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REFERENCE MATERIALS FOR TRACE ACTINIDE CONTENT IN PLUTONIUM OXIDE

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ABSTRACT

Nuclear forensic analyses of plutonium (Pu) materials encountered outside nuclear safeguards control can include chemical composition, isotopic composition, and the concentration of various contaminants. Results from these measurements provide insights into how and when the Pu was produced and help place limits on potential uses and provenance of the material. As part of a program to enhance nuclear forensic analytical capabilities, the United States Department of Homeland Security sponsored the development of nuclear forensic reference materials, including plutonium oxides, NFRM Pu-1 and NFRM Pu-2. These were prepared and characterized for americium (Am), neptunium (Np) and uranium (U) occurring as trace constituents in Pu. The starting material for these reference materials were an oxidized Pu metal (NFRM Pu-1) and a Pu oxalate precipitate (NFRM Pu-2). Both were calcined (≤ 750 °C) and then dispensed to individual sample units comprised of 200 mg of oxide in robust quartz glass vials. Characterization was performed on randomly selected units by controlled potential coulometry for Pu assay and thermal ionization mass spectrometry (TIMS) for isotopic composition. Characterization of Am mass fractions was performed by isotope dilution mass spectrometry (IDMS). Np mass fractions were measured by externally calibrated inductively couple plasma mass spectrometry (ICP-MS). U mass fraction measurements were by IDMS and isotopic composition analyses were by TIMS. Characterized attributes are provided for a reference date of 01 January 2019. Both materials have a Pu-239 isotope amount fraction of greater than 93% and are nominally PuO_2 with a Pu mass fraction of approximately 0.88 g g^{-1}. Mass fractions of trace actinide constituents range from 800 µg g^{-1} for Am to 30 µg g^{-1} for Np. The trace constituents are homogenously distributed within the Pu oxide material. Monoisotopic Am-241 is consistent with ingrowth from decay of Pu-241. U-234, U-235, and U-236 are primarily ingrown from decay of Pu isotopes but a significant proportion of measured U-238 appears to be due to process related contamination of the Pu oxide or analysis blank. Monoisotopic Np-237 also appears be a combination of ingrowth from Am-241 since purification and a homogenously distributed contaminant in the Pu oxide.

INTRODUCTION

Special nuclear materials, such as plutonium, have the potential to be used as fissile material for a nuclear device and are, therefore, of particular concern for nuclear safeguards and counter terrorism efforts. Analyses of plutonium encountered outside of nuclear safeguards control can yield important information for law enforcement and non-proliferation efforts by providing insight into

how and when materials were produced and by providing constraints on the intended use and provenance of the materials [1-3]. Analytical reference materials are necessary for method development, method validation, and measurement quality control but standards for trace constituents in plutonium are not commercially available.

The Department of Homeland Security (DHS) Countering Weapons of Mass Destruction Office (CWMD) funded the production and characterization of two Nuclear Forensic Reference Materials (NFRMs) for trace actinide mass fraction (concentration) and isotope-amount ratios (isotopic composition) in plutonium oxide. The target actinide trace elements for the new reference materials are americium, neptunium, and uranium. Production and attribute measurement were performed by Los Alamos National Laboratory (LANL). Lawrence Livermore National Laboratory (LLNL) and Oak Ridge National Laboratory (ORNL) performed additional attribute measurements. The Radioactivity Group within the Radiation Physics Division at the National Institute of Standards and Technology (NIST) collated and evaluated analytical results for the new reference materials.

REFERENCE MATERIAL PREPARATION

Two plutonium oxides (PuO_2) were chosen as stock for the new reference materials. One of the materials, NFRM Pu-1, is an oxidized portion of a plutonium metal rod that was part of the double-electrorefined metal used to create Certified Reference Material (CRM) 126-A plutonium assay and isotopic reference material [4]. The second, NFRM Pu-2, is an oxide created from a set of plutonium solids that were dissolved, purified by anion exchange, and then recovered as a plutonium (III) oxalate precipitate. Based on results from a loss-on-ignition (LOI) study performed by the LANL production facility, the plutonium materials were calcined to temperatures of 750° C and 650° C for the Pu-1 and Pu-2 materials respectively. Heating in air to these temperatures resulted in only 0.2% to 0.3% decrease in mass. Individual units were created from the bulk oxides by transferring approximately 200 mg of PuO_2 to cleaned quartz vials using a benchtop riffler. The vials were then sealed with robust plastic caps and each unit vial was wiped down, labelled, and sealed in mylar sleeves for storage. A total of 160 units were prepared for NFRM Pu-1 and 45 units of NFRM Pu-2.

CHARACTERIZATION ANALYSES

Measurements of the reference materials to establish attribute values (“Characterization” measurements) were primarily performed at LANL on 10 samples of NFRM Pu-1 and 5 samples NFRM Pu-2 that were chosen from throughout the production runs. In addition, 2 samples of each material were transferred to ORNL and to LLNL for analyses to verify the Characterization measurement results (“Verification” measurements). As part of a related project, 2 units of each material were sent to 4 United States Department of Energy laboratories as blind samples for a Methodology Benchmarking Study (MBS) funded by DHS.

Table 1 is a summary of methods for the analyses performed on the NFRM Pu-1 and NFRM Pu-2 materials. The Characterization measurements included Controlled Potential Coulometry (CPC) for plutonium assay, extensive Thermal Ionization Mass Spectrometry (TIMS) analyses for plutonium and uranium isotope amount ratios, Isotope Dilution Mass Spectrometry (IDMS) for uranium and americium mass fraction, and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for neptunium mass fraction. The CPC analyses used relatively large amounts of the plutonium oxide (approximately 100 mg per analysis) so these were performed on 5 of the NFRM Pu-1 samples and

2 of the NFRM Pu-2 samples. All other Characterization measurements were performed on the remaining samples for each material (5 for NFRM Pu-1 and 3 for NFRM Pu-2). Verification analyses were performed on 2 subsamples from each NFRM unit sent to ORNL and LLNL. The measurements for the MBS were performed independently from the reference material project and the results were not used to determine attribute values.

Table 1. Characterization and Verification Measurement Method Summary

Attribute	Laboratory	Method	Equipment	Reference Materials
Pu Mass Fraction	**LANL**	**CPC**	**---**	**Calibration: CRM 126-A**
	LLNL	IDMS	Multi-Collector ICP-MS	Tracer: ^{244}Pu Mass Bias Cal: CRM 137
	ORNL	IDMS	Multi-Collector ICP-MS	Tracer: ^{242}Pu CRM 130 Mass Bias Cal: CRM 137
Pu Isotope Amount Ratios	**LANL**	**Mass Spectrometry**	**Multi-Collector TIMS**	**Mass Bias Cal: CRM 126-A**
	LLNL	Mass Spectrometry α Spectrometry	Multi-Collector ICP-MS Ortec Alpha Ensemble	Mass Bias Cal: CRM 137
	ORNL	Mass Spectrometry α Spectrometry	Multi-Collector ICP-MS Canberra Alpha Analyst	Mass Bias Cal: CRM 137
Am Mass Fraction	LANL	Gamma Spectrometry	Gas Proportional Counter NaI(Tl) Dector	Calibration: NIST Traceable ^{241}Am-doped epoxy tubes.
	LLNL	**IDMS**	**Multi-Collector ICP-MS**	**Tracer: NFRM Am-243** **Mass Bias Cal: CRM U010**
	ORNL	**IDMS**	**Multi-Collector ICP-MS**	**Tracer: NFRM Am-243** **Mass Bias Cal: CRM 137**
Np Mass Fraction	**LANL**	**Mass Spectrometry**	**Quadruple ICP-MS**	**Internal Sensitivity Cal:** **Rh MSRH 10PPM**
	LLNL	Mass Spectrometry	Multi-Collector ICP-MS	Yield Tracer: ^{239}Np Sensitivity: ^{237}Np Working Standard
	ORNL	HPLC to Mass Spectrometry	Quadrupole ICP-MS	Cal: ^{239}Np Internal Std Sensitivity Cal: IPL 1066-39
U Mass Fraction	**LANL**	**IDMS**	**Multi-Collector TIMS**	**Tracer: ^{233}U Working Standard** **Mass Bias Cal: IRMM 199**
	LLNL	IDMS	Multi-Collector ICP-MS	Tracer: ^{233}U Working Standard Mass Bias Cal: CRM U010
	ORNL	IDMS	Multi-Collector ICP-MS	Tracer: ^{233}U CRM 111-A Mass Bias Cal: CRM 900
U Isotope Amount Ratios	**LANL**	**Mass Spectrometry**	**Multi-Collector TIMS**	**Mass Bias Cal: CRM U750**
	LLNL	Mass Spectrometry	Multi-Collector ICP-MS	Mass Bias Cal: CRM U010
	ORNL	Mass Spectrometry	Multi-Collector ICP-MS	Mass Bias Cal: CRM U900

Analysis methods used to determine attribute values for the reference materials are in bold.

Plutonium isotope ratio mass spectrometric analyses were performed on 2 multi-collector mass spectrometers; referred to at LANL as VG3 and VG2, but the U isotopic analysis were only analyzed on the VG3 instrument. The ^{241}Am mass fractions were originally planned to be characterized using gamma spectrometry-based measurements performed at LANL but data analysis (see Discussion section) indicated a high probability that the LANL gamma spectrometry results were systematically biased. As a result, IDMS-based americium measurements performed by

ORNL and LLNL were used to calculate the reference value for ^{241}Am and the LANL data was used to help estimate a data-set variability component for reference value uncertainty models.

ANALYTICAL RESULTS

For this study, results from 7 different measurements data sets (LANL, LLNL, ORNL and 4 Methodology Benchmarking Study data sets) were compared. To use this extensive set of measurement data for establishing reference values and for assessment of measurement variability, it was necessary to decay correct the data to a common reference date. For some nuclides this is a multi-step process that requires calculation of both ingrowth and loss from radioactive decay using equations derived from Bateman [6] and then summing the decay corrected starting mass fraction with one or more sources of ingrown nuclide. The analytical results, presented below, and the following discussion will be based on data that is decay corrected to a date of 01 January 2019.

Plutonium Mass fraction:

The results for the plutonium mass fraction of the NFRM Pu-1 and Pu-2 oxides are (0.87840 ± 0.00090) g g^{-1} and (0.87896 ± 0.00097) g g^{-1}, respectively. The CPC Characterization measurements data is highly repeatable, but IDMS Verification measurements results for both materials indicate mass fraction values that are significantly lower for both NFRM Pu-1 (-0.6 % on average) and NFRM Pu-2 (-0.7 and -1.0 % on average). The uncertainties for the plutonium IDMS measurements, however, are relatively large (≥ 0.5%) and the data show a level of measurement variability that is similar in magnitude to the expanded uncertainties cited by the laboratories.

Plutonium Isotope Amount Ratios:

The plutonium isotope amount ratio analyses of NFRM Pu-1 performed at LANL do not indicate statistically significant sample-to-sample variability at the 95% confidence level but there do appear to be marginal systematic biases between measurement instruments (Figure 1A). The n(^{242}Pu)/n(^{239}Pu) ratios have a particularly well-defined bias between mass spectrometers with the VG3 measurement results being slightly higher than the VG2 results. The Verification measurement data are largely in agreement with the Characterization data (Verification values within uncertainties of Characterization measurements) but statistically significant differences between "data sets" are indicated for most of the isotope amount ratios. The CRM 126-A plutonium metal reference material and the NFRM Pu-1 oxide share a common source material, so decay corrected values for the certified isotopic composition were also compared to the measured value for the oxide.

The distributions of the NFRM Pu-2 isotope amount ratio measurement results are broadly similar to the NFRM Pu-1 results (Figure 1B). Again, the values for Characterization measurements do not indicate sample-to-sample variability at the 95% confidence level, the Verification results are consistent with the Characterization measurements, but there appears to be a well-defined instrumental bias for the n(^{242}Pu)/n(^{239}Pu) ratio results. Also, as observed for NFRM Pu-1, there is a small but statistically significant bias between measurement data sets for both n(^{240}Pu)/n(^{239}Pu) and the n(^{242}Pu)/n(^{239}Pu) ratios.

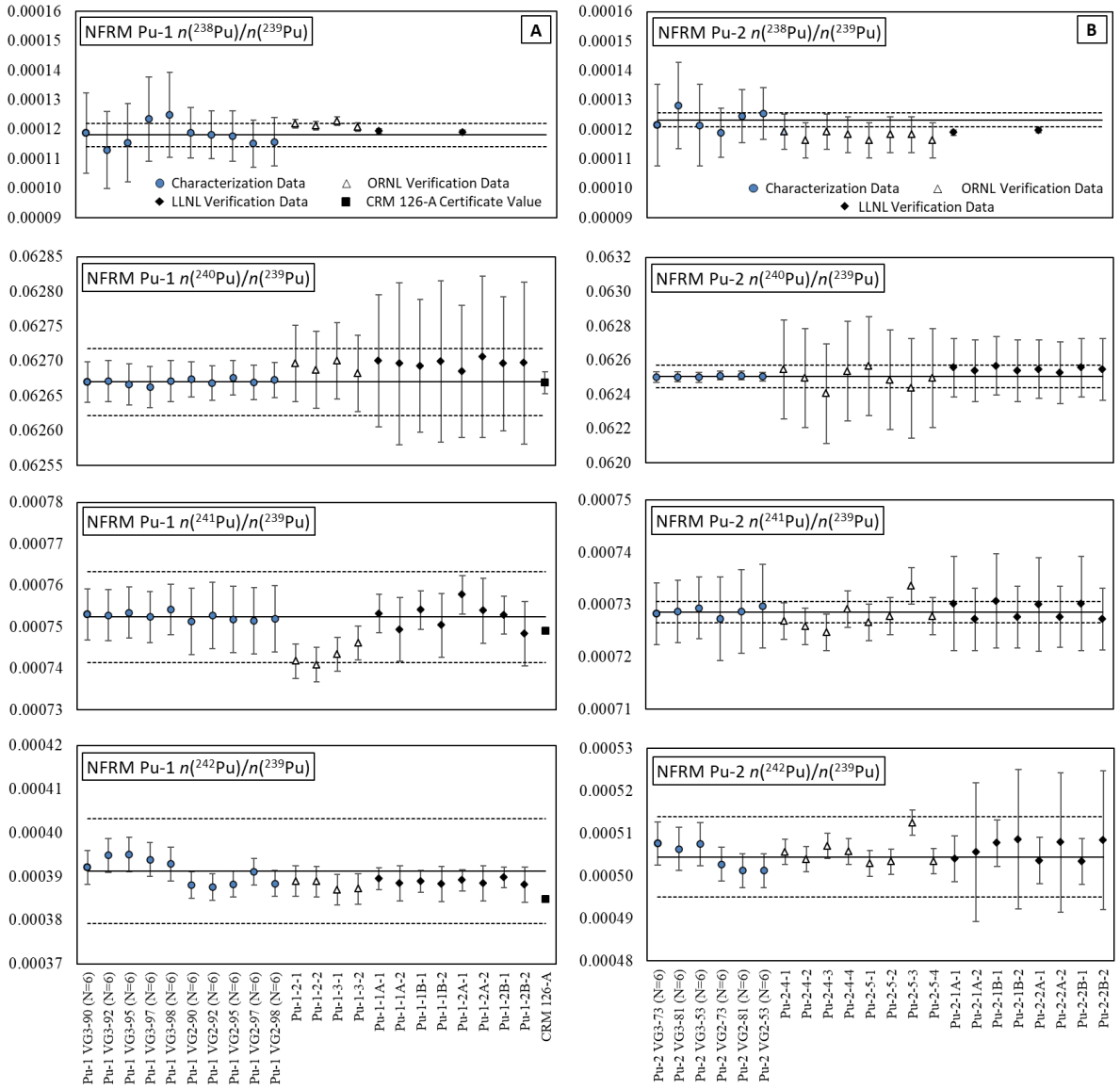


Figure 1. NFRM Pu-1 and NFRM Pu-2 Plutonium Isotope Amount Ratio Data. Uncertainties for data points are expanded uncertainties ($k = 2$) as reported by the analysis laboratories. Reference values for NFRM Pu-1 are shown as solid lines and the expanded uncertainty envelopes are bounded by horizontal lines.

<u>^{241}Am ^{227}Np and U Mass Fraction</u>:

The ^{241}Am mass fraction measurement result are highly consistent within each measurement data set but there are well-defined statistically significant biases between data sets for both NFRM Pu-1 (Figure 2A) and NFRM Pu-2 (Figure 2A). Within uncertainties, the ingrowth corrected ^{241}Am information value from the CRM 126-A certificate is consistent with the NFRM Pu-1 calculated reference value. The ^{237}Np mass fraction data are also highly consistent within measurement data sets but there are statistically significant biases between data sets for both NFRM Pu-1 (Figure 2C) and NFRM Pu-2 (Figure 2D). The ingrowth corrected ^{237}Np information value from the CRM 126-A certificate is slightly higher than the Characterization data but otherwise consistent with the reference value for NFRM Pu-1.

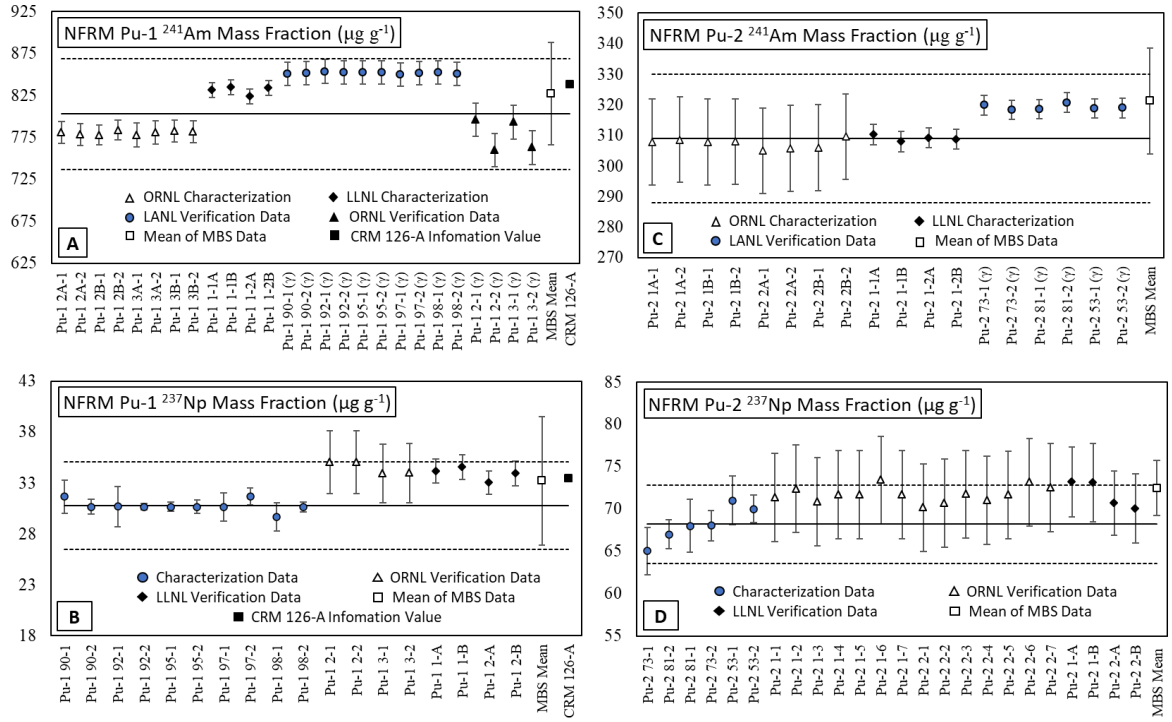
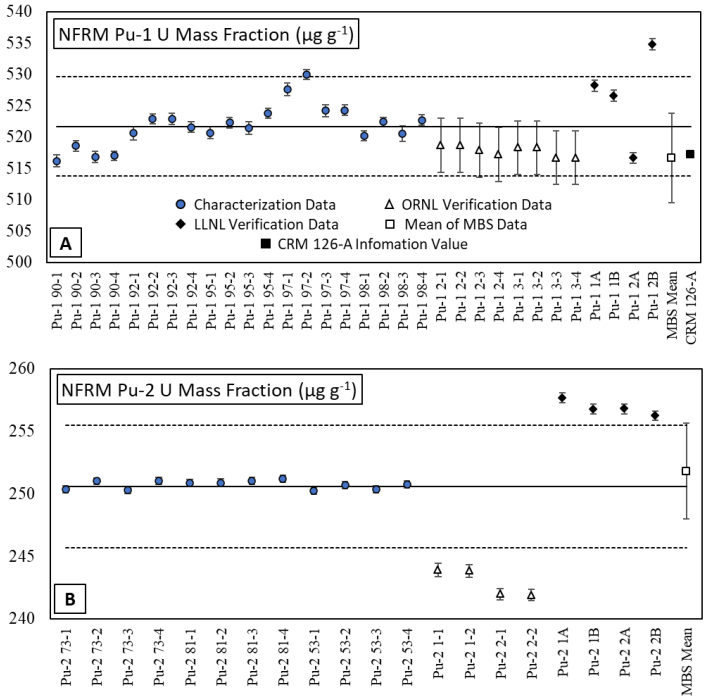


Figure 2. ^{241}Am and ^{237}Np mass fraction measurement data for NFRM Pu-1 and NFRM Pu-2. Uncertainties are expanded uncertainties (k = 2) for decay corrected mass fraction values. Reference values are shown as solid lines and the expanded uncertainty envelope for the reference values is bounded by dashed lines.

Figure 3. Uranium mass fraction measurement data for the NFRM Pu-1 and NFRM Pu-2. Uncertainties for data points are expanded uncertainties (k = 2) for the decay corrected mass fraction values. The calculated reference values are shown as solid horizontal lines and the expanded uncertainty envelope for the reference values is bounded by the dashed horizontal lines.



The measurement results for uranium mass fractions are shown for NFRM Pu-1 in Figure 3A and for NFRM Pu-2 in Figure 3B. The Characterization and Verification measurements indicate greater

variability for uranium relative to the variability observed for plutonium or other trace actinides. The NFRM Pu-1 analyses display a statistically significant sample-to-sample difference in uranium mass fraction that is not observed for the other trace actinide elements in either material. The measurement results for NFRM Pu-1 and Pu-2 show systematic differences between data sets, with NFRM Pu-2 having particularly large differences between the verification laboratories (6% relative difference between ORNL and LLNL verification data). NFRM Pu-1 is generally consistent with the ingrowth-corrected uranium mass fraction value cited in the CRM 126-A certificate.

U Isotope Amount Ratios:

Ingrowth-corrected isotope amount ratio measurement results are shown in Figure 4A for NFRM Pu-1 and Figure 4B Pu-2. The isotope amount ratios for the materials indicate compositions that are consistent with uranium isotopes primarily being plutonium daughter products. The $n(^{234}U)/n(^{235}U)$ and $n(^{236}U)/n(^{235}U)$ isotopic data are internally consistent for the various data sets but the $n(^{238}U)/n(^{235}U)$ data display a statistically significant sample-to-sample bias. A statistically significant variability between data, as observed for other attributes, is also observed in the isotopic data for both materials. Despite these differences, the measurement data sets for the $n(^{234}U)/n(^{235}U)$ and $n(^{236}U)/n(^{235}U)$ ratios are characterized by overlapping measurement uncertainties, indicating a reasonable level of consistency between samples and between data sets. The isotopic data for NFRM Pu-2, however, and the $n(^{238}U)/n(^{235}U)$ isotope amount ratios for NFRM Pu-1 display differences between data sets that are greater than uncertainties cited by the analysis laboratories.

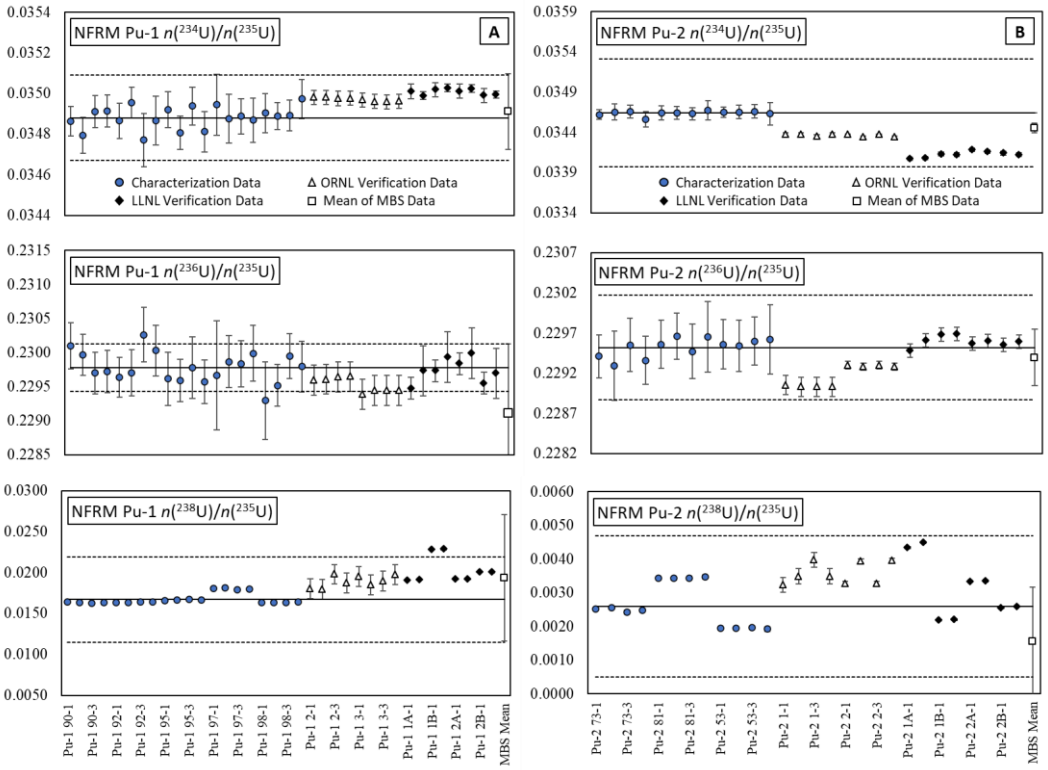


Figure 4. Uranium isotope amount ratio data for NFRM Pu-1 and NFRM Pu-2. Uncertainties for data points are expanded uncertainties (k = 2) as reported by the analysis laboratories. The reference values for NFRM Pu-1 are shown as solid horizontal lines and the expanded uncertainty envelopes for the reference values are bounded by the dashed horizontal lines.

Model Radiochronometric Ages:

The reference values determined in this project were used to calculate model ages for the various actinide parent-daughter systems. The most robust Pu-U radiochronometers (^{238}Pu-^{234}U, ^{239}Pu-^{235}U, and ^{240}Pu-^{236}U) yield concordant dates that are consistent with the processing history for both NFRM Pu-1 (Figure 5A) and Pu-2 (Figure 5B). In both materials, the results of the ^{242}Pu-^{238}U radiochronometer indicate model ages that are impossibly old by multiple orders of magnitude, therefore most of the ^{238}U in these materials is not due to ingrowth since purification. The LANL gamma spectrometry-based ^{241}Pu-^{241}Am ages are slightly older than U-Pu ages but IDMS-based ^{241}Pu-^{241}Am ages are consistent with the other model uranium ages and the production history for the materials. This is an indication that the gamma spectrometry measurements for ^{241}Am mass fraction have a positive bias. Using decay-corrected plutonium compositions and the Bateman equations, the amount of radiogenic ^{237}Np formed since the last purification of the plutonium materials can be estimated. Based on these calculations, a little more than half of the ^{237}Np in Pu-1 (16 μg g^{-1}) and most of the ^{237}Np in Pu-2 (63 μg g^{-1}) is not due to ingrowth since purification and might have been carried through with plutonium during purification steps.

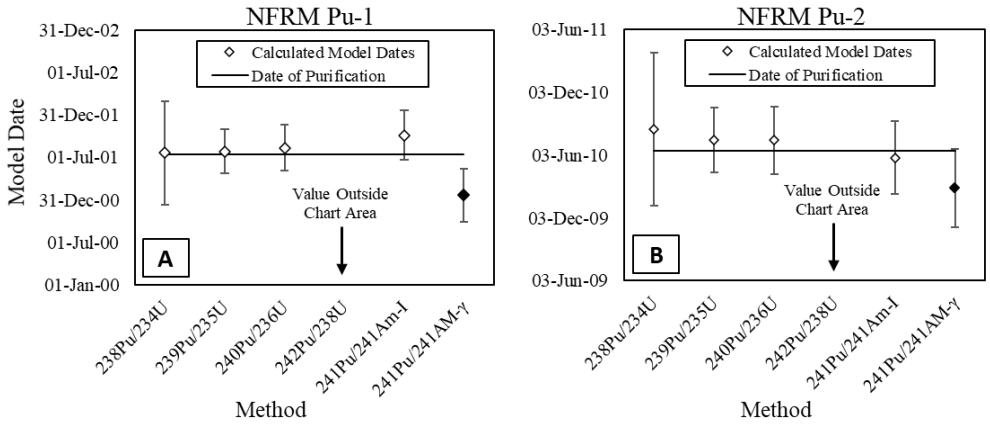


Figure 5. Model purification dates for measured attribute reference Values. Date uncertainties are expanded uncertainties (k = 2). The values shown as filled diamonds were calculated using gamma spectrometry-based ^{241}Am mass fraction results.

DISCUSSION

A high-quality reference material should be fit-for-purpose, stable and homogeneous [6]. Characterized attribute values should be evaluated for measurement reproducibility and metrological traceability and should have measurement uncertainties consistent with international standards, i.e. [7]. The NFRM Pu-1 and Pu-2 project described in this report was planned and executed to address these criteria.

Plutonium dioxide (PuO_2) was chosen as the base materials for NFRM Pu-1 and Pu-2 to provide plutonium in a relatively stable form for long-term use as an analytical reference material. LOI experiments performed in association with calcining during material preparation showed that the final calcining temperatures resulted in only 0.2% to 0.3% changes in mass for the plutonium oxides. This level of mass difference is much smaller than the relative uncertainties associated with mass fractions of Am, Np, or U (from 1.5% to 14%), therefore this potential change in assay represents an insignificant source of bias. The isotopes comprising the plutonium material and the characterized trace actinide components are all radioactive. As a result, the relative proportions of characterized nuclides will change over time. This is a well understood process and the

documentation for the reference materials will specify how to calculate the reference values for the NFRM materials based on dates when separations and analyses are performed by the user.

The NFRM Pu-1 and Pu-2 materials were anticipated to be homogenous for plutonium composition and trace actinides. The Pu-1 material was created from oxidized double-electrorefined plutonium metal that had been extensively tested during CRM 126-A certification for variability of the plutonium isotopic composition and mass fraction. Although the Pu-2 oxide was created from a mixture of different solid materials, these solids were combined into a single solution, and passed through an anion exchange column before conversion to oxide.

The analytical data for uranium and americium indicate that these elements are primarily plutonium decay products formed since purification of the NFRM materials. As such, they should be homogenously distributed in the oxides. Comparison of sample data consistently indicate that there is no statistically significant sample-to-sample bias for these elements, with the exception of the ^{238}U nuclide. Age dating systematics for the uranium isotopes show that much of ^{238}U in both materials is a contaminant. These trends can be explained by the presence of at least two sources of uranium in the plutonium material, with the primary source being *in situ* radiogenic uranium and a small proportion of a contaminant uranium with a natural or near natural composition (hence the lack of any significant effects on uranium isotopes other than ^{238}U) [8]. This heterogeneity is, however, small compared to the variability between Characterization, Verification, and MBS data sets and should be encompassed in the data-set variability components incorporated into the reference material uncertainty budgets.

Although most of the ^{237}Np present in both materials does not appear to be associated with ingrowth since the last purification of the plutonium materials, it does appear to be homogenously distributed at the resolution of the characterization and verification measurements. This is consistent with incomplete separation of neptunium from plutonium during NFRM production, rather than the result of subsequent contamination.

Measurement reproducibility (as defined in the VIM [6]) for each characterized attribute of NFRM Pu-1 and Pu-2 was evaluated using the distribution of independent measurement data sets from the verification laboratories and the MBS. For most attributes, the independent data sets have overlapping expanded uncertainties for measured values indicating nominal agreement between data sets. The most prominent exceptions to this are the systematic difference between ^{241}Am mass fraction measurements by IDMS and gamma spectrometry and the variability of some uranium isotope ratio and mass fraction data sets. To compensate for this variability, conservative uncertainty components for data set variability were included in the budget for the attributes. Accordingly, the reference values for the characterized attribute value are reproducible within cited uncertainties.

The attribute values for the NFRM Pu-1 and Pu-2 oxide materials are metrologically traceable to the SI units kg and mol. Characterization measurements were performed using various methods that are secondarily traceable by relying on internal or external calibrations as described in Table 1. The mass faction values are traceable to the kg through mass measurements performed on calibrate balances and conversion of element amounts (i.e. mols) to mass using evaluated atomic masses for nuclides [9]. The isotope amount ratios are traceable to the mol through direct calibration of measurements instruments with certified isotopic reference materials.

CONCLUSION

NFRM Pu-1 and NFRM Pu-2 contain measurable quantities of neptunium, americium, and uranium. The isotopic composition of uranium was quantifiable but the neptunium and americium in these materials are mono-isotopic within the capabilities of the measurement techniques utilized. The characterized attributes for the trace constituents are sufficiently homogeneous, traceable, and reproducible for these materials to be fit-for-purpose as trace actinide nuclear forensic reference materials. For additional details about the reference materials and information about obtaining samples, please contact the corresponding author.

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REFERENCES

1. Kristo, M.J., Tumey, S.J.: The state of nuclear forensics. Nucl. Instrum. Meth. in Phys. Res. B **294**, 656 (2013)
2. Keegan, E., Kristo, M.J., Toole, K., Kips, R., Young, E.: Nuclear Forensics: Scientific analysis supporting law enforcement and nuclear security investigations. Anal. Chem. **88**, 1498 (2016)
3. Moody, K.J.: Determination of Plutonium Metal Origins. Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-120253(1995)
4. New Brunswick Laboratory: Certificate of Analysis CRM 126-A Plutonium Metal Assay and Isotopic Standard, NBL Program Office, Oak Ridge, TN, USA. (2013)
5. Reid, A.: Simulating decay chains using spreadsheets, Physics Education, 48:18 (2012) https://iopscience.iop.org/article/10.1088/0031-9120/47/1/F08/pdf. Accessed: December 2019
6. Joint Committee for Guides in Metrology: International vocabulary of metrology -Basic and general concepts and terms (VIM), JCGM 200 (2012)
7. Joint Committee for Guides in Metrology: Evaluation of measurement data – Guide to the expression of uncertainty in measurement (GUM). JCGM 100, 2008 (E/F). (2008)
8. Sturm, M., Richter, S., Aregbe, Y., Wellum, R., Mialle, S., Mayer K., Prohaska T.: Evaluation of chronometers in plutonium age determination for nuclear forensics: What if the 'Pu/U clocks' do not match? J. Radioanal. Nuc. Chem. 302, 399 (2014)
9. Wang, M., Audi, G., Wapstra, A.H., Kondev, F.G., MacCormick, M., Xu, X., and Pfeiffer, B.: The AME2012 atomic mass evaluation (II). Table, graphs, and references. Chin. Phys. C, **36(12)**, 1603 (2012).