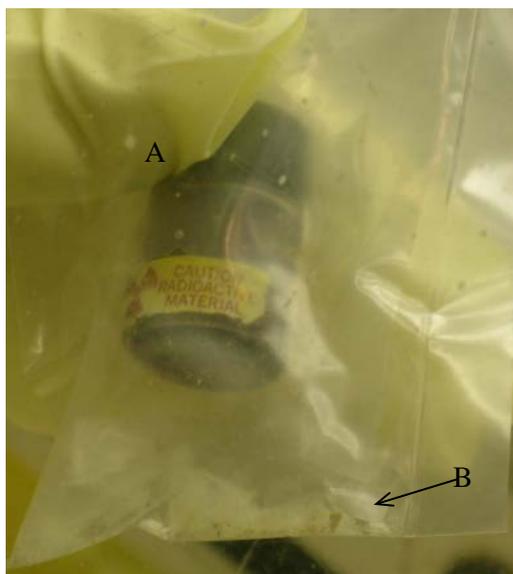
materials in conjunction with NBL and NIST; (4) demonstrated excellence in providing high quality measurements; and (5) a robust QA program.

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 ($\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), 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 preceded 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
<i>LANL uncertainties</i>	<i>0.001</i>	<i>0.008</i>	<i>0.008</i>	<i>0.0008</i>	<i>0.002</i>
Certified Value, (decay corrected)	0.228	78.703	19.040	0.786	1.244
<i>Certificate uncertainties, 95% confidence interval</i>	<i>0.007</i>	<i>0.015</i>	<i>0.015</i>	<i>0.005</i>	<i>0.003</i>
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 °C and 650 °C respectively. For relatively pure PuO₂ 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 <ul style="list-style-type: none"> · 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.

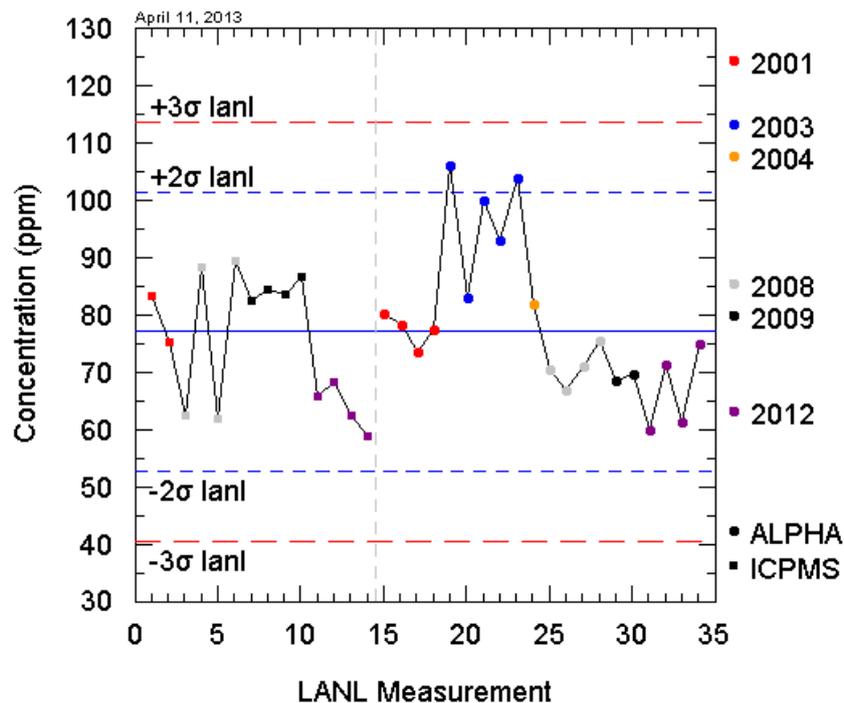
3.3 Performance assessment protocols

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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