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Preparation of Small, Well Characterized
Plutonium Oxide Reference Materials
and Demonstration of the Usefulness of
Such Materials for Nondestructive Analysis

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by

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ABSTRACT

Calibration of neutron coincidence and multiplicity counters for passive nondestructive analysis (NDA) of plutonium requires knowledge of the detector efficiency parameters. These are most often determined empirically. Bias from multiplication and unknown impurities may be incurred even with small plutonium metal samples. Five sets of small, pure plutonium metal standards prepared with well-known geometry and very low levels of impurities now contribute to determining accurate multiplication corrections. Recent measurements of these metal standards, with small but well-defined multiplication and negligible yield of other than fission neutrons, demonstrate an improved characterization and calibration of neutron coincidence/multiplicity counters. The precise knowledge of the mass and isotopic composition of each standard also contributes significantly to verifying the accuracy of the most precise calorimetry and gamma-ray spectroscopy measurements. Because the requisite range of NDA measurements is dominated by materials that are compounds of plutonium, often with impurity admixtures, it is also necessary to perform accurate corrections for multiplication in materials whose neutron yields come from both fission and α, n reactions. This includes materials for which α ("alpha," the ratio of α, n to spontaneous-fission neutrons) is large. Multiplicity measurements must be able to measure both multiplication and α in order to determine the mass of plutonium. The value of α for the pure plutonium metal standards is essentially zero. We have now prepared five sets of small, plutonium oxide reference materials with small multiplication, similar to the metal standards, and very low or well characterized levels of impurities so that α is well known. These new materials will support the verification of neutron multiplicity measurements for which a determination of α is required in order to obtain the mass of plutonium. This report documents the benefits of the new metal reference materials for NDA measurements, the fabrication of the new oxide standards, and the preliminary verification of the reference values for these oxide standards by calorimetry.

I. INTRODUCTION

Neutron time-correlation counting has been used extensively during the past 20 years for the nondestructive analysis (NDA) of nuclear material. Advantages of the technique include the good penetrability of neutrons and the unique origin of time-correlated neutrons to (the fission of) nuclear material. Passive neutron coincidence and multiplicity counting are useful in the independent verification or NDA of the plutonium mass of an item.

Certain detector parameters such as efficiency, doubles gate fraction, and triples gate fraction must be determined in order to calibrate neutron coincidence and multiplicity counters. A multiplicity measurement in particular must use the three measured quantities (singles, doubles, and triples neutron rates) to determine three unknowns for each item: i) effective ^{240}Pu mass; ii) “alpha” (α), the ratio of α, n to spontaneous-fission neutrons; and iii) multiplication. Nonmultiplying, pure plutonium metal standards with no significant neutron yield other than that from spontaneous fission of the ^{240}Pu effective mass would be ideal for determining a multiplicity counter’s calibration: efficiency, doubles gate fraction, and triples gate fraction. Sources of ^{252}Cf are used in practice, and empirical corrections are necessary to obtain the required calibration parameters for ^{240}Pu . Reliance on the use of small plutonium metal and oxide items that are impure or not well characterized can introduce biases because of the unknown multiplication and impurity concentrations in these materials. Pure plutonium metal standards developed recently prevent these biases. Very precise NDA measurements have recently verified the reference masses of the metal standards.

Small, pure, well-characterized oxide standards would also be ideal calibration standards for multiplicity counting because of the precise knowledge of α for such materials. Five new sets of plutonium oxide standards prepared recently respond to this need.

This paper presents the recent results of calorimetry and neutron multiplicity measurements of the five sets of pure metal standards. It also describes the specification, preparation, and preliminary verification of five new sets of small, pure plutonium oxide standards with known geometries and well-known or low levels of impurities. These standards, paired with the metal standards, are designed specifically for the improved calibration and characterization of neutron coincidence and multiplicity counters for unbiased results. A previous review report on NDA standards [1] identified the need for these reference materials for neutron NDA. Another previous report documents the preparation of the pure plutonium metal standards [2].

II. STANDARDS SPECIFICATIONS

A. Impurity Limits

Impurities in plutonium can contribute to neutron emission in two ways. 1) Very small concentrations of ^{244}Cm and ^{252}Cf can yield spontaneous fission neutrons in addition to the yield from the effective ^{240}Pu content. 2) Low-Z elements can contribute to total neutron yield of plutonium metal or oxide through (α, n) reactions.

Source neutrons from pure plutonium metal arise from spontaneous fission, primarily from the even isotopes of ^{238}Pu , ^{240}Pu , and ^{242}Pu , or neutron-induced fission of the odd isotopes of ^{239}Pu and ^{241}Pu . Source neutrons from pure plutonium oxide arise both from fission and (α, n) reactions on ^{17}O and ^{18}O target nuclei. Very small concentrations of the impurities of ^{244}Cm and ^{252}Cf can also yield spontaneous fission neutrons that bias measurements of plutonium. Limits on the allowable concentrations of ^{244}Cm and ^{252}Cf calculated from basic nuclear yield data represent the isotope content that contributes 1% of the spontaneous fission neutron yield for pure weapons-grade plutonium. These are given in Table I as micrograms of impurity per gram of plutonium.

Table I. Impurity Limits for Spontaneously Fissioning Isotopes	
Isotope	$\mu\text{g/g Pu}$ (upper limit)
^{244}Cm	0.0563
^{252}Cf	0.000000260

Low-Z elements including oxygen also contribute to total neutron yield through (α, n) reactions. Energy spectra of (α, n) neutrons differ from those of fission neutrons. Therefore, the neutron detection efficiency differs for these two sources. Verifying that the multiplicity analysis determines α accurately requires standards whose contributions to the neutron energy spectrum from both fission and (α, n) reactions are well known so that accurate reference values for α can be assigned to each standard. Candidates are small (very low-multiplication) standards composed of very pure oxide or oxide with very low (or very well defined) impurity concentrations. Upper limits on the allowable concentrations of ten impurity elements were calculated using basic nuclear and atomic data with a simple stopping power model [3]. Again, each limit represents the element content that contributes 1% of the spontaneous-fission neutron specific yield for pure weapons-grade plutonium in oxide form. These limits are given in Table II.

Table II. Impurity Limits for Moisture and Elements that Produce (α,n) Neutrons	
Element	$\mu\text{g/g Pu}$ (upper limit)
Be	1
B	4
F	14
Li	61
Na	76
Mg	98
Al	214
Si	1141
Cl	1378
C	873
H ₂ O	1000

A limit for moisture (H₂O) also appears in Table II. Hydrogen moderates the neutron energy spectrum, altering the neutron detection efficiency for large samples. The reasonable (achievable in practice, with minimal impact on neutron energies because these standards are so small) limit for moisture content is given in Table II. By limiting impurities in the oxide standards and determining these impurity contents precisely, it is possible to calculate α precisely for the oxide standards.

B. Multiplication

An ideal neutron standard is nonmultiplying, but even the smallest items have some multiplication. Therefore, the sample multiplication of a calibration standard must be well known. Neutron multiplication is a complicated function of the sample composition (including impurities), density, and geometry. The best calibration standard is one with the smallest multiplication possible in order to have the minimum effect on the neutron emission rate. The least multiplying practical geometry is a thin disc. Monte Carlo simulations determine multiplication effects of plutonium metal discs of known mass and geometry. Therefore, the pure plutonium metal disk standards are reference materials for determining multiplication in a multiplicity measurement. A counter that is verified to measure multiplication with the pure metal disk standards is also verified to measure multiplication with the oxide standards. Used together with the metal standards, the oxide standards become reference materials for determining α in a multiplicity measurement.

Table III gives the target mass, diameter, and estimated thickness of PuO₂ powder for each of the three oxide standard sizes. The oxide density of 1.5 g/cm³ determines the required height of each of the three container sizes conservatively, to assure ease of fabrication in a glovebox environment.

Table III. Masses and Dimensions (Radius, Thickness) of PuO₂ in the Oxide Standards*

Nominal Pu Mass (g)	Radius (cm)	Nominal Oxide Powder Thickness (cm)
2	1.34	0.272
5	1.34	0.679
10	1.34	1.358
* Assumes 0.87 g Pu/g PuO ₂ , $\rho_{\text{oxide}} = 1.5 \text{ g/cm}^3$		

III. FABRICATION OF THE OXIDE STANDARDS

A. Purification of Starting Metal

The plutonium metal starting materials for the oxide standards originate from the same metal purification processes used to obtain starting material for the metal standards. High-purity metal is required to achieve the impurity levels described in Table II.

Electrorefining purifies bulk quantities of crude plutonium metal [4]. A typical electrorefining cell for plutonium processing operations is shown in Fig. 1. A crude batch of plutonium alloy is placed in the anode compartment of the crucible beneath a cast salt electrolyte. The cell system is heated to melt the salt and metal. Impure molten plutonium metal in contact with the positive electrode is the anode. The current that is defined by the transport of positive plutonium ions from the anode through the molten salt to the cathode determines the production rate of electrolytically purified plutonium. Reduced at the cathode, metallic plutonium settles to the bottom of the crucible in the product compartment. Purified plutonium is recovered as an annular metal ring beneath the solidified electrolyte at the conclusion of the electrorefining process.

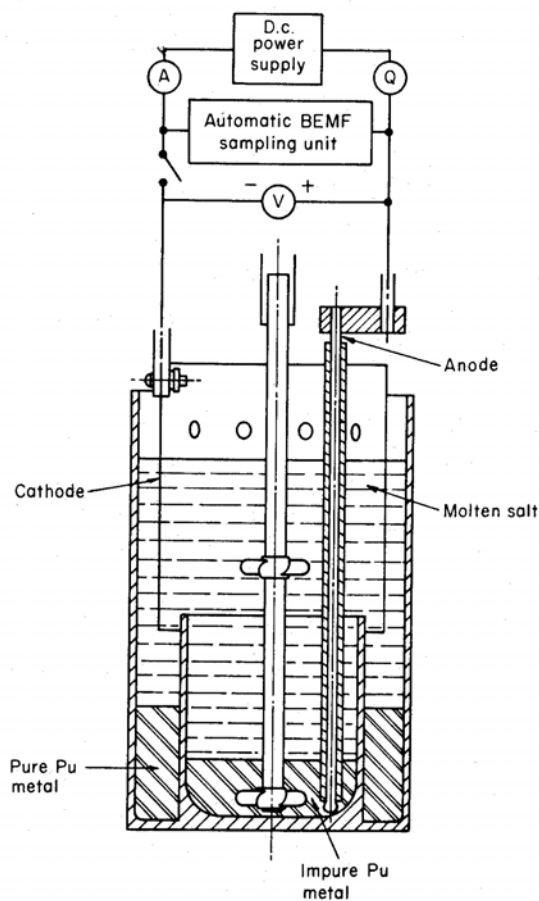


Figure 1. Schematic of electrorefining cell showing the electrodes, electrolyte (molten salt), impure plutonium metal (anode), and purified plutonium metal product. A mechanical stirrer at the center of the cell spans its vertical length.

Plutonium is an actinide metal with six allotropes. Alpha is the hardest and least ductile of the six, and delta is the softest and most ductile. The metal product of electrorefining is alpha-phase plutonium. Fabrication of the plutonium metal standards required conversion to the softest (delta) phase to minimize the risk of breakage in rolling and punching the thin metal discs. The softness and ductility of delta metal is not required for the fabrication of the plutonium oxide standards. However, conversion of alpha-phase plutonium metal to the delta-phase is a vacuum distillation process (involving the addition of gallium) that further purifies the plutonium metal. Minimizing impurities is very important for the oxide standards. The distillation is repeated three times for maximum purification. The plutonium is then cast into an ingot in the furnace shown in Fig. 2.

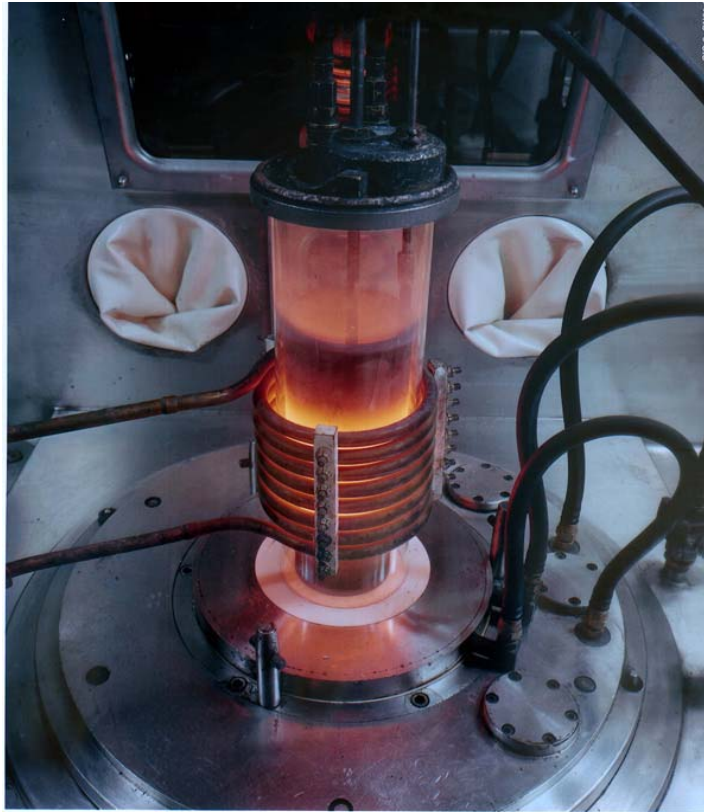


Figure 2. Furnace for casting plutonium metal into an ingot is pictured during operation.

B. Preparation of the Oxide

The purified plutonium metal is converted to oxide and then calcined at an elevated temperature. The calcined oxide is sieved and blended. Samples are taken for destructive analysis before weighing the oxide into the capsules for welding.

Processing and handling choices minimize the pickup of impurities during oxidation, calcination and subsequent mechanical handling steps. Mechanical handling and containment of the oxide was done exclusively with new equipment, tools, and containers and limited to the essential steps. All analytical samples were contained in new glass vials. Issues of impurities dictate specific requirements and procedures for oxidation and calcination.

Metal would seem to be an obvious choice of crucible material for the oxidation step. Crucible materials such as tantalum introduce no impurities that contribute to the α, n neutron yield. However, because tantalum and other metals alloy with plutonium, the surfaces of metal crucibles must be oxidized before introducing plutonium metal into the crucible. The oxides that make up all crucible surfaces, including metallic oxides such as Ta_2O_5 , WO_3 , and ceramics (MgO , SiO_2 , CaO , etc.) are stable at room temperature. Nonetheless, the thermodynamics of the oxidation reaction that forms the crucible material must be compared to that of the reaction carried out within the crucible to determine the chemical stability of the crucible material for the intended reaction.

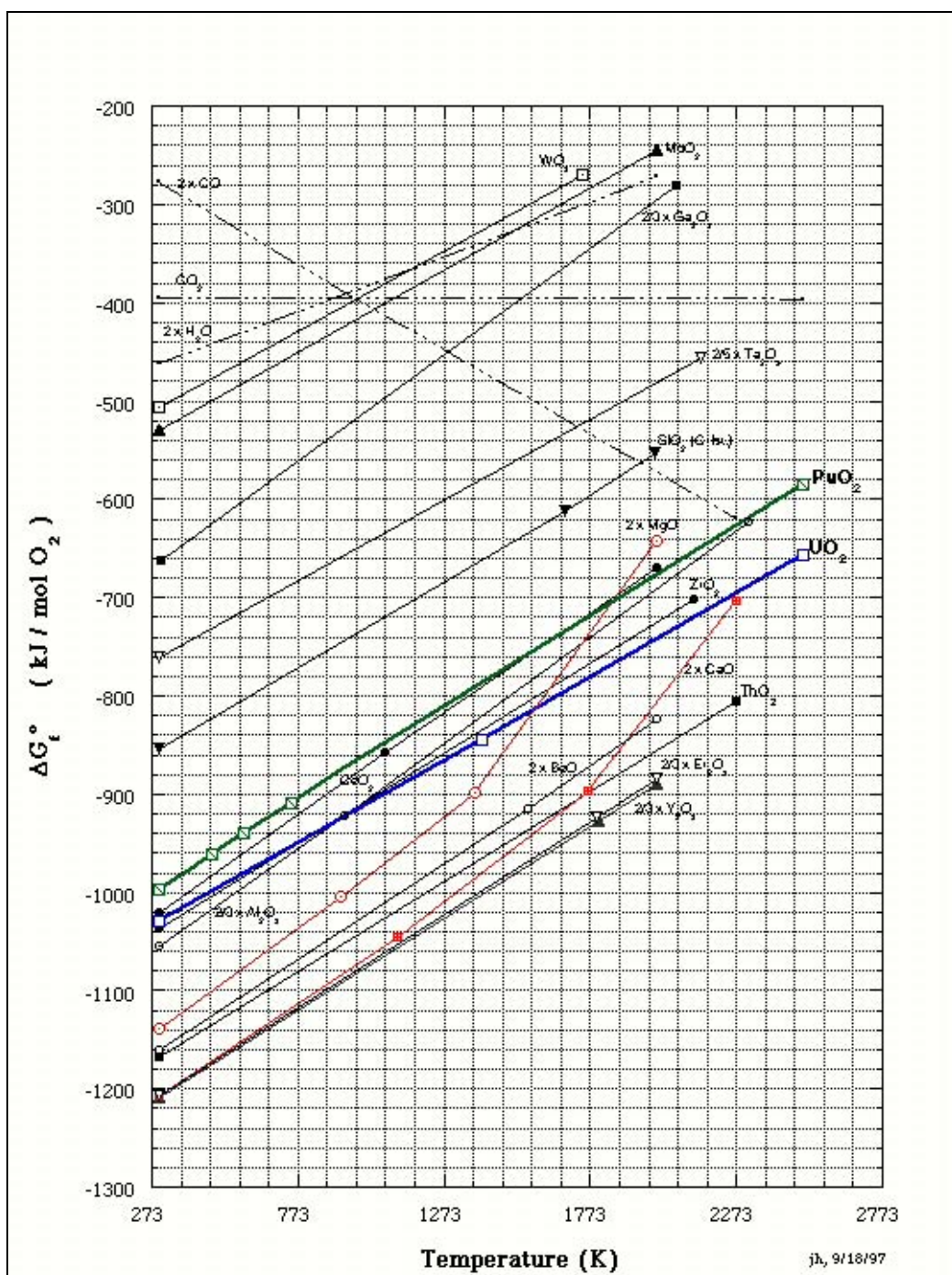


Figure 3. The free energies of oxide formation per mole of O_2 are plotted vs. absolute temperature for plutonium (green), uranium (blue) and materials, such as MgO and CaO (red), commonly involved in actinide processing.

Figure 3 is a plot of the free energies of oxide formation *per mole of O₂* for plutonium and other common materials including those of crucible surfaces. The oxides of those materials with free-energy curves above that of plutonium are thermodynamically unstable to plutonium oxidation. The resulting dissociation of these oxides during the oxidation of plutonium will introduce contaminants into the PuO₂ as it forms. Therefore, plutonium oxidation should not be carried out in materials such as Ta₂O₅, WO₃ and SiO₂. The ceramics CaO and MgO (below 1100 °C for MgO), both highlighted in red in Fig. 3, are thermodynamic options. Ceramic CaO is a better choice from the impurity standpoint. (Calcium does not contribute to the α, n neutron yield.) Because the CaO ceramic is more fragile than MgO and dissolves in some molten pyrochemical salts, CaO crucibles were not on hand. Despite the potential for magnesium to contribute to the α, n neutron yield, a ceramic MgO crucible was used to oxidize the pure plutonium metal and calcine the oxide.

Oxidation of the pure metal was performed at 430 °C to avoid melting the plutonium metal before complete conversion. Complete conversion required two eight-hour periods—two hours to ramp up to temperature, four hours at 430 °C, and two hours to cool. Unknown to the project team at the time is that the oxide was rolled and sieved in common equipment (a departure from the procedure) between the two oxidation steps. The use of common equipment is likely to result in contamination of the oxide.

Subsequently calcining the oxide by the “ramp-and-soak” method —raising its temperature slowly (in five hours) to 950–1000 °C, firing at this temperature for two hours, and cooling slowly (in five hours)—reduces its susceptibility to moisture pickup. The converted oxide was calcined by this method in the same MgO crucible used to oxidize it.

A 40-mesh screen removed 15% of the oxide mass from the remaining bulk. The 85% “fines” powder was blended in a polyethylene container. Sampling and weighing of the blended powder into the certified capsules followed immediately. The weighing steps were complete within two days of the start of calcining. The oxide material remained in a dry-argon glovebox from the time of completion of the calcining to the welding of the standards.

C. Mitigating Moisture Issues

Issues of moisture dictate specific requirements and procedures beyond oxidation and through the first steps of fabricating the encapsulated standards and performing measurements on the analytical samples.

Low moisture content is targeted for the standards. It is most important that the standards and analytical samples have the same moisture content. Steps for fabricating the standards and handling the oxide adhered to the following mandates for minimizing moisture pickup and assuring uniform moisture content in the standards and the analytical samples:

- Convert metal to oxide in a dry-air glovebox environment.
- Elevate the oxide temperature (950–1000 °C) for an extended calcination period.
- Minimize the time between calcining and both the sampling and weighing steps.
- Perform all handling and fabrication steps after calcining in a dry-argon atmosphere.

- Sample the bulk oxide and determine volatile content by measuring loss (in mass) on ignition (LOI) at the time of fabrication of the standards.
 - Minimize time between the sampling and moisture-measurement steps.
 - Use new glass vials for all analytical samples.
 - Use fused-glass seals for archival samples.
 - Obtain the net weight of oxide and the gross weight of sealed vial for each analytical sample.
 - Store analytical samples in dry argon until they are transferred for destructive analysis.
- Additional mandates for the analysis of samples further reduce moisture or mitigate moisture issues:
- Compare gross weights of the analytical samples received to those of the shipped vials.
 - Measure the LOI of each analytical sample received.
 - Minimize time between LOI measurements and plutonium assay (g Pu/g) of samples.



Figure 4. Set C (of the five sets) of encapsulated plutonium oxide standards is pictured. The outer diameter and height of each capsule is 3.2 and 4.2 cm, respectively. The identification numbers were etched onto the individual capsule parts prior to assembly and welding.

IV. SAMPLING AND ANALYSES TO OBTAIN REFERENCE VALUES

Five five-gram samples for destructive chemical analysis were taken from different parts of the bulk. Each was analyzed independently by the Los Alamos analytical chemistry group. The mean of the five analysis results is the reference value. The standard deviation includes any effects of inhomogeneity of the bulk material. Each sample was sealed in a glass tube, and each sealed tube

was weighed prior to removal from the glovebox for transfer to the analytical chemistry group. The sampling, packaging, and weighing were performed in a dry-argon atmosphere.

Five two-gram archive samples were taken from different parts of the bulk. Each sample was sealed in a glass tube, and each sealed tube was weighed prior to removal from the glove box for storage. The sampling, packaging, and weighing were performed in a dry-argon atmosphere.

Two ten-gram samples were also taken from different parts of the bulk for moisture analysis at the Los Alamos Plutonium Facility by measuring LOI. The LOI result measures volatiles, giving an upper limit on the moisture content. Each LOI sample was sealed in a glass tube prior to transfer to the LOI glove box. The sampling and packaging were performed in a dry-argon atmosphere. Each LOI sample was split in two parts and the LOI measurement was performed on each. The mean LOI result, $331 \pm 23 \text{ } \mu\text{g/g Pu}$, is compared to LOI results obtained two months later by the analytical chemistry group (refer to IV.B).

The Los Alamos analytical chemistry group used multiple techniques to measure the five samples.

- Mass spectrometry for plutonium isotopic distribution, and gamma-ray counting for ^{241}Am . These results are in Table IV.
- Alpha spectrometry for the spontaneously fissioning isotopes ^{244}Cm and ^{252}Cf . These results are in Table V.
- Various techniques for the impurity elements listed in Table II: Be, B, F, Li, Na, Mg, Al, Si, Cl, and C. These results are in Table VI.
- Measurements of LOI for volatiles, including moisture. These were performed at the time of the dissolution of samples for Coulometric titration. The results are in Table VI.
- Coulometric titration for plutonium assay (g Pu/g sample). The results are in Table VII.

A. Isotopic Distribution

Table IV gives the destructive analytical results for isotope mass fractions of the five oxide samples. Mass spectrometry measured the ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu and ^{242}Pu fractions, and gamma-ray counting determined ^{241}Am . The ^{241}Am was reported as the fraction of the oxide mass. This result, divided by the mean result for plutonium mass fraction (g Pu/g sample, Table VII) gives the fraction of ^{241}Am relative to plutonium mass, as reported in Table IV.

Table IV. Reference values for isotope mass fractions as of 5/23/2002						
Sample ID	²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu	²⁴¹ Am*
7675AS	0.0116	93.9802	5.8321	0.1347	0.0413	197.5
7675BS	0.0111	93.9828	5.8297	0.1351	0.0413	196.3
7675CS	0.0123	93.9813	5.8302	0.1352	0.0409	202.0
7675DS	0.0113	93.9841	5.8286	0.1347	0.0412	203.2
7675ES	0.0115	93.9836	5.8287	0.1350	0.0411	205.5
Mean	0.0116	93.9824	5.8299	0.1349	0.0412	200.9
1σ mean	0.0002	0.0007	0.0006	0.0001	0.0001	1.7
* $\mu\text{g/g Pu (5/23/02)}$						

B. Impurity Determination

Alpha spectroscopy measures the content of spontaneously fissioning impurities ²⁴⁴Cm and ²⁵²Cf. Table V gives these results. The measured ²⁴⁴Cm conforms to its specified upper limit from Table I. Alpha spectroscopy is not sensitive enough to measure ²⁵²Cf at the level of the desired limit.

Table V. Measured impurities: spontaneously fissioning isotopes		
Isotope	$\mu\text{g/g Pu (upper limit)}$	$\mu\text{g/g Pu (measured)}$
²⁴⁴ Cm	0.0563	<0.03
²⁵² Cf	0.000000260	<0.005

The upper limit for each impurity element in Table II is also given in column 2 of Table VI alongside the measured impurity content in column 3. The standard deviation in the mean of the five sample analysis results is indicated in column 3 when the analysis sensitivity is sufficient to yield an absolute impurity fraction. Only the limiting sensitivity of the analytical technique is reported in column 3 when the analysis sensitivity is not sufficient to yield an absolute impurity fraction. Column 4 indicates the method of impurity analysis. The measured concentration of each impurity including the measured (upper limit on) moisture is less than the specified upper limit except for fluorine, which exceeds the upper limit by a factor of 20. The fluorine content is well established, however, because the relative standard deviation in the mean fluorine content is 1%.

Table VI. Measured impurities^a: moisture and elements that produce (α,n) neutrons			
Element	$\mu\text{g/g Pu}$ (upper limit)	$\mu\text{g/g Pu}$ (measured)	Method
Be	1	<0.2	ICP-MS*
B	4	2.0 ± 0.7	ICP-MS*
F	14	289 ± 3	IC***
Li	61	<2	ICP-MS*
Na	76	<29	ICP-AES**
Mg	98	15 ± 4	ICP-AES**
Al	214	4.3 ± 1.3	ICP-MS*
Si	1141	<23	ICP-AES**
Cl	1378	23 ± 12	IC***
C	873	18 ± 3	Combustion – IR
H ₂ O	1000	$<620 \pm 78$ ****	Combustion – LOI
^a Impurities were measured and reported as the fraction of the oxide mass. This result, divided by the mean result for plutonium mass fraction (g Pu/g sample, Table VII) gives the impurity fraction relative to plutonium mass that is listed here. * Inductively coupled plasma – mass spectroscopy ** Inductively coupled plasma – atomic emission spectroscopy *** Ion Chromatography **** Measured on 5/20/02			

The measured upper limit of $620 \pm 78 \mu\text{g/g Pu}$ for moisture is listed in Table VI. While less than the prescribed limit of $1000 \mu\text{g/g Pu}$ for moisture, it exceeds that measured at the time/location of fabrication of the standards ($331 \pm 23 \mu\text{g/g Pu}$) by nearly a factor of two. This incremental amount ($289 \pm 78 \mu\text{g/g Pu}$) is likely to represent additional moisture (relative to the standards) and not another volatile component in the analytical samples. This increment is the source of a very small ($\sim 0.03\%$) negative bias in the reference value for plutonium mass fraction.

C. Coulometric Assay

Table VII gives the plutonium mass fractions determined by Coulometric titration of the oxide samples. The standard deviation in the five assay results (0.02% relative standard deviation) is within the relative precision of 0.1% reported for Coulometry.

Table VII. Plutonium assay (g Pu/g oxide)	
Sample ID	Pu mass fraction (%) 5/20/02
7675AS	87.13
7675BS	87.10
7675CS	87.11
7675DS	87.09
7675ES	87.12
1 σ	0.016
Mean \pm 1 σ_{mean}	87.110 \pm 0.007

D. Traceability

The analysis methods for plutonium assay and isotopics are based on standards certified by New Brunswick Laboratory. The routine analytical procedures include measurements of certified standards.

V. CONTAINERS AND ENCAPSULATION

The capsules for the standards are nested stainless steel cylinders, certified by the American National Standards Institute (ANSI). Figure 8 is a drawing of the capsule. Figure 9 is a photograph of the disassembled capsule parts. The alternative dimensions of the retaining cylinder are illustrated by the three examples included for this piece. An ANSI-certified welder performs the capsule welding in a helium-atmosphere glovebox.

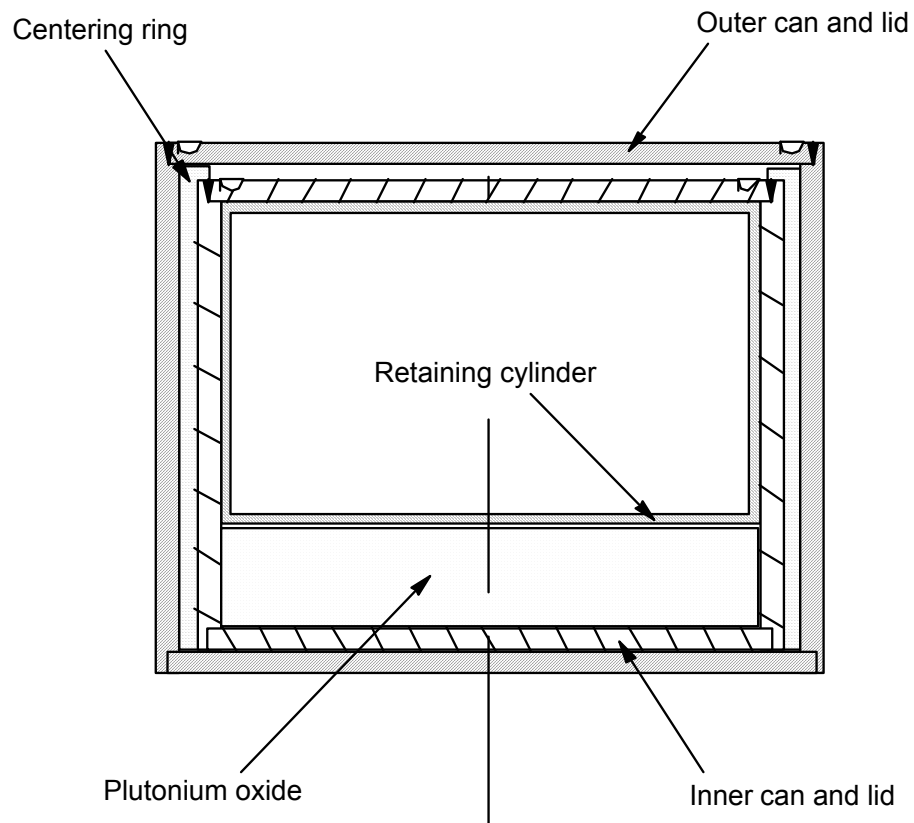


Figure 5. Drawing of the stainless steel container for the oxide standards. Three different retaining- cylinder heights accommodate the thickness of the three nominal PuO_2 masses (Table III). Welds are indicated for inner and outer cans.



Figure 6. Photograph of stainless steel capsule parts. The “inner can” is at the right. Its “lid” is one of the three “retaining cylinders” (center). The “outer can” and its “centering ring” and “lid” (top to bottom) are at the left.

VI. MASS DETERMINATION

The plutonium oxide masses for the standards were weighed using an analytical balance accurate to 0.0001 g. The analytical balance was checked with weights in the range of 1–10 g that are certified by the National Institute of Science and Technology. The oxide masses are listed in the second column of Table VIII. The plutonium mass of each standard is obtained by multiplying the oxide mass by the average plutonium assay (g Pu/g oxide) listed in Table VII.

Table VIII. Determination of Plutonium Mass in Oxide Standards (5/20/02)

Oxide Standard ID	Oxide Mass (g) ± 0.0007 g	Plutonium Mass (g)	Relative error* (%)	Absolute error (g)
A1	2.301	2.0044	0.054	0.0011
A2	5.702	4.9670	0.047	0.0023
A3	11.413	9.9419	0.045	0.0045
B1	2.295	1.9992	0.054	0.0011
B2	5.705	4.9696	0.047	0.0023
B3	11.409	9.9384	0.045	0.0045
C1	2.298	2.0018	0.054	0.0011
C2	5.706	4.9705	0.047	0.0023
C3	11.405	9.9349	0.045	0.0045
D1	2.302	2.0053	0.054	0.0011
D2	5.702	4.9670	0.047	0.0023
D3	11.411	9.9401	0.045	0.0045
E1	2.300	2.0035	0.054	0.0011
E2	5.703	4.9679	0.047	0.0023
E3	11.399	9.9297	0.045	0.0045
* Based on the uncertainty in the oxide mass and expected precision of 0.045% in Coulometry mean.				

VII. PROCEDURE FOR USE OF THE OXIDE STANDARDS

The primary purpose of the plutonium metal and oxide standards is for better determination of certain neutron detector parameters required for calibrating neutron coincidence and neutron multiplicity analysis of plutonium-bearing materials. Some of the basic concepts of neutron coincidence and multiplicity counting must be defined in order to define procedures for uses of the standards. Refer to Ref. 5 and the references therein for an introduction to neutron coincidence

counting. An introduction to neutron multiplicity counting is given in the application guide [6] and the references therein.

There are two measured multiplicity distributions (0s, 1s, 2s, 3s, 4s, 5s, etc.) of neutron pulses: the multiple counts in the “real-plus-accidental” (R+A) gate and the “accidental” (A) gate. The two distributions are the same within statistical errors for a purely random (in time) pulse stream. A time-correlated pulse stream with fission neutron pulses has more higher order multiplicity events in the R+A distribution than in the A distribution. Analysis algorithms in the INCC [7] software analyze the two distributions to obtain the number of time-correlated double, triple, and quadruple pulses, etc. The term “doubles” (D) refers to the number of correlated pulse pairs in the pulse stream; “triples” (T) indicates the number of correlated triplets; “singles” (S) designates the total number of neutron counts. In practice, triple events are usually the highest correlations that can be obtained with reasonable statistical precision. A standard shift register circuit determines S and D but cannot determine T. A multiplicity shift register determines S, D, and T.

The neutron source multiplicity distribution is the neutron multiplicity probability distribution per event. An event for plutonium oxide can be, for example, a ^{240}Pu spontaneous fission or an (α, n) reaction on ^{17}O followed by a neutron-induced fission of ^{239}Pu . This example highlights some of the many variables associated with the composition of plutonium-bearing materials that affect the neutron source multiplicity distribution. It emphasizes the usefulness of small oxide samples that are very well characterized—determining the fundamental response of a multiplicity counter using a neutron source with a known multiplicity distribution. Passive neutron multiplicity analysis (PNMA) uses factorial moments of the measured multiplicity distribution of neutrons from spontaneous- and induced-fission and from (α, n) reactions.

The background-corrected rates S, D, and T for a plutonium oxide sample with a very small mass are given by

$$S = F\varepsilon\nu_{s1}(1+\alpha), \quad (1)$$

$$D = \frac{1}{2}F\varepsilon^2 f_d \nu_{s2}, \text{ and} \quad (2)$$

$$T = \frac{1}{6}F\varepsilon^3 f_t \nu_{s3}, \quad (3)$$

where

F = the rate of source (spontaneous-fission) events,

α = ratio of (α, n) to spontaneous-fission neutrons,

ε = detector efficiency,

f_d, f_t = double and triple gate fractions, and

$\nu_{s1}, \nu_{s2}, \nu_{s3} = 1^{\text{st}}, 2^{\text{nd}}, \text{ and } 3^{\text{rd}}$ factorial moments of the neutron (spontaneous-fission) source distribution.

The gate fractions account for the fact that the R+A gate is not open long enough to count all the correlated neutrons.

Ideally, an analysis based on the doubles counts should provide a unique signature for plutonium and should also determine the effective mass of ^{240}Pu in the sample. The effective mass of ^{240}Pu is the mass of ^{240}Pu that gives the same D response as the D produced by all of the even isotopes (the ^{240}Pu -effective) in the sample:

$$^{240}\text{Pu}_{\text{eff}} = 2.52^{238}\text{Pu} + ^{240}\text{Pu} + 1.68^{242}\text{Pu} . \quad (4)$$

The total plutonium mass is then obtained from the plutonium isotopic composition:

$$^{\text{Total}}\text{Pu} = ^{240}\text{Pu}_{\text{eff}} / (2.52c_{238} + c_{240} + 1.68c_{242}) , \quad (5)$$

where c_{238} , c_{240} , and c_{242} are mass fractions of the corresponding plutonium isotopes in the sample.

The parameters that are obtained by using the small plutonium oxide standards are, in order, ε , f_d , and f_t , using equations (1) – (4),

where

$$F = ^{240}\text{Pu}_{\text{eff}} 473.5 , \quad (6)$$

$$\varepsilon = S / (F \nu_{s1} (1 + \alpha)) , \quad (7)$$

$$f_d = 2\nu_{s1}D / (\varepsilon\nu_{s2}S) , \text{ and} \quad (8)$$

$$f_t = 3f_d\nu_{s2}T / (\varepsilon\nu_{s3}D) . \quad (9)$$

The parameters ν_{s1} , ν_{s2} , and ν_{s3} , respectively, are 2.154, 3.789, and 5.211.

The parameters in Eqs. (7) – (9) are obtained for all three standards in a given set. The results are extrapolated back to zero mass to obtain the final values. Equation (7) requires a value for α . A calculated value of α for these standards is 1.76. Fluorine, not oxygen, is the primary contributor.

The quantities f_d and f_t should be determined with a precision from counting statistics of 0.5% or better. This will require a minimum of 3-hour counts per standard in a detector with $\varepsilon = 50\%$.

The results for ε , f_d , and f_t obtained using the three oxide standards with a known α value should match those obtained with the metal standards for a given multiplicity counter. A first test of models on which the multiplicity analysis is based is to calibrate with both sets of standards: the small oxide standards (with known α) and the small metal standards.

VIII. VERIFICATION RESULTS AND WORKING EXAMPLE OF UTILIZATION

A. Metal Standards

Calorimetry was used to verify the reference plutonium masses of 12 of the metal standards (only of four of the five sets because the fifth set was transferred to the end user before these measurements were made). The new 5-cm-diameter solid-state calorimeter measured the heat produced by each sample. This high-sensitivity calorimeter has a signal-to-noise ratio equivalent to that of its predecessor of similar design [8]. The calorimeter calibration is based on NIST-traceable ^{238}Pu heat standards. The isotopic distribution from mass spectrometry (coupled with gamma-ray spectrometry for ^{241}Am determination) gives the specific power used to obtain the calorimetry result for plutonium mass of each of the 12 standards.

These verification data are plotted in Figure 7 as the ratio of the reference mass to the calorimetry result vs. reference mass. Each data point is the average result of the five to seven calorimetry measurements performed on each standard. Each error bar is the standard deviation in the mean of the multiple measurement results. There is no apparent bias, and the relative standard deviation in the 12 ratios is 0.10%. This standard deviation includes calorimetry uncertainty. It also includes weighing uncertainty, sampling effects, uncertainties in the analytical chemistry and mass spectrometry measurements, and sample contamination effects. The calorimetry accuracy is 0.1%. Therefore, these results indicate that all sources of error besides calorimetry uncertainty are smaller than 0.1%.

Gamma-ray spectroscopy using the FRAM isotopic analysis [9] verified the reference isotopic distributions of the fifteen metal standards. The agreement with the reference isotopics from mass spectrometry is illustrated by the following comparison. The heat measurements from calorimetry were reinterpreted with the FRAM isotopic distribution results for specific power. The mean plutonium mass ratio (reference/calorimetry) using FRAM results for specific power is 1.0015 compared to 0.9995 obtained with the calorimetry data (see Fig. 7) based on specific power from mass spectrometry. The relative standard deviation in the 12 ratios using FRAM results for specific power is 0.10%, the same as that obtained with the calorimetry data based on specific power from mass spectrometry. The two mean results agree within the summed standard deviations.

Neutron multiplicity counting provides a working example of utilization of the standards. The 64%-efficient epithermal neutron multiplicity counter (ENMC, Ref. 10) measured the plutonium masses of the fifteen plutonium metal standards. The calibration of the ENMC was set by the standards themselves. The effective ^{240}Pu mass measured by the ENMC was interpreted using the mass spectrometric results for isotopic distribution to determine the plutonium mass of each of the 15 standards.

The multiplicity data are plotted in Figure 8 as the ratio of reference mass to the ENMC result vs. reference mass. The overall bias is effectively zero as the calibration is established using these materials. A small, mass-dependent systematic effect contributes to the relative standard deviation of 0.21% in the 15 ratios. The source of this effect has not yet been determined. However, it is important to note that no previous NDA reference materials are sufficiently pure and well characterized to measure effects of this magnitude.

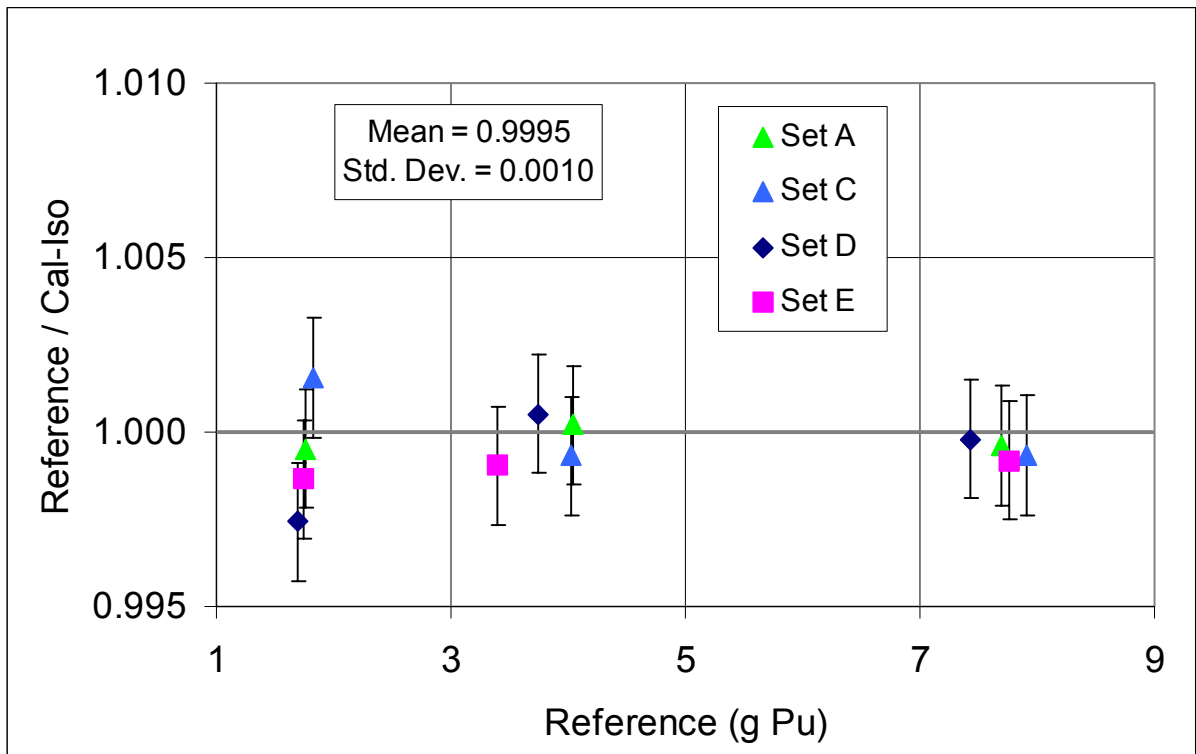


Figure 7. The ratio of the reference value for plutonium mass of each of 12 pure plutonium metal standards to the calorimetry result for plutonium mass is plotted vs. the reference value. The relative standard deviation of 0.10% matches the calorimetry accuracy, indicating that other contributions to the uncertainty in the plutonium mass (analytical chemistry uncertainty, sampling effects, contaminants) are smaller than 0.1%.

B. Oxide Standards

Measurements with the new 5-cm-diameter solid-state calorimeter to verify the reference plutonium masses of the five sets of small plutonium oxide standards are in progress. Preliminary results indicate that the reference values for plutonium mass are lower than the calorimetry result by approximately $0.5 \pm 0.1\%$. This consistent discrepancy is far too large to be caused by contamination or moisture effects. The magnitude of the possible moisture effect was measured to be a factor of 16 less than the observed discrepancy (0.03% compared to 0.5% for the discrepancy. Refer to IV.C). Furthermore, these NDA measurements have been performed using the same calorimeter that was used to verify the plutonium metal standards with the results summarized in VII.A. The plutonium metal standards have been measured for control purposes throughout the period in which the calorimetry measurements have been performed on the oxide standards.

Measurements of the oxide standards with the ENMC will begin soon.

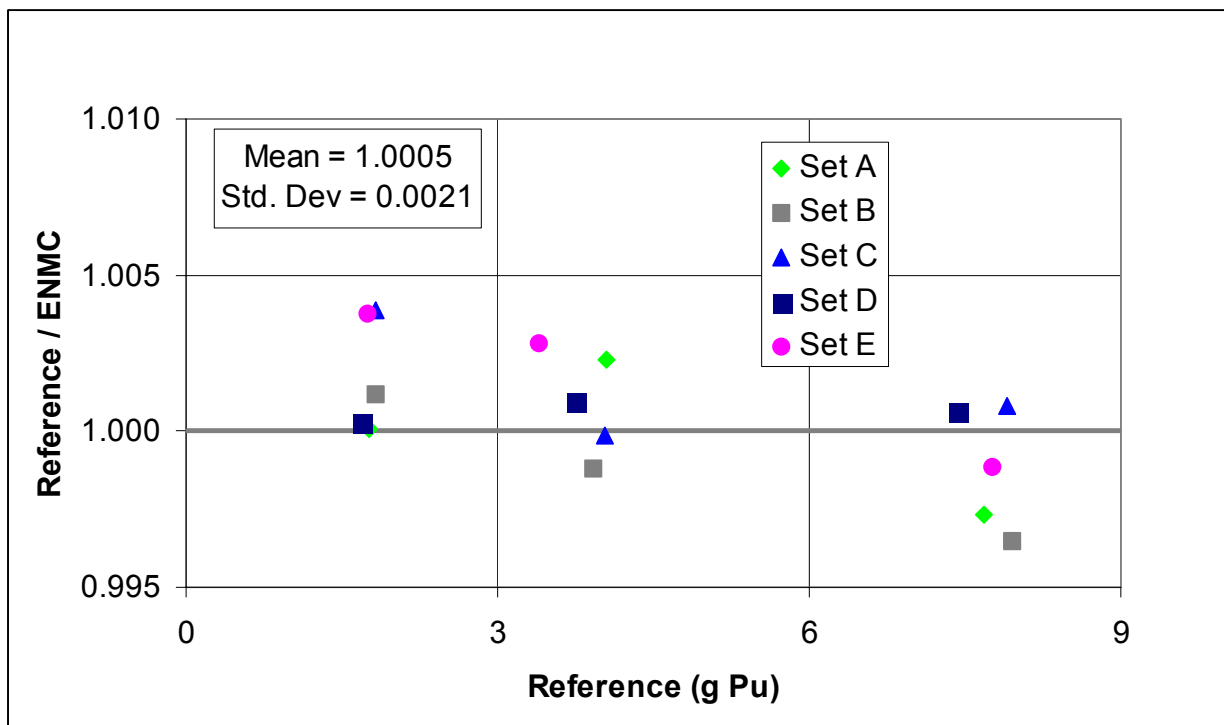


Figure 8. The ratio of the reference value for plutonium mass of each of 15 pure plutonium metal standards to the ENMC result for plutonium mass is plotted vs. the reference value. A small, mass-dependent systematic effect contributes to the relative standard deviation of 0.21%.

IX. SUMMARY AND RECOMMENDATIONS

The preparation of five sets of small, well-characterized plutonium oxide standards is complete. The fabrication of these materials is more complex than that of the small plutonium metal standards because of considerations related to additional chemical (oxidation) and physical (calcining) treatment and mechanical handling (sieving, blending) not required in the fabrication of the metal standards. Constraints added to the fabrication processes to minimize the impact of these extra procedures on the purity and characterization of the standards were successful for the most part.

Although the desired purity was not achieved for one important element (fluorine, present in the standards with a concentration of $289 \pm 3 \mu\text{g F/g Pu}$), the measured concentration of every other impurity—including moisture—with a designated concentration limit is well below the prescribed upper limit. The empirical result for moisture pickup between the time of standards fabrication and the time of dissolution of samples for destructive analysis was less than 0.03%, which becomes a known negative bias in the reference values reported (in Table VIII) as the plutonium mass of each standard.

The origin of the unexpectedly high fluorine content is uncertain. The possibility of the presence of a CaF_2 coating on the surface of the MgO crucible¹¹ was considered and dismissed. The specification on the composition of MgO ceramic crucibles at the facility does not include calcium or fluorine, and the facility itself does not apply a CaF_2 coating to magnesia crucibles. Analysis of the highly pure metal starting material performed after analysis of the oxide samples was complete gave a fluorine concentration of $45 \pm 5 \mu\text{g F/g Pu}$ for the starting metal. This is higher than the prescribed upper limit for the fluorine content ($14 \mu\text{g F/g Pu}$) in the standards but is lower by a factor of 6.4 than the very high fluorine concentration measured in the oxide samples. Because the measured fluorine content is well characterized and uniform ($1\sigma_{\text{mean}} = \pm 1\%$) among the five analytical samples of the oxide, the usefulness of the standards for neutron multiplicity counting may be impacted very little by the fluorine discrepancy.

It is likely that the fluorine contamination occurred during the rolling and sieving of the oxide that was carried out by the operator between the two oxidation steps. (Refer to Section III.B.) This practice is routinely performed to assure complete conversion in the second oxidation step. Unfortunately, the operator was not aware of contamination issues, and the project team was unaware of this routine procedure between the two conversion steps. Because conversion of metal to oxide is typically performed on the less pure “dross” (surface metal) and metal that adheres to processing hardware from a casting, the common equipment used to roll and sieve (roller, tray, and sieve) is contaminated with salts. The salts include CaF_2 that lines graphite molds.

The high costs of the chemical, physical, and mechanical steps involved in preparing the oxide add to the significant expenses of sampling, weighing the oxide, welding the capsules, and analyzing the samples. These latter costs substantiate interim sampling/analysis steps in the preparation of oxide standards. Concurrent analysis of impurities in three interim samples—taken from the 1) purified metal, 2) calcined oxide and 3) physically and mechanically treated oxide—is both justified and essential for future efforts to prepare very pure oxide for standards.

The high uniformity ($1\sigma = \pm 0.1\%$) in the ratio of the calorimetry verification result to the reference value for plutonium mass of the 15 oxide standards is consistent with the results obtained with the metal standards. It is also consistent with the best expectations for the variety of uncertainties (calorimetry precision, as well as weighing uncertainty, sampling effects, uncertainties in the analytical chemistry and mass spectrometry measurements, and sample-contamination effects) that contribute to this overall uncertainty. The current discrepancy of $\sim 0.5 \pm 0.1\%$ between calorimetry (the verification results) and the reference values for plutonium mass of the standards is an important issue that must be resolved in order for these materials to be useful as NDA standards.

Chemical effects have been considered as a possible source of positive bias in calorimetry. No reasonable chemical mechanism has been identified to date. Calorimetry measurements of the oxide standards will continue for an extended period (along with measurements of the metal standards as control references) to determine if the bias between calorimetry and the reference result for the oxide standards decreases.

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REFERENCES

1. S. -T. Hsue, J. E. Stewart, T. E. Sampson, G. Butler, C. R. Rudy, and P. M. Rinard, "Guide to Nondestructive Assay Standards: Preparation Criteria, Availability, and Practical Considerations," Los Alamos National Laboratory report LA-13340-MS (October 1997).
2. S. -T. Hsue, J. E. Stewart, and M. S. Krick, "Preparation of Pure Plutonium Metal Standards for Nondestructive Assay," Los Alamos National Laboratory report LA-13760-MS (2001).
3. Mojtaba Taherzadeh, "Neutron Characteristics of Plutonium Dioxide Fuel," National Aeronautics and Space Administration (NASA) Technical Report 32-1555, rev. 1, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (December 1, 1972).
4. L. J. Mullins, J. A. Leary, A. N. Morgan, and W. J. Mariman, "Plutonium Electrorefining," Los Alamos Scientific Laboratory report LA-2666 (1962).
5. D. T. Reilly, N. Ensslin, H. A. Smith, Jr., and S. Kreiner, "Passive Nondestructive Assay of Nuclear Materials (PANDA) Manual," NUREG/CR-5550 (US Government Printing Office, Washington, D.C., 1991). Los Alamos National Laboratory document LA-UR-90-732 (1991).
6. N. Ensslin, W. C. Harker, M. S. Krick, D. G. Langner, M. M. Pickrell, and J. E. Stewart, "Application Guide to Neutron Multiplicity Counting," Los Alamos National Laboratory report LA-13422-M (November 1998).
7. W. C. Harker and M. S. Krick. "INCC Software Users Manual," Los Alamos National Laboratory document LA-UR-99-1291 (July 1998).
8. D. S. Bracken and P. A. Hypes, "Solid-State Calorimeter," Los Alamos National Laboratory document LA-UR-00-3087. (Proceedings of the 41st Annual Meeting of the Institute of Nuclear Material Management, New Orleans, LA, July 16-20, 2002, paper no. 000063.)
9. T. E. Sampson, T. A. Kelley and D. T. Vo, "Improvements in PC/FRAM Isotopic Analysis Software," Proceedings of Sixth International Conference, Facility Operations – Safeguards Interface, Jackson Hole, WY, September 20-24, 1999, pp. 206-211.
10. J. E. Stewart, H. O. Menlove, D. R. Mayo, W. H. Geist, L. A. Carrillo and G. D. Herrera "The Epithermal Neutron Multiplicity Counter Design and Performance Manual: More Rapid Plutonium Inventory Verifications by Factors of 5-20," Los Alamos National Laboratory report LA-13743-M (August 2000).
11. J. J. Katz, G. T. Seaborg and L. R. Morss, "The Chemistry of the Actinides," Volume I, Second Edition, New York: Chapman and Hill, 1986, p. 620.

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