New reference materials for trace-levels of actinide elements in plutonium

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Abstract.
Two plutonium oxides were prepared as unique reference materials for measurement of actinide elements present as trace constituents. Each reference material unit is approximately 200 mg of PuO_2 in a quartz glass bottle. Characterized attributes of the oxides included mass fractions of plutonium, americium, neptunium, and uranium. Isotope-amount ratios were also determined for plutonium and uranium, but neptunium and americium were observed to be monoisotopic ^{237}Np and ^{241}Am. Measurements for characterization and verification of the attributes show that plutonium and trace actinides are homogeneous with the exception of limited heterogeneity for uranium, primarily observed for the ^{238}U isotope. Model purification ages calculated from measured americium and uranium attribute values are consistent with material histories and indicate that the actinide impurities are primarily from decay of plutonium isotopes.

Introduction

Special nuclear materials (SNM) such as plutonium, highly enriched uranium (HEU), and ^{233}U have the potential to be used as fissile material for a nuclear device. Accordingly, they are of particular concern from the perspective of nuclear safeguards and counter terrorism. Since the early 1990s, there have been multiple incidences of illicit trafficking of HEU and plutonium materials [1]. Analyses of SNM 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 [2-4]. These analyses, typically described as "nuclear forensics", frequently include measurements of physical characteristics, chemical composition, and the concentrations and isotopic compositions of the SNM and various trace constituents.

Several nuclear forensic studies have been performed that focus specifically on plutonium, e.g. [5-11]. These studies show that quantifying trace actinide constituents in plutonium is essential for illuminating the history of these materials. For instance, the amounts of americium and uranium relative to plutonium can be used to determine model ages of purification. The isotopic composition of trace uranium and relative amounts of americium, neptunium, and uranium nuclides might provide an indication of a specific purification process. This data, in

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conjunction with plutonium isotopic composition, could also potentially be used to constrain reactor types and irradiation conditions for production of plutonium [5].

Well-characterized analytical reference materials play an essential role in assuring data quality for nuclear forensic analyses of plutonium and are critical to meet evidentiary standards [12]. Appropriate reference materials are necessary for method development and validation, for instrument calibration, and as known samples for quality control measurements. Accordingly, Reference material providers such as the Commission d'ETAblissement des Méthodes d'Analyse, the European Commission's Joint Research Center Geel, the United States National Nuclear Security Administration's NBL Program Office, and the National Institute of Standards and Technology (NIST) have produced a variety of plutonium certified reference materials (CRMs). These include assay and radioactivity standards, isotopic reference materials, and enriched isotope spikes. Most of these CRMs were developed for fuel cycle or environmental analysis of plutonium but two reference material have been characterized specifically for nuclear forensic analyses; the NIST SRM 4340 Plutonium-241 Radioactivity Standard [13] and a high purity ^{244}Pu spike for measurement of trace amounts of plutonium [14]. Aside from these materials, however, the availability of plutonium standards appropriate for nuclear forensics analyses is limited [15-16]. To compensate for the paucity of nuclear forensic standards, some researchers have made use of available plutonium certified refence materials to demonstrate analytical methods even though these materials have not been certified for the attributes of interest, e.g. [7, 8, 11, 17].

As part of a program to enhance nuclear forensic analytical capabilities, the United States Department of Homeland Security (DHS) sponsored a series of projects to develop new reference materials specifically for nuclear forensic measurements. The work described here is one such project which included the preparation of two plutonium nuclear forensic reference materials (NFRMs) with different levels of trace actinide impurities. These new reference materials are designated NFRM Pu-1 and NFRM Pu-2. They are comprised of PuO_2 powders that have been characterized for plutonium mass fraction; plutonium isotope-amount ratios; americium, neptunium, and uranium mass fraction; and uranium isotope-amount ratios. Preparation and characterization of the reference materials was performed by researchers at Los Alamos National Laboratory (LANL). Verification analyses were performed by both Lawrence Livermore National Laboratory (LLNL) and Oak Ridge National Laboratory (ORNL). Units of the materials were also distributed to several United States Department of Energy (DOE) national laboratories as part of a DHS-sponsored Methodology Benchmarking Study (MBS) to assess nuclear forensic analytical capabilities.

Experimental

Unit Production

During initial project planning, it was determined that creating reference materials by doping a highly purified plutonium with known quantities other actinides was not feasible within the project time frame and budget. Instead, a review was performed of plutonium in the LANL inventory to identify materials that: a) are relatively low in ^{241}Pu; b) are in a relatively stable form for long term storage; c) are comprised of a homogenous batch of processed plutonium (i.e. not mixed solids); and d) represent product from common large scale processing activities. The chosen materials have significantly different processing histories. NFRM Pu-1 is an oxide formed from a plutonium metal rod that was part of the feedstock used to create the CRM 126-A plutonium metal assay and isotopic standard [18]. The plutonium metal was double electro-refined on 15 July 2001 [17] prior to being cast into rods. After the CRM 126-A production was complete, the excess rod was wrapped in tantalum foil and allowed to oxidize by exposure to air within a glove box. The oxide chosen for NFRM Pu-2 was created from remanent solid materials from Pu production processing that were dissolved in 2 batches and combined into a single 7 mol L-1 nitric acid solution. This plutonium solution was passed through a column containing Reillex HPQ[1] anion exchange resin (Vertellus, Indianapolis, IN, USA) on 15 June 2010. The column was then rinsed with 6.2 mol L-1 nitric acid and the plutonium was stripped from the column with a solution of 0.45 mol L-1 nitric acid. The purified plutonium solution was then converted to oxide by performing Pu(III) oxalate precipitation and calcining in air at 600 °C.

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[1] Certain commercial equipment, instruments, software, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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. The LANL production facility performed loss-on-ignition studies on the stock oxide materials specifically to assess the calcining temperature that would result in relatively small changes in mass due to loss of volatile components but without producing a phase change that would render the plutonium oxide difficult to process [19]. Based on this work, an additional calcining step was performed on both stock materials specifically for this project. NFRM Pu-1 and Pu-2 were calcined in air to temperatures of 750 °C and 650 °C respectively which resulted in only 0.2 % to 0.3 % decrease in mass.

Individual units for the two reference materials were prepared in a glove box that had been cleared-out and wiped down to reduce the potential for contamination by particulates from materials that were previously present in the glovebox. The 2 sets of NFRM units were prepared independently and equipment used was either new, wiped down, or washed between materials to prevent cross contamination. The reference material units were prepared by transferring approximately 200 mg of PuO_2 into custom-made quartz screw top vials (Precision Glass Blowing, Centennial, CO, USA) using a benchtop micro riffler apparatus (Quantachrome Instruments, Boynton Beach, FL, USA). A total of 160 units of NFRM Pu-1 and 45 units of Pu-2 were created. The bottles were sealed with robust plastic caps fitted with tin (Sn) metal foil liners to assure a tight seal and mitigate alpha radiation damage to the plastic caps. After filling, these unit bottles were wiped down, labelled, and heat sealed in metalized Mylar sleeves for storage and handling.

Material Characterization and Verification Analyses

A total of 10 randomly selected samples from the NFRM Pu-1 production run and 5 from the NFRM Pu-2 production run were analyzed at LANL for characterization of reference materials attributes. Both LLNL and ORNL performed verification measurements on at least 2 splits from each of 2 reference material units. The mass of the PuO_2 sample splits processed for characterization and verification measurements was approximately 25 mg or smaller (this does not include Pu mass fraction characterization, see proceeding section). Table 1 summarizes the characterization and verification analyses performed for this project. Measurement used to define attribute values are describe in more detail below. For the DHS-funded MBS, two units of both materials were sent as blind samples to each of 4 DOE laboratories. Although these laboratories included LANL, LLNL, and ORNL as well as Savanah River National Laboratory, the measurements for the study were independent of characterization or verification measurements performed by these same facilities. The measurement results from the MBS and the verification measurements were not used to derive the attribute values but were used to assess accuracy of the characterization data and the adequacy of measurement uncertainty estimates.

Plutonium Mass Fraction Measurements for Material Characterization

Plutonium mass fraction characterization measurements were made by controlled potential coulometry (CPC) as described in [20]. Analyses were performed, in duplicate, on 5 units of NFRM Pu-1 and 2 units of NFRM Pu-2. The LANL procedure for the CPC analyses consumed relatively large proportions of the reference material units (approximately 100 mg per analysis), so units selected for characterization by CPC were used solely for these measurements. A calibration factor for the analyses was determined by measuring the current necessary to oxidize a known quantity of Pu(III) to Pu(IV) in a solution made from CRM 126-A. The amount of plutonium in the analyzed NFRM samples was then calculated based on the product of the calibration factor and the current necessary to oxidize the plutonium in the solutions prepared from the oxides. Corrections for analytical interferences resulting from oxidation of trace iron in the plutonium were determined by measuring the iron content of samples using a spectrophotometric method as described [21]. The mass fraction was then calculated based on the mass of plutonium measured in the solution relative to the mass of dissolved oxide.

Table 1. Summary of Analyses for Characterization and Verification of NFRM Pu-1 and Pu-2 Attribute Values

Attribute	Laboratory	Analysis Method[a]	Measurement Instruments[b]	Calibration Material [c]	Isotopic Tracer [c]
Pu Mass Fraction	**LANL**	**CPC**	---	**CRM 126-A**	---
	LLNL	IDMS	Nu Plasma HR MC-ICP-MS	CRM 137	^{244}Pu WRM
	ORNL	IDMS (NFRM Pu-2)	ThermoFisher Neptune MC-ICP-MS	CRM 137	CRM 130 (^{242}Pu)
Pu Isotope -Amount Ratios	**LANL**	**Mass Spectrometry**	**Isotopx Sector 54 & VG 354 MC-TIMS**	**CRM 126-A**	---
	LLNL	Mass Spectrometry α Spectrometry (^{238}Pu)	Nu Plasma HR MC-ICP-MS Ortec Alpha Ensemble α Spectrometer	CRM 137	---
	ORNL	Mass Spectrometry α Spectrometry (^{238}Pu)	ThermoFisher Neptune MC-ICP-MS Canberra Alpha Analyst	CRM 137	---
Am Mass Fraction	LANL	γ Spectrometry	Protean Gas Proportional Counter Packard Cobra NaI(Tl) γ Counter	^{241}Am-doped epoxy tubes.	---
	LLNL	**IDMS**	**Nu Plasma HR MC-ICP-MS**	**CRM U010**	**NFRM Am-243**
	ORNL	**IDMS**	**ThermoFisher Neptune MC-ICP-MS**	**CRM 137**	**NFRM Am-243**
Np Mass Fraction	**LANL**	**Mass Spectrometry**	**VG Elemental PlasmaQuad PQ2 ICP-MS**	**Internal: Rh MSRH 10PPM**	---
	LLNL	Mass Spectrometry	Nu Plasma HR MC-ICP-MS	Yield: ^{239}Np WRM Sensitivity: ^{237}Np WRM	---
	ORNL	Quadrupole Mass Spectrometry	ThermoFisher Series2 Quadrupole ICP-MS	Yield: ^{239}Np WRM Sensitivity: ^{237}Np WRM Internal: ^{233}U WRM	---
U Mass Fraction	**LANL**	**IDMS**	**Isotopx VG 354 MC-TIMS**	**^{233}U WRM**	**IRMM 199**
	LLNL	IDMS	Nu Plasma HR MC-ICP-MS	^{233}U WRM	U010
	ORNL	IDMS	ThermoFisher Neptune MC-ICP-MS	CRM 111-A (^{233}U)	CRM 900
U Isotope -Amount Ratios	LANL	IDMS	**Isotopx VG 354 MC-TIMS**	**CRM U750**	---
	LLNL	Mass Spectrometry	Nu Plasma HR MC-ICP-MS	CRM U010	---
	ORNL	Mass Spectrometry	ThermoFisher Neptune MC-ICP-MS	CRM U900	---

[a] Analyses highlighted in bold were used for attribute values. "WRM" is lab-specific working reference material. Other abbreviations are as defined in the text.

[b] Referenced instrument manufacturers include Canberra (Mirion Technologies, Meriden, CT, USA), Nu (Ametek, Wrexham, UK), Ortec (Oak Ridge, TN, USA), Packard Instruments (Downers Grove, IL, USA), Protean Instruments (Knoxville, TN, USA) and ThermoFisher Scientific (Waltham, MA, USA).

[c] CRMs 111-A, 130, 137, U010, U750 and U900 are from NBL Program Office (Oak Ridge, TN, USA).

Isotope-amount Ratio Measurements for Material Characterization

Plutonium and uranium isotopic ratios were measured for reference material characterization at LANL by Mult-collector thermal ionization mass spectrometry (MC-TIMS). A total of 5 NFRM Pu-1 units and 3 NFRM Pu-2 units were sampled for isotopic analyses. Plutonium samples were subdivided for the analyses with small portions of each sample transferred into clean glass vials for separation and collection of plutonium and larger portions separated for uranium. For the plutonium isotopic analyses, concentrated nitric acid was added drop-wise to each sample to dissolve the plutonium and resulting solution was then evaporated to dryness. Dry samples were reconstituted in 12 mol L^{-1} hydrochloric acid and transferred to an anion-exchange column (Lewatit MP5080, 60-150 mesh, Birmingham, NJ) to isolate plutonium from potential isobaric actinides. The plutonium fraction was selectively stripped from the column with a mixed hydrochloric (7 mol L^{-1}) and hydroiodic (0.2 mol L^{-1}) acid solution and collected in a glass vial. The recovered plutonium solution was evaporated to dryness on a hotplate, reconstituted in concentrated nitric acid, and evaporated to dryness again.

Each of the plutonium samples was analyzed in triplicate using two mass spectrometers designated as VG3 (Sector 54, Isotopx Ltd. Cheshire, UK) and VG2 (VG 354, Isotopx Ltd. Cheshire, UK). The dried samples were reconstituted using a quantity of high purity 1 mol L^{-1} nitric acid necessary to achieve the desired dilution factor for the plutonium isotopic analysis. Sample solutions were loaded onto rhenium filaments and dried. The sample filaments were mounted onto VG instrument sample turrets along with two blank ionization filaments in a triple-filament geometry. Plutonium isotopes ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu were measured using the total evaporation analysis method [22] on multi-collector Faraday cup systems with 10^{11} Ω amplifiers. Multiple analyses of CRM 126-A interspersed with the characterization samples were performed for correction of mass dependent isotope fractionation.

For uranium isotope-amount ratio measurements, plutonium samples were dissolved and dried down as previous described. Concentrated nitric acid was added to each vial and then evaporated to dryness. Dry samples were reconstituted in 12 mol L^{-1} hydrochloric acid and transferred to an MP5080 anion-exchange column. The uranium fraction was selectively stripped from the column with a dilute hydrochloric acid solution (0.1 mol L^{-1}) and collected in a glass vial. The recovered uranium solution was evaporated to dryness on a hotplate, reconstituted in concentrated nitric acid, and again evaporated to dryness.

Uranium samples were analyzed in duplicate on the VG3 TIMS instrument. The dried samples were reconstituted using high purity 1 mol L^{-1} nitric acid. A portion of each sample solution was loaded onto a rhenium filament, dried, and mounted into the instrument sample turret. The VG3 TIMS is equipped with a Daly detector and a photomultiplier tube. A dynamic ion counting method was used to sequentially measure the uranium isotopes ^{234}U, ^{235}U, ^{236}U, and ^{238}U. Multiple analyses of CRM U750, interspersed with the characterization samples, were performed for calibration of mass dependent isotope fraction during uranium measurements.

Trace Actinide Mass Fraction Measurements for Material Characterization

Americium in both reference materials is assumed to be monoisotopic ^{241}Am based on $n(^{243}\text{Am})/n(^{241}\text{Am})$ ratio measurements made as part of this study. The results of measurements on unspiked samples indicate values below detection limits ($< 1.0 \times 10^{-5}$). The ^{241}Am mass fraction measurements by gamma spectrometry-based methods performed at LANL appear to have a small systematic bias (see Radiochronometry section). Accordingly, the results of isotope dilution mass spectrometry (IDMS) measurements performed by ORNL and LLNL were used to establish the reference values for ^{241}Am mass fractions and the LANL data was used to help estimate a data-set variability component for the uncertainty models.

LLNL and ORNL both performed ^{241}Am mass fraction measurements by IDMS using a high purity ^{243}Am spike that was prepared and calibrated for activity concentration by the National Physical Laboratory in the UK. The molar concentration of this spike material was verified at LLNL by IDMS using a ^{241}Am activity standard (SRM 4322C; NIST Gaithersburg, MD, USA) as an isotopic spike. Both laboratories performed similar analytical procedures. At each laboratory, 2 samples of NFRM Pu-1 and 2 samples of NFRM Pu-2 were dissolved and separate aliquots of each sample solution were spiked with ^{243}Am. The americium was then separated from plutonium using chromatography methods. LLNL purified the spiked americium samples using 3 successive columns prepared with AG1x8 100-200 mesh anion exchange resin (Bio-Rad, Hercules, CA, USA). For the first column, the plutonium was dissolved in 8 mol L^{-1} HNO_3 and loaded onto the column, then the americium was eluted with 8 mol L^{-1} HNO_3 rinse.

The americium was loaded onto the second column in 9 mol L^{-1} HNO_3 and eluted in 9 mol L^{-1} HCl. The americium was then loaded onto the third column in a mixed acetone-HCl solution (75:25) and eluted with concentrated HCl. ORNL purified the americium IDMS samples by loading sample aliquots on TRU columns (Eichrom, Lisle, IL USA) in HNO_3, rinsing the plutonium off the column with a $NaNO_2$ solution, and then eluting the americium with 8 ml L^{-1} HCl. The separated Am IDMS solutions were analyzed by the labs for the $n(^{243}\text{Am})/n(^{241}\text{Am})$ ratio by multi-collector inductively-couple plasma mass spectrometry (MC-ICP-MS: Neptune at ORNL, Nu Plasma at LLNL) and the measured isotopic ratios were corrected for mass dependent fractionation using either a plutonium (CRM 137 at ORNL) or a uranium (CRM U010 at LLNL) isotopic reference material.

Neptunium in NFRM Pu-1 and NFRM Pu-2 is also monoisotopic at the resolution of measurements made for this study, with a $n(^{236}\text{Np})/n(^{237}\text{Np})$ ratio of less than 1.0 $\times 10^{-6}$. The ^{237}Np mass fraction was characterized by measurements at LANL performed on a VG Elemental PlasmaQuad PQ2 ICP-MS (ThermoFisher Scientific, Waltham, MA, USA). A total of 5 sample of NFRM Pu-1 were analyzed in duplicate and 3 samples of the NFRM Pu-2 were analyzed in duplicate. The samples were spiked with a known amount of rhodium internal standard (MSRH 10PPM, Delta Scientific laboratory Products, Mississauga ON, Canada) and each sample was then analyzed for signal intensity on the quadrupole mass spectrometer with the rhodium signal intensity used to correct for transmission efficiency.

Uranium mass fraction was measured using IDMS. Four separate IDMS analyses were made from each of 5 NFRM Pu-1 samples and 3 NFRM Pu-2 samples. For each analysis, an aliquot of plutonium solution was transferred to a clean glass vial that contained a known amount of a LANL in-house ^{233}U working standard. Several drops of 1 mol L^{-1} hydrofluoric acid were added to the vial then dried. The dry samples were reconstituted in 12 mol L^{-1} hydrochloric acid and transferred to an anion-exchange column where the uranium fraction was selectively stripped with a dilute hydrochloric acid (0.1 mol L^{-1}) and collected in a glass vial. As described for the uranium isotopic analyses (above), the IDMS samples were converted to a nitrate solution and analyzed in duplicate for the $n(^{233}\text{U})/n(^{235}\text{U})$ ratio by ion counting on the VG3 TIMS. Replicate analyses of IRMM 199 (Joint Research Center, Geel, Belgium) were used to correct for mass dependent isotope fractionation.

Results and Measurement Uncertainties

The intent of the project was to develop a representative set of measurements results for the reference material production runs and to use the mean values of this data to establish the attribute values. The resulting reference values for NFRM Pu-1 and Pu-2 are provided in Table 2. Measurement result and reference values are corrected for ingrowth and/or decay [23] to a reference date of 01 January 2019. Evaluated half-lives used for these corrections were obtained from the Decay Data Evaluation Program [24-27] and atomic masses from [28] were used to calculate molar masses necessary for mass fraction calculations. Uncertainties for the reference material attribute values were modelled using uncertainty propagation software (GUM Workbench 2.4.1, Metrodata, Grenzach-Wyhlen, Germany). These uncertainties are expanded with a coverage factor (*k*) of 2 for an approximately 95 % level of confidence and are consistent with GUM protocols [29-30]. Detailed uncertainty budgets for each attribute value will be provided with documentation for the reference materials.

Two different statistical values were used to represent the observed measurement variability for the plutonium isotope-amount ratio and trace actinide mass fraction results. Standard uncertainty (i.e. standard error of the mean) is the statistical quantity normally used to describe measurement variability, but this assumes a random distribution of measurement results around a single “true” value. The mean values and standard uncertainties of the LANL characterization measurements (except for Am mass fraction) were used for the uncertainty models. These characterization measurements, however, are not necessarily more accurate than the verification measurements or results from the MBS. So, a discrete component for variability between measurements data sets was also included in the uncertainty models for the attribute values. This variability component accounts for systematic biases that were not recognized or were not adequately incorporated into uncertainty models for individual measurements (sometimes called “dark” uncertainty” [31]). This “data-set” variability component was estimated by subdividing all available measurement results (characterization, verification, and MBS data) into data sets by analysis laboratory, measurement campaign, and/or analysis method and then performing Analysis of Variance (ANOVA) to obtain between-data set standard uncertainties, as recommended by GUM protocols [29]. For measured attributes that appear to indicate compositional heterogeneity (see uranium measurement results below), sample variability was not isolated from measurements variability or variability between the multiple data sets. Instead, it was assumed that the data-set variability component is sufficiently conservative to cover both the relatively small degrees of observed heterogeneity as well as the larger variability between data sets.

Uncertainty components such as weighing variability or internal measurement variability (i.e. statistics from a single mass spectrometry analysis) were not evaluated as discrete components. Multiple separate sample dissolutions were performed for the characterization analyses of both NFRM Pu-1 and NFRM Pu-2 and replicate measurements were made from prepared analysis samples. Therefore, any random variability associated with weighing or internal measurement variability was assumed to be represented in the observed dispersion of the measurement results.

Table 2. Reference Values for Characterized Attributes

Attribute[a]	**NFRM Pu-1**			**NFRM Pu-2**		
	Value		*U (k u_c)*[b]	Value		*U (k u_c)*[b]
Pu Mass Fraction (g g^{-1})	0.878 40	±	0.000 90	0.878 96	±	0.000 97
Pu Isotope-amount Ratios						
$n(^{238}\text{Pu})/n(^{239}\text{Pu})$	0.000 118 1	±	0.000 003 9	0.000 123 3	±	0.000 002 4
$n(^{240}\text{Pu})/n(^{239}\text{Pu})$	0.062 670	±	0.000 048	0.062 505	±	0.000 067
$n(^{241}\text{Pu})/n(^{239}\text{Pu})$	0.000 752	±	0.000 011	0.000 723 6	±	0.000 002 0
$n(^{242}\text{Pu})/n(^{239}\text{Pu})$	0.000 391	±	0.000 012	0.000 504 5	±	0.000 009 5
U Isotope-amount Ratios						
$n(^{234}\text{U})/n(^{235}\text{U})$	0.034 83	±	0.000 37	0.034 64	±	0.000 67
$n(^{236}\text{U})/n(^{235}\text{U})$	0.229 78	±	0.000 35	0.229 52	±	0.000 67
$n(^{238}\text{U})/n(^{235}\text{U})$	0.016 7	±	0.004 8	0.002 6	±	0.002 1
^{241}Am Mass Fraction (µg g^{-1})	803	±	66	309	±	21
^{237}Np Mass Fraction (µg g^{-1})	30.8	±	4.3	68.2	±	4.6
U Mass Fraction (µg g^{-1})	521.9	±	7.9	250.6	±	4.9

[a] Reference date for attribute values is 01 January 2019.

[b] Expanded uncertainties (*U*) are combined standard uncertainties (u_c) with a coverage factor (*k*) of 2 to yield an approximate confidence level of 95 %.

Plutonium Mass Fraction

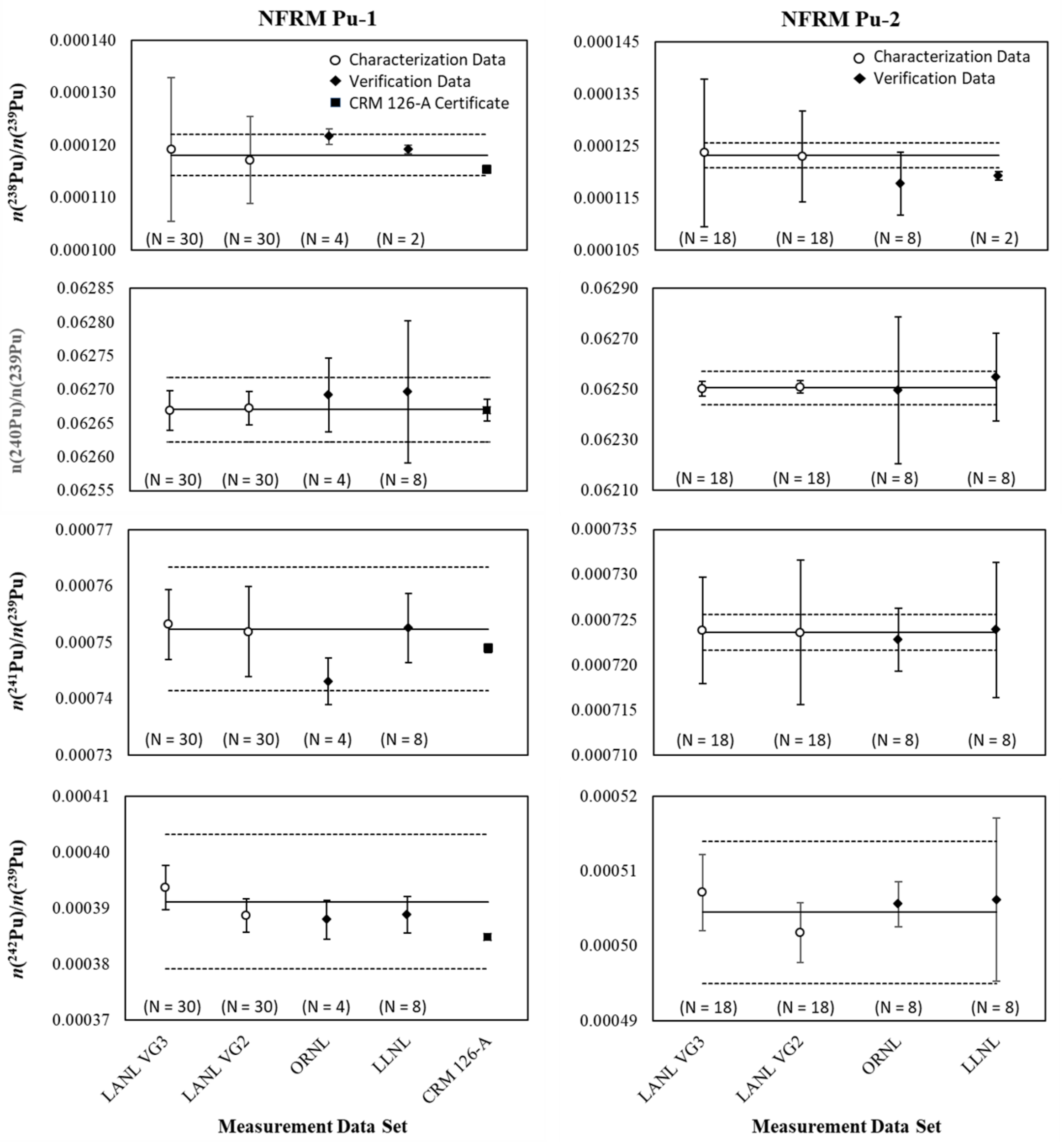
The reference values for mass fractions of the NFRM Pu-1 and NFRM Pu-2 oxides (Table 2) are slightly lower than the theoretical mass fraction value of 0.882 g g^{-1} for a pure stoichiometric PuO_2. This difference is consistent with plutonium that has a relatively small proportion (< 0.4 %) of impurities. The CPC characterization measurements used to establish the reference values were highly repeatable with a relative standard deviation of less than 0.05 % for both NFRM Pu-1 and NFRM Pu-2. IDMS verification measurements by LLNL indicate lower mass fraction values for both NFRM Pu-1 (average = (0.8733 ± 0.0059) g g^{-1}) and NFRM Pu-2 (average = (0.8729 ± 0.0040) g g^{-1}). The uncertainties for the LLNL plutonium IDMS data are relatively large (≥ 0.5 %) and measurements show a level of measurement variability (0.15 % to 0.35 % RSD) that is similar in magnitude to the expanded uncertainties cited for individual measurements. ORNL only provided mass fraction data for NFRM Pu-2 and these results are also systematically lower (average = (0.8626 ± 0.0065) g g^{-1}) but with large uncertainties for individual measurements (0.75 %) and significant measurement variability (0.4 % RSD).

Uncertainties for the plutonium mass fraction reference values are dominated by the repeatability of the CPC measurements and the Type B evaluated uncertainty associated with individual measurements. Uncertainty components associated with the molar mass of the plutonium materials and decay corrections were minor contributions to the overall uncertainty.

Plutonium Isotope-amount Ratios

NFRM Pu-1 reference values and measurement uncertainties for plutonium isotope-amount ratios are provided in Table 2. The reference values, characterization data, and verification data for plutonium isotope-amount ratios are summarized in Fig. 1. Analyses performed at LANL for characterization do not indicate statistically significant sample-to-sample variability at the 95 % confidence level for NFRM Pu-1. A systematic bias associated with measurement instruments is, however, indicated by Student's t-tests with the n(^{242}Pu)/n(^{239}Pu) ratio results having a particularly well-defined bias between mass spectrometers (*t* critical = 2.0, *t* statistics 7.7). Verification measurement data are largely in agreement with the characterization measurements (i.e. measured values overlap within uncertainties) but statistically significant differences between the 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 isotope-amount ratios were compared to the measured values for the oxide. The CRM 126-A values are consistent with the LANL measurements for n(^{238}Pu)/n(^{239}Pu), n(^{240}Pu)/n(^{239}Pu), and n(^{241}Pu)/n(^{239}Pu) ratios. The reference material value for n(^{242}Pu)/n(^{239}Pu) is also consistent with the VG2 characterization measurements but is lower than results for the VG3 instrument.

Fig. 1.



NFRM Pu-1 and Pu-2 average plutonium isotope-amount ratio data. Uncertainties for data points are average expanded uncertainties (U) as reported by the analysis laboratories ($k = 2$). Reference values are shown as solid horizontal lines and the expanded uncertainty envelopes are bounded by the dashed horizontal lines. Number of analyses for each measurements data set are shown in parenthesis.

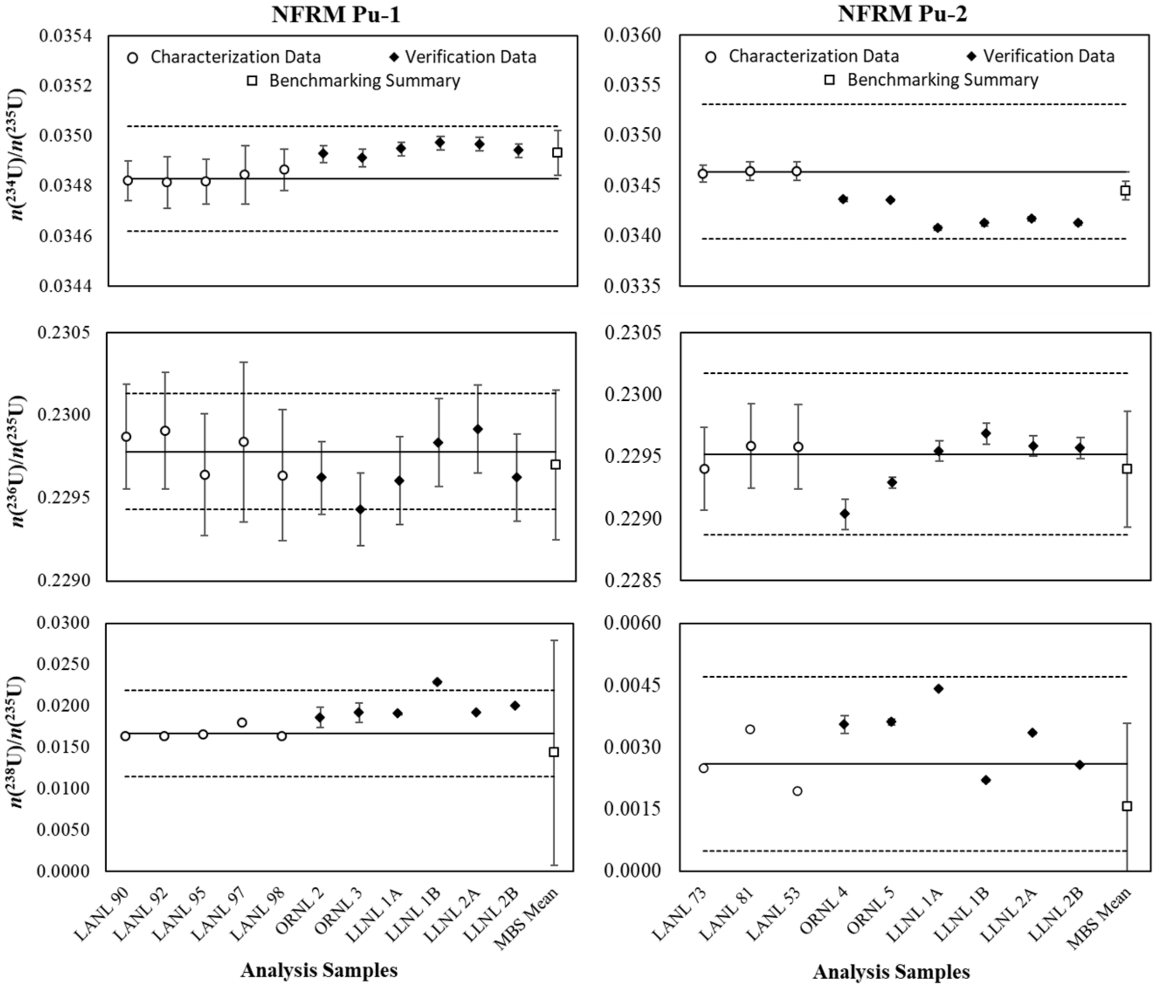
The distribution of the NFRM Pu-2 isotope-amount ratio measurement results is similar to the NFRM Pu-1 results (Table 2, Fig. 1). The measured characterization values do not indicate sample-to-sample variability at the 95 % confidence level, the verification results are consistent with the characterization measurements, and there appears to be a well-defined instrumental bias for the $\mathrm{n}(^{242}\mathrm{Pu})/\mathrm{n}(^{239}\mathrm{Pu})$ ratio results (t critical = 2.0, t statistic = 7.6). Similarly, there are a small but statistically significant biases between measurement data sets for both $n(^{240}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ and the $n(^{242}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ ratios.

Uranium Isotope-amount Ratios

Reference values and measured isotope-amount ratios for uranium in NFRM Pu-1 and Pu-2 (Table 2, Fig. 2) indicate compositions that are consistent with daughter products from plutonium decay. The $n(^{234}\text{U})/n(^{235}\text{U})$ and $n(^{236}\text{U})/n(^{235}\text{U})$ isotopic data are internally consistent for the various data sets but the $n(^{238}\text{U})/n(^{235}\text{U})$ characterization data display a statistically significant sample-to-sample bias (F critical =3.1, F statistic = 338 for Pu-1 and F critical =4.2, F statistic = 19 for Pu-2). The statistically significant variability between data sets observed for the plutonium isotopic composition is also observed in the uranium isotopic data. Despite these systematic differences, the measurements for the $n(^{234}\text{U})/n(^{235}\text{U})$ and $n(^{236}\text{U})/n(^{235}\text{U})$ ratios in NFRM Pu-1 have overlapping measurement uncertainties for characterization and verification measurements, indicating a reasonable level of consistency between samples and between data sets. The isotope-amount ratio data for NFRM Pu-2 and the $n(^{238}\text{U})/n(^{235}\text{U})$ ratios for NFRM Pu-1, however, display differences between data sets that are greater than uncertainties cited by the analysis laboratories.

The uncertainties for the $n(^{234}\text{U})/n(^{235}\text{U})$ and $n(^{236}\text{U})/n(^{235}\text{U})$ reference values for both NFRM materials are dominated by the between data-set variability component and uncertainties for ingrowth from decay of plutonium isotopes. Measurement repeatability and the uncertainty for the CRM U750 calibration standard also contribute to the uncertainty but corrections for uranium blank and instrument background are insignificant. For the $n(^{238}\text{U})/n(^{235}\text{U})$ ratios, however, it is the blank corrections uncertainty, the between data-set variability component, and the measurement variability component that account for the observed measurement uncertainty.

Fig. 2.



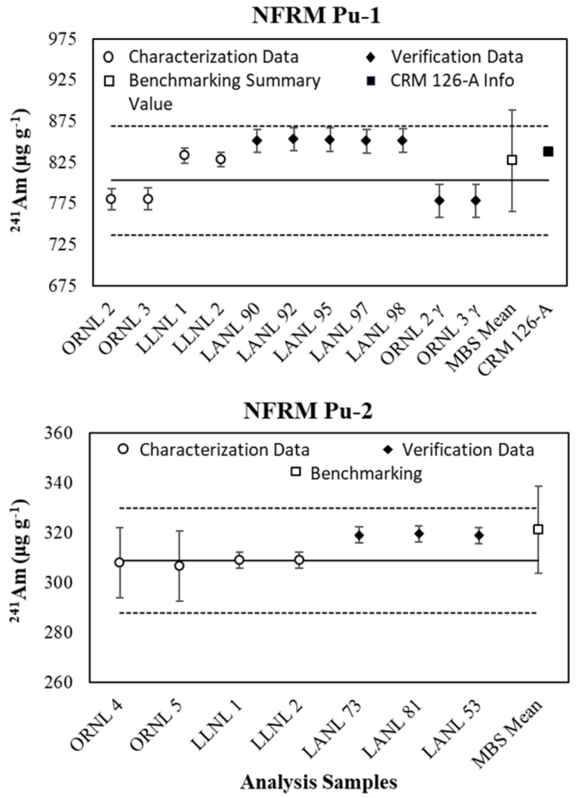
NFRM Pu-1 and NFRM Pu-2 uranium Isotope-amount Ratio Data. Uncertainties for data points are expanded uncertainties for the corrected isotope-amount ratios ($k = 2$). The calculated reference values are shown as solid horizontal lines and the expanded uncertainty envelope for the reference values is bounded by the dashed horizontal lines. The "MBS Mean" data points are the average of measurements from the Methodology Benchmarking Study and the associated error bars represent 2 standard deviations of the data.

Americium Mass Fraction

The ^{241}Am mass fraction data (Table 2, Fig. 3) are highly consistent within each measurement data set but well-defined statistically significant biases between data sets are observed for both NFRM Pu-1 (*F* critical = 2.2, *F* statistic of 199 for an) and NFRM Pu-2 (*F* critical = 2.5, *F* statistic = 602). This is at least partially due to higher mass fraction values indicated by gamma spectrometry-based analyses performed at LANL. ORNL and LLNL used the same IDMS measurement technique and the same ^{243}Am isotopic tracer, but there are also systematic differences between the measurements result from these labs. This bias could be due to the use of a plutonium isotopic reference material for mass bias correction of the n(^{243}Am)/n(^{241}Am) ratio measured at ORNL and a uranium reference material used at LLNL. The ingrowth corrected ^{241}Am information value from the CRM 126-A certificate is, within uncertainties, consistent with the NFRM Pu-1 IDMS characterization results from LLNL and summarized data from the Methodology Benchmarking study overlap with both the LLNL and ORNL characterization data for both materials.

The uncertainty for the calculated NFRM Pu-1 refence value is due largely to the Type B evaluated uncertainties for the IDMS measurements, such as ^{243}Am spike calibration and the mass spectrometry calibration standards. The decay/ingrowth correction uncertainties and the variability components represent minor uncertainty contributions. The NFRM Pu-2 uncertainty budget has a similar distribution with the exception that the between data-set variability is the largest single component.

Fig. 3.

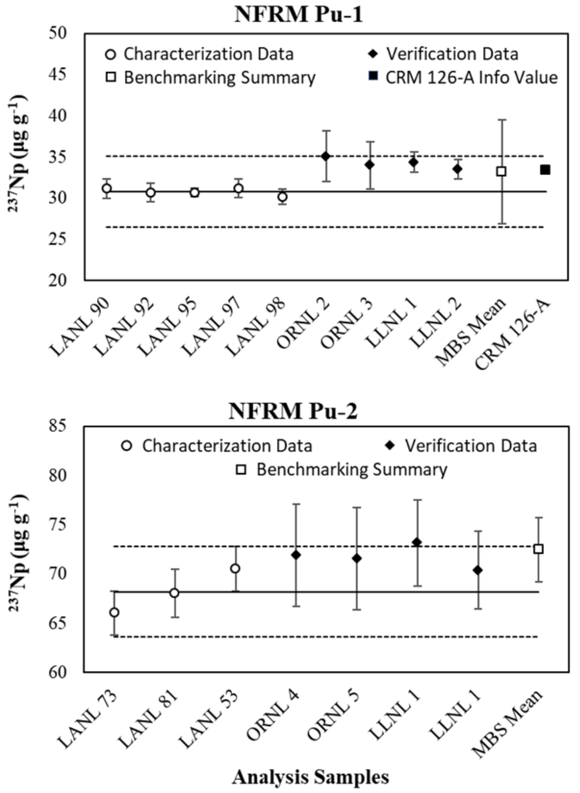


Americium Mass Fraction Data. Uncertainties for the measurements are expanded uncertainties for mass fraction values ($k = 2$). The calculated reference values are shown as solid horizontal lines and the expanded uncertainty envelope for the reference values is bounded by the dashed horizontal lines. The MBS Mean data point is the average of measurements and the associated error bars represent 2 standard deviations of the data.

Neptunium Mass Fraction

The ^{237}Np mass fraction data (Table 2, Fig. 4) are consistent within measurement data sets but there are statistically significant biases between data sets for both NFRM Pu-1 (F critical = 2.6, F statistic = 27 for an) and NFRM Pu-2 (F critical = 2.7, F statistic = 8). 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. The verification measurements and summarized Methodology Benchmarking data are also slightly higher than the characterization data for both NFRM Pu-1 and Pu-2 but, within uncertainties, are consistent with the characterization measurements. The uncertainties for the NFRM Pu-1 and Pu-2 ^{237}Np mass fraction reference values are mainly due to Type A evaluated measurement variability and data-set variability components with significant contributions from the Type B evaluated uncertainties for the measurement method.

Fig. 4.



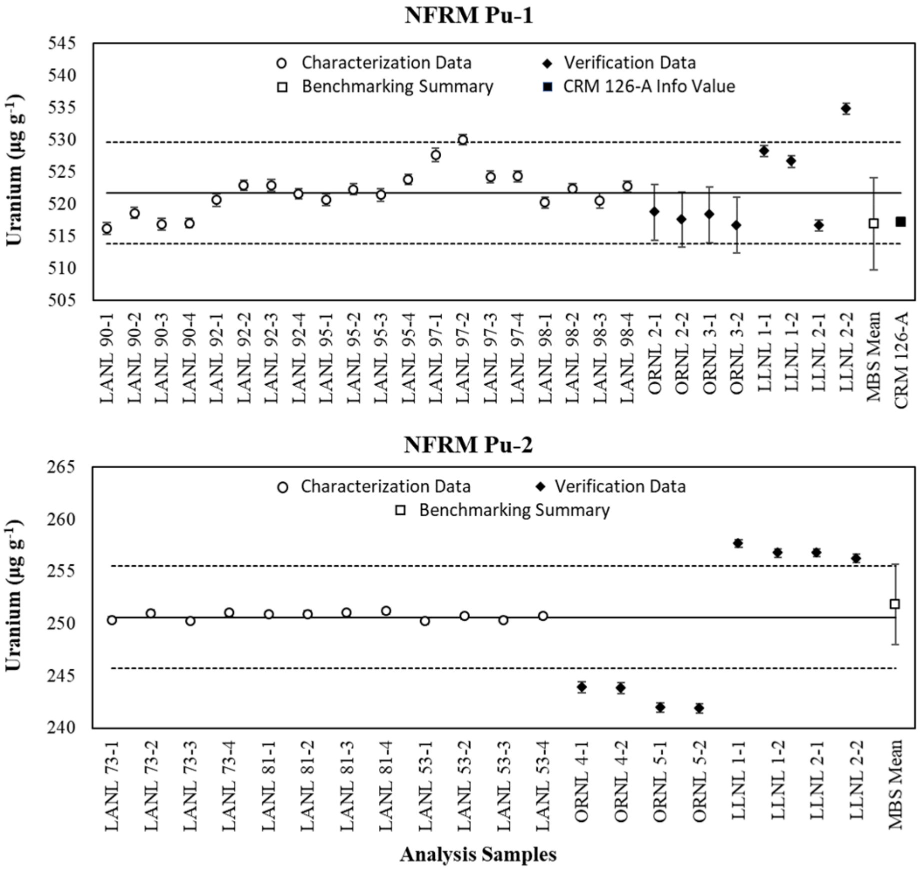
Neptunium Mass Fraction Data. Uncertainties for data points are expanded uncertainties for the corrected mass fractions ($k = 2$). The calculated reference values are shown as solid horizontal lines and the expanded uncertainty envelope for the reference values is bounded by the dashed horizontal lines. The MBS Mean data point is the average of measurements and the associated error bars represent 2 standard deviations of the data.

Uranium Mass Fraction

The reference values (Table 2) and the measurement data for uranium mass fractions in NFRM Pu-1 and NFRM Pu-2 are shown in Fig. 5. The characterization and verification measurement results for uranium in NFRM Pu-1 display a greater degree of variability between analysis samples than other trace actinides as indicated by a statistically significant sample-to-sample difference (F critical = 2.1, F statistic = 2.8) in uranium mass fraction. This degree of variability is not observed in NFRM Pu-2 or for the other trace actinide elements in either material. The apparent heterogeneity may be related to a larger proportion of non-radiogenic uranium in NFRM Pu-1 as indicated by the measured $n(^{238}\text{U})/n(^{235}\text{U})$ and the ^{242}Pu-^{238}U radiochronometric calculations described in the proceeding section.

The measurement results for NFRM Pu-1 and Pu-2 also show systematic differences between data sets, with NFRM Pu-2 having particularly large differences between the verification laboratories (6 % average relative difference between ORNL and LLNL verification data). Despite this variability, the measured uranium mass fraction data for NFRM Pu-1 overlaps with the ingrowth-corrected uranium mass fraction value cited in the CRM 126-A certificate and characterization values for both reference materials are consistent with the Methodology Benchmarking data. The reference value for NFRM Pu-1 encompasses the preponderance of available data but the NFRM Pu-2 reference value is between the measured verification values. Due to this variability, it is the between data-set uncertainties component that dominates reference value uncertainty budgets with only minor contribution from other components.

Fig. 5



Uranium Mass Fraction Data. Uncertainties for data points are expanded uncertainties for the corrected mass fractions ($k = 2$). 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 MBS Mean data points are the average of measurements from the study and the associated error bars represent 2 standard deviations of the data.

Model Radiometric Ages

The reference values determined in this project were used to calculate model ages for the various parent-daughter actinide isotopic systems (Table 3). By comparing these ages to the histories of the NFRM Pu-1 and NFRM Pu-2 starting materials it is possible to estimate the proportions of the trace actinide constituents that are present from ingrowth and any contaminants due to incomplete purification, material processing, or analysis blanks. The most robust Pu-U radiochronometers (^{238}Pu-^{234}U, ^{239}Pu-^{235}U, and ^{240}Pu-^{236}U) yield concordant ages that encompass purification dates from the processing history for both NFRM Pu-1 and Pu-2. The NFRM Pu-1 dates also overlap with a consensus model age value of 15 March 2001 ± 100 days proposed for CRM 126-A by Mathew et al. [17]. This indicates that the ^{234}U, ^{235}U, and ^{236}U measured in these NFRMs is primarily formed from *in situ* radioactive decay of Pu. The results of the ^{242}Pu- ^{238}U radiochronometer indicate model ages that are impossibly old by thousands of years for NFRM Pu-1 and hundreds for NFRM Pu-2, therefore most of the ^{238}U in these materials cannot be due to ingrowth since purification. Based on the processing history of the materials, the long half-life of the ^{242}Pu nuclide, and the relatively low abundance of ^{238}U in NFRM Pu-1 and Pu-2, the proportion of non-radiogenic ^{238}U is estimated to be 99.86 % and 98.9 %, respectively. Based on the relatively tight clustering of model ages of the ^{238}Pu-^{234}U, ^{239}Pu-^{235}U, and ^{240}Pu-^{236}U radiochronometers, it likely that this ^{238}U is from uranium that is not significantly enriched [32]. If a natural or nearly natural uranium isotopic composition is assumed, then approximately 4.8 µg g^{-1} of uranium in NFRM Pu-1 and 0.2 µg g^{-1} in NFRM Pu-2 is from incomplete separation, contamination from processing, analysis blank or some combination of sources.

IDMS-based ^{241}Pu- ^{241}Am ages are consistent with U-Pu model uranium ages and with the production history for the materials but the gamma spectrometry-based ^{241}Pu- ^{241}Am radiochronometer indicates ages that are slightly older. The average difference between the decay corrected ^{241}Am mass fraction by gamma spectrometry and by IDMS is approximately 49 µg for NFRM Pu-1 and 9 µg for NFRM Pu-2. This corresponds to LANL gamma spectrometry-based measurements being approximately 7 % higher than IDMS data for both materials. Considering the different processing histories of these two oxides it is unlikely that the materials would have an identical proportion of excess ^{241}Am making a bias in the γ spectrometry measurement the more likely explanation for the discrepancy. Therefore, the IDMS measurements for ^{241}Am by LLNL and ORNL were used for calculation of ^{241}Am mass fraction reference values.

Table 3. Calculated Model Purification Dates[a]

	NFRM Pu-1:			**NFRM Pu-2:**		
Radiochronometer	Electro-refined: 15 July 2001			Anion Exchange: 15 June 2010		
	Date		*U (k u_c)*[b]	Date		*U (k u_c)*[b]
^{238}Pu- ^{234}U	20 July 2001	±	223 days	18 Aug 2010	±	88 days
^{239}Pu- ^{235}U	27 July 2001	±	95 days	16 July 2010	±	62 days
^{240}Pu- ^{236}U	11 Aug 2001	±	99 days	18 July 2010	±	62 days
^{241}Pu- ^{241}Am (IDMS)	5 Oct 2001	±	113 days	26 May 2010	±	66 days
^{241}Pu- ^{241}Am (γ-spec)[c]	*15 Jan 2001*	±	*106 days*	*27 Feb 2010*	±	*36 days*
^{242}Pu- ^{238}U[c]	*9411 BCE*	±	*960 years*	*1339 CE*	±	*360 years*

[a] Model purification dates based on measured attributes for plutonium and trace actinides.

[b] Uncertainties are expanded uncertainties ($k = 2$).

[c] Values in italics are considered unreliable due to measurement bias (^{241}Am γ spectrometry) or significant proportions of extraneous daughter product nuclide (^{238}U).

Radiochronometry for the ^{241}Am-^{237}Np system is more complicated due to the simultaneous ingrowth and decay of ^{241}Am. Using decay-corrected plutonium compositions and the Bateman equations [23], the amount of radiogenic ^{237}Np formed since the last purification of the plutonium materials can be estimated. For NFRM Pu-1, approximately 13 µg g^{-1} of ^{237}Np has formed since the Pu-metal was electrorefined in 2001. Approximately 2.2 µg g^{-1} of ^{237}Np has grown in since the NFRM Pu-2 material was passed through an anion exchange column on 15 June 2010. 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}) was probably carried through with the plutonium during purification.

Discussion

Detailed requirements for production and certification of reference materials are outline in ISO Guide 35 [33] and ISO 17034 [34]. These requirements include evaluation of measurement reproducibility and metrological traceability, material stability and homogeneity, and the assignment of GUM compliant measurement uncertainties. Although NFRM Pu-1 and Pu-2 are not certified reference materials, as defined in [35], the project described in this report was planned and executed to address many of the requirement for high quality reference materials such as those outlined in the ISO documents.

Stability

Plutonium dioxide (PuO_2) was chosen as the base materials for NFRM Pu-1 and Pu-2 due to the relative stability of this chemical form. Stock material preparation at LANL included loss-on-ignition studies specifically to assess the calcining temperature that would result in relatively small changes in mass due to loss of volatile components. It was observed that heating calcining resulted in only 0.2 % to 0.3 % decrease in mass. Also, the reference material units are stored in capped quartz glass bottles which, in turn, are heat-sealed in metalized Mylar foil pouches. Therefore, it is not anticipated that the composition of the oxides will change significantly under normal storage conditions. It is possible, however, that the oxides will absorb some moisture from the environment when units are opened for handling and processing. The observed changes in mass of the plutonium oxides during calcining are significantly smaller than uncertainties associated with the mass fractions of Am, Np, or U. Furthermore, plutonium mass fraction and isotopic composition attributes of NFRM Pu-1 and NFRM Pu-2 were characterized primarily for the purpose of allowing quantitative ingrowth corrections to be made for the trace actinide constituents in the materials. These reference materials are not intended for use as plutonium assay standards. Accordingly, even a 0.3 % change in mass for the plutonium oxide should not have a negative impact on the fitness of the reference materials for their intended purpose.

The isotopes comprising the plutonium material and the characterized trace actinide components are 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 material will provide recommendations for performing necessary corrections to the NFRM reference values based on dates when separations and analyses are performed by the user.

Homogeneity

The Pu-1 material was created from oxidized plutonium metal that had been extensively tested for variability of the plutonium isotopic composition and mass fraction as part of the CRM 126-A certification process. The Pu-2 oxide was created from a single volume of plutonium solution that was purified, precipitated, and converted to oxide. As such the NFRM Pu-1 and Pu-2 stock materials were presumed to be homogenous for plutonium composition and trace actinides. The analytical data for uranium and americium indicate that these elements are primarily plutonium decay products formed since the NFRM materials were purified and converted to solids. As such, they should be homogenously distributed within the oxides. Measurement data consistently show 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 indicate that much of ^{238}U in both materials is a contaminant. Also, the uranium isotopic data display a significant sample-to-sample variability for the abundance of ^{238}U but not for the other uranium isotopes. 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 but variable proportion of a contaminant uranium with a natural or near natural composition (hence the lack of significant effects on uranium isotopes other than ^{238}U). This contaminant could be present in the oxide itself or could also be due to processing and measurement instrument blank during characterization.

Although much of the ^{237}Np present in both materials is not associated with ingrowth since the last purification of the plutonium materials, the nuclide appears to be homogenously distributed at the resolution of the characterization and verification measurements. This is consistent with the “excess” neptunium being the result of incomplete separation from plutonium during production of the stock material, rather than the result of subsequent contamination.

Considered as a whole, the NFRM Pu-1 and Pu-2 materials are homogeneous at the 25 mg sample size for the plutonium mass fraction and isotopic composition, ^{241}Am mass fraction, ^{237}Np mass fraction and the ^{234}U, ^{235}U, and ^{236}U isotopes. The distribution of ^{238}U in both materials is heterogenous, possibly resulting in a recognizable variability in the mass fraction of uranium in NFRM Pu-1. This heterogeneity is, however, similar in magnitude to the variability between Characterization, Verification, and MBS data sets and should be encompassed in the combined components for attribute measurement variability and data-set variability that were incorporated into the reference material uncertainty budgets.

Reproducibility

Measurement reproducibility (as defined in [34]) 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 differences between ^{241}Am mass fraction measurements by IDMS and gamma spectrometry and the variability of some uranium isotope ratio and mass fraction data. To compensate for this variability, conservative uncertainty components for data-set variability were included in the budgets for the attributes. Accordingly, the reference values for the characterized attribute value are reproducible within cited uncertainties.

Traceability

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. Table 4 provides the traceability information for the reference values including the measurement method used to determine the attribute value, calibration materials used, and the SI unit to which the value is traceable.

Table 4. Attribute Traceability for NFRM Pu-1 and NFRM Pu-2 oxides

Attribute	Method[a]	Traceability	SI Unit
Pu Mass Fraction ($g\ g^{-1}$)	CPC	Sample mass: Calibrated electronic balances Coulometric calibration: CRM 126-A plutonium standard	kg
Pu Isotope-Amount Ratios (mol/mol)	TIMS	Instrument calibration: CRM 126-A plutonium standard	mol
^{241}Am Mass Fraction[b] ($\mu g\ g^{-1}$)	IDMS	Spike & sample mass: Calibrated electronic balances ^{243}Am spike calibration: DDEP evaluated half-life Instrument Calibration: CRM U010 uranium standard & CRM 137 Plutonium standard	kg
^{237}Np Mass Fraction ($\mu g\ g^{-1}$)	ICP-MS	Spike & sample mass: Calibrated electronic balances Instrument calibration: MSRH 10PPM (internal standard)	kg
U Mass Fraction[c] ($\mu g\ g^{-1}$)	IDMS	Spike & sample mass: Calibrated electronic balances ^{233}U spike calibration: CRM 112-A uranium standard Instrument calibration: IRMM 199 uranium standard	kg
U Isotope-Amount Ratios (mol/mol)	TIMS	Instrument calibration: CRM U750 uranium standard	mol

[a] Abbreviations for methods are as defined in the text.

[b] A primary calibration for activity concentration of the ^{243}Am spike was performed by the National Physical Laboratory in the United Kingdom. This value was converted to amount using the DDEP evaluated half-life for ^{243}Am [24].

[c] CRM 112-A (NBL Program Office, Oak Ridge, TN, USA) was used as a reverse spike to calibrate the LANL ^{233}U spike for amount of uranium.

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 resolution of the measurement methods used for the project. The plutonium isotope-amount ratios and the mass fractions of americium, neptunium, and plutonium appear to be homogeneous for both reference materials but there is evidence of limited heterogeneity for uranium mass fraction and isotope-amount ratios. This heterogeneity was captured in conservative uncertainty components that were applied to the reference values. Other significant sources of variability or bias for the measured attribute values were also quantified so the state of knowledge for the measured values is realistically represented by the estimated uncertainties. The characterized attributes values for NFRM Pu-1 and NFRM Pu-2 are sufficiently homogeneous, traceable, and reproducible that these materials are fit-for-purpose as nuclear forensic reference materials for measurement of trace actinides in plutonium. Further, model ages calculated from the reference values for the ^{238}Pu-^{234}U, ^{239}Pu-^{235}U, ^{240}Pu-^{236}U, and ^{241}Pu-^{241}Am parent-daughter pairs are consistent with material processing histories and with one another. Therefore, these materials may also be useful as test samples for plutonium radiochronometric measurements.

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