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Importance of ^{241}Am Determination in the Characterization of PuO_2 Standards for Calorimetric Assay

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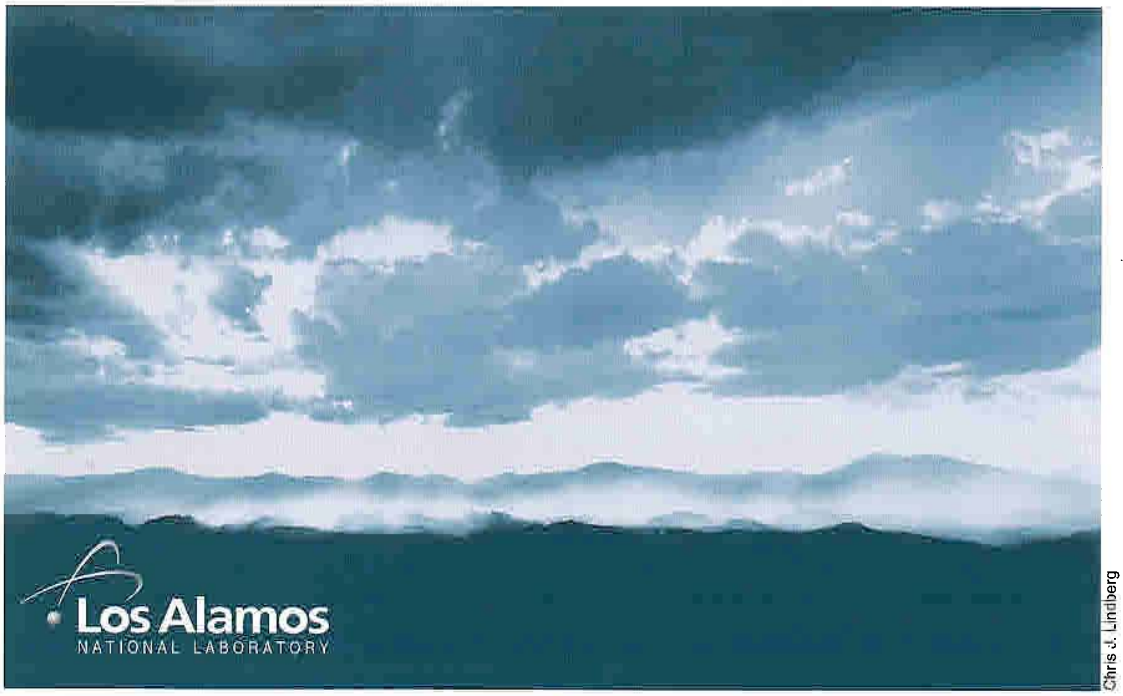

Importance of ^{241}Am Determination in the Characterization of PuO_2 Standards for Calorimetric Assay

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ABSTRACT

Plutonium dioxide (PuO_2) standards are often used both as heat standards and isotopic standards for calorimetric assay. Calorimetric assay is the combination of the power in watts measured in a calorimeter with the effective specific power (P_{eff}) in watts/g Pu, determined either by nondestructive gamma-ray assay or by destructive mass spectrometry, to yield the total elemental plutonium mass in the sample. To use a PuO_2 sample as a heat standard for calorimetry, one must determine both the plutonium mass and P_{eff} with very small uncertainties and then calculate the sample watts from the known plutonium mass, specific powers, and isotopic composition.

Well-characterized PuO_2 standards have plutonium mass values determined by analytical chemistry with a precision and accuracy on the order of 0.1%–0.2 % relative to the total mass of the sample. Mass spectrometry, typically used to determine the isotopic fractions of plutonium standards, is very accurate and precise for the major isotopes but is somewhat less precise for low-abundance isotopes. The characterization of the $^{241}Am/Pu$ ratio in the standard is also of great importance because ^{241}Am can contribute significantly to P_{eff} and to the heat output of the standard. The determination of the $^{241}Am/Pu$ ratio in a plutonium-bearing sample is a process that is less standardized than mass spectrometry. There are no certified reference materials (CRMs) traceable to the national measurement system for ^{241}Am in plutonium, and routine analytical $^{241}Am/Pu$ ratio measurements often exhibit uncertainties of several percent relative to the total plutonium or greater.

The usefulness of a PuO_2 standard for calorimetric assay is seriously degraded if the ^{241}Am concentration has a large uncertainty. The discussion in this paper quantifies the effect of the ^{241}Am characterization uncertainty on the total uncertainty of P_{eff} and suggests target values for ^{241}Am uncertainty required to characterize PuO_2 materials used for calorimetric assay standards.

Introduction

Plutonium dioxide (PuO_2) standards are often used both as heat standards and isotopic standards for the calorimetric assay of plutonium. Equation 1 displays how calorimetric assay obtains the plutonium mass by combining the power in watts (measured in a calorimeter) with the effective specific power determined either by nondestructive gamma-ray isotopic analysis or by destructive mass spectrometry.

$$M = \frac{W}{P_{eff}}, \qquad (1)$$

M is the plutonium mass in grams, W is the measured sample power in watts, and P_{eff} is the effective specific power in watts/g Pu. The effective specific power is determined from the sum over all heat-producing isotopes.

$$P_{eff} = \sum_i P_i * f_i, \qquad (2)$$

P_i is the specific power in watts/g isotope for isotope i and f_i is the mass fraction of isotope i relative to total plutonium. Note that ^{241}Am is included in this sum because it is present in most plutonium samples and produces a significant amount of heat. Small amounts of americium can contribute significantly to the total heat produced by a PuO_2 item because americium has a very high specific power compared to plutonium isotopes. For example, in typical low burnup plutonium with 6% ^{240}Pu and 0.3% ^{241}Am, the ^{241}Am contributes approximately 13% of the total power. For this reason, the ^{241}Am/Pu ratio must be accurately and precisely known in a plutonium-bearing sample used as a standard for calorimetric assay. The remainder of this paper will quantify the effect that errors have in the ^{241}Am/Pu ratio have on P_{eff}.

Calorimetric Assay Data

The accepted values for the specific powers of the plutonium isotopes and ^{241}Am are given in Table I (1).

Table I. Specific Power Values P_i for the Isotopes of Plutonium

Isotope	Half-Life (yr)	Specific Power (mW/g isotope)	Standard Deviation (mW/g isotope)	Relative Standard Deviation (%)
^{238}Pu	87.74	567.57	0.26	0.046
^{239}Pu	24119	1.9288	0.0003	0.016
^{240}Pu	6564	7.0824	0.002	0.028
^{241}Pu	14.348	3.412	0.002	0.064
^{242}Pu	376300	0.1159	0.0003	0.26
^{241}Am	433.6	114.2	0.42	0.37

The uncertainties in the P_i values are seldom considered in a calculation of the sample power because they do not contribute to the random error of the sample power.

Propagation of Error for P_{eff}

We calculate the effective specific power from the isotopic composition according to Eq. 2. For this analysis we consider only the errors in the plutonium and americium isotopic fractions f_i and consider that the specific powers P_i are without error. In fact, the P_i values are not without error (see Table I) but only contribute to a systematic error in P_{eff}. The random errors in the isotopic fractions arise mainly from counting statistics for gamma spectroscopy and from the differences in repeated measurements for mass spectrometry. Equation 3 propagates the variance in P_{eff} considering only uncertainties in the isotopic fractions f_i and neglecting the correlations between the f_i.

$$(\Delta P_{eff})^2 = \sum_i \left(\frac{\partial P_{eff}}{\partial f_i}\right)^2 (\Delta f_i)^2 \quad = \sum_i (P_i)^2 (\Delta f_i)^2 \qquad (3)$$

In the succeeding paragraphs we examine the magnitude of each isotopic component in the sum to determine the major contributors to the variance in P_{eff}.

Isotopic Composition and Uncertainties: First Example

In 2003, Los Alamos National Laboratory personnel prepared a 5-kg PuO_2 standard for use in the ARIES (Advanced Retirement and Integrated Extraction System) Nondestructive Assay (NDA) System[2]. One of the principal uses of this standard was to standardize and control calorimetric assay measurements that used nondestructive gamma-ray spectroscopy for determining the isotopic fractions. The results of the mass spectrometry measurements for the plutonium isotopic fractions and the gamma counting for ^{241}Am with a NaI detector for this standard (MC-0006) are listed in Table II and completely described in Smith and Bluhm (3).

Smith and Bluhm state that "for isotope ratio measurements" (by mass spectrometry), "the confidence limits (95%) are typically less than 0.1% relative or 10^{-5} absolute, whichever is greater." For the gamma-counting measurement of ^{241}Am, Smith and Bluhm stated a measurement uncertainty of ± 5% RSD . These uncertainties are representative of "routine" analytical measurements because no extra special precautions were undertaken in the measurements.

Table II. Mass Spectrometry and Gamma-Counting (^{241}Am) Measurements for Standard MC-006 (3)

Isotope	Mass % wrt Plutonium	Relative Error* (% RSD)
Pu-238	0.0092	2.7
Pu-239	94.051	0.003
Pu-240	5.7985	0.08
Pu-241	0.1106	1.4
Pu-242	0.0308	1.1
Am-241	0.2191	7.1

* % RSD of a single measurement calculated from repeated measurements

For the purpose of calculation in this example, we have assumed an insignificantly different isotopic composition along with a ^{241}Am concentration that is more appropriate for plutonium from weapons disposition. We have assigned errors that are the larger of the errors in Table II or the a priori errors stated in the previous paragraph. These assumed values are listed in Table III and are used for the calculations in this example.

Table III. Assumed Weapons Plutonium Isotopic Composition and Relative Errors from Mass Spectrometry (Gamma Count for ^{241}Am) as % RSD

Isotope	Mass % wrt Plutonium	Relative Error (% RSD)
Pu-238	0.010	2.7
Pu-239	94.050	0.05
Pu-240	5.800	0.08
Pu-241	0.100	1.4
Pu-242	0.040	1.1
Am-241	0.300	7.1

P-effective = 2.6276 mW/g Pu for the isotopic distribution in Table III using the constants in Table I. This value is used in subsequent calculations of the % RSD in P_{eff}.

Table IV displays the individual variance components from the sum in Eq. 3 using the isotopic and error data from Table III. From Table IV we see that over 99% of the variance of P_{eff} comes from ^{241}Am. The % RSD in P_{eff} is actually poorer than that arising from a typical gamma-ray isotopic measurement as demonstrated below in Table V.

Table IV. Variance Components (Eq. 3) of P_{eff} for Mass Spectrometry (Gamma Counting for ^{241}Am). Errors and Isotopic Distribution of Table III.

Isotope	Mass %	(% RSD)	$(P_i)^2(\Delta f_i)^2$
Pu-238	0.010	2.7	2.35E-06
Pu-239	94.050	0.05	8.23E-07
Pu-240	5.800	0.08	1.08E-07
Pu-241	0.100	1.4	2.28E-09
Pu-242	0.040	1.1	2.60E-13
Am-241	0.300	7.1	5.92E-04
		Variance of P_{eff}	5.95E-04
		Std. Dev. of P_{eff}	2.44E-02
		% RSD in P_{eff}	0.93

In Table V we calculate Eq. 3 using % RSDs (column 3) that are typical for the analysis of a gamma-ray spectrum from disposition plutonium with the FRAM[4] gamma- ray isotopic analysis software.

Table V. Variance Components for P_{eff} for a Typical FRAM Gamma-Ray Isotopic Analysis Measurement.

Isotope	Mass %	(% RSD)	$(P_i)^2(\Delta f_i)^2$
Pu-238	0.010	7.0	1.58E-05
Pu-239	94.050	0.15	7.40E-06
Pu-240	5.800	2.0	6.75E-05
Pu-241	0.100	0.3	1.05E-10
Pu-242	0.040	10.0	2.15E-11
Am-241	0.300	1.0	1.17E-05
		Variance of P_{eff}	1.02E-04
		Std. Dev. of P_{eff}	1.01E-02
		% RSD in P_{eff}	0.39

The total variance in P_{eff} for the gamma-ray isotopic analysis measurement is 6 times smaller than the variance calculated for mass spectrometry with gamma counting for ^{241}Am. That is, the 7% error (Table IV) in the ^{241}Am concentration from the analytical characterization of the calorimetric assay standard created a larger uncertainty in P_{eff} than the nondestructive gamma-isotopic measurement (Table V) that was meant to be standardized by the standard.

The % RSD in P_{eff} calculated for this FRAM gamma-ray isotopic analysis measurement agrees very well with that observed from repeated measurements. This shows that the assumptions in Eq. 3 are valid.

A Second Example with Higher Burnup Plutonium: The CALEX II Standard
The Department of Energy has a program for the preparation and characterization of a 2-kg PuO_2 sample containing 12% ^{240}Pu for use in calorimetric assay. Preliminary values for the characterization were reported at the 2002 Safeguards Measurement Evaluation Program meeting. The preliminary isotopic values and uncertainties from mass spectrometry and gamma counting for ^{241}Am are given in Table VI.

The errors here represent the errors typical of measurements undertaken with the extra care and preparation characteristic of standards analytical measurements. The values in Table VI yield a P_{eff} of 3.67282 mW/g Pu.

Table VI. Preliminary Isotopic Values and Errors for the CALEX II Standard.

Isotope	Mass % wrt Plutonium	Relative Error (% RSD)
Pu-238	0.078	0.26
Pu-239	86.701	0.004
Pu-240	12.190	0.033
Pu-241	0.824	0.22
Pu-242	0.208	0.34
Am-241	0.585	2.1

Table VII displays the variance components of P_{eff} for the preliminary characterization of the CALEX II standard.

Table VII. Variance Components (Eq. 3) of P_{eff} for Mass Spectrometry (Gamma Counting for ^{241}Am) for the CALEX II Standard.

Isotope	Mass %	(% RSD)	$(P_i)^2(\Delta f_i)^2$
Pu-238	0.078	0.26	1.27E-06
Pu-239	86.701	0.004	4.47E-09
Pu-240	12.190	0.033	8.12E-08
Pu-241	0.824	0.22	3.82E-09
Pu-242	0.208	0.34	6.71E-13
Am-241	0.585	2.1	1.97E-04
		Variance of P_{eff}	1.98E-04
		Std. Dev. of P_{eff}	1.41E-02
		% RSD in P_{eff}	0.38

Even for a standard characterized with the extra care associated with standards measurements, the uncertainty in ^{241}Am contributes over 99% of the variance in P_{eff}. For this example, the % RSD in P_{eff} from the analytical characterization is more in line with what is typically seen for gamma-ray isotopic analysis measurements of this type (4).

Nevertheless, the uncertainty of 0.38 % RSD is still not good enough for a standard to be used for calorimetric assay. It is often said that the uncertainty in the standard should be 10 times less than the uncertainty in the method standardized. While this may not be possible in many cases, for CALEX II, the characterization should be good enough to

produce an uncertainty in P_{eff} of < 0.15% relative so the uncertainty in the standard is more than 2 times smaller than the uncertainty in the measurement to be standardized.

What ^{241}Am Error Yields a Good Standard for Calorimetric Assay?

We have shown that mass spectrometry combined with an imprecise ^{241}Am analysis does not produce a good standard for the calorimetric assay of plutonium, yielding a larger uncertainty in P_{eff} than the gamma-ray isotopic measurement it is meant to standardize.

In Fig. 1 we display the error in P_{eff} as a function of the random error in ^{241}Am characterization for the weapons plutonium example. The conditions use the weapons-grade isotopic distribution and uncertainties of Table III, varying only the ^{241}Am uncertainty.

Americium-241 contributes about 50% of the total variance when its error is 0.5% RSD. At this point, the error in P_{eff} is about 0.1% relative. This is a good target for the P_{eff} error in a standard for calorimetric assay. Reducing ^{241}Am errors below 0.5% does not materially improve the error in P_{eff}..

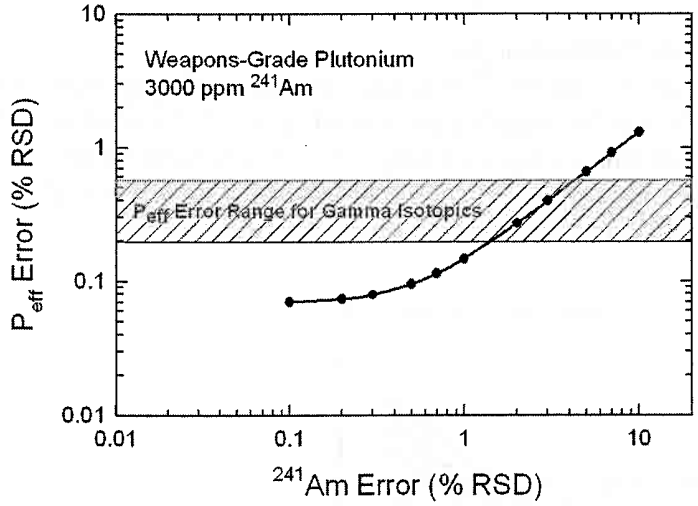

Fig. 1. Error in P_{eff} as a function of ^{241}Am error assuming typical mass spectrometry errors for the plutonium isotopic fractions.

In Fig. 2 we display the error in P_{eff} as a function of the random error in ^{241}Am for the CALEX II example. The conditions use the preliminary CALEX II isotopic distribution and uncertainties of Table VII, varying only the ^{241}Am uncertainty.

Americium-241 contributes about 50% of the total variance when its error is 0.2% RSD. At this point, the error in P_{eff} is about 0.05% relative. A ^{241}Am error of 0.5% produces an uncertainty of 0.1% RSD in P_{eff}.

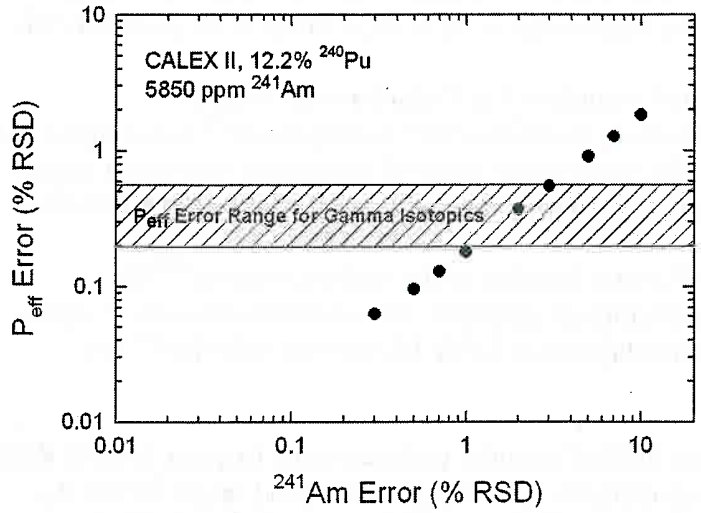

Fig. 2. Error in P_{eff} as a function of ^{241}Am error assuming preliminary mass spectrometry errors for the plutonium isotopic fractions in the CALEX II standard.

Variation of P_{eff} Error with ^{241}Am Concentration

Clearly, the error in P_{eff} depends not only on the ^{241}Am error but also on the magnitude of the ^{241}Am concentration. Figure 3 uses the weapons plutonium isotopic composition and errors of Table III and computes the error in P_{eff} for a range of ^{241}Am concentrations. Higher concentrations of ^{241}Am require lower ^{241}Am errors to keep the P_{eff} error in the 0.1%–0.15 % RSD range.

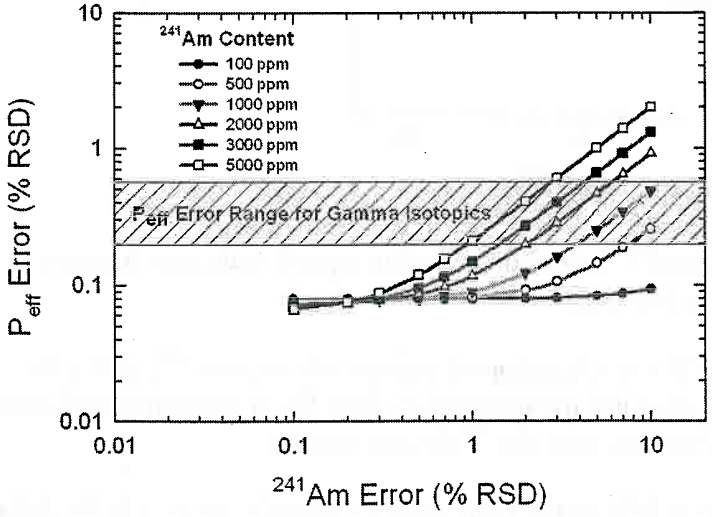

Fig. 3. Errors in P_{eff} for typical weapons plutonium mass spectrometry for a range of ^{241}Am concentrations.

Limiting Cases

We can estimate the uncertainty in P_{eff} caused by the uncertainties in the P_i values from Table I by simply reversing P_i and f_i in Eq. 3 and assuming no uncertainty in the f_i values. Carrying out the calculation using the errors in Table I and the isotopic distribution of Table III in the same fashion as illustrated in Table IV gives the RSD of P_{eff} of 0.05% when only the uncertainties in the P_i values are considered. This error represents the systematic error present in the calculation of P_{eff} arising from the errors in the fundamental P_i values from Table I.

It is interesting to note that the limiting value of the error in P_{eff} is 0.079% considering only the weapons plutonium isotopes, no americium, and the "routine" mass spectrometry errors of Table III. For the example of the CALEX II standard with its standards grade mass spectrometry, the limiting error in P_{eff} is 0.039% for a ^{241}Am concentration of zero

Conclusion

Routine and even "standards grade" analytical measurements of the ^{241}Am/Pu ratio in plutonium samples typically have an uncertainty of several percent (relative) or greater when gamma counting is used for ^{241}Am. This uncertainty contributes to and often completely dominates the uncertainty in the effective specific power P_{eff} calculated from the analytical ^{241}Am measurement when coupled with mass spectrometry measurement of the plutonium isotopic fractions. The magnitude of the uncertainty in the analytical determination of P_{eff} is usually greater than the uncertainty in P_{eff} from nondestructive gamma-ray isotopic measurements, the technique meant to be standardized by the analytical measurements.

We have shown that the analytical characterization of the ^{241}Am/Pu ratio in a weapons plutonium-bearing standard for calorimetric assay should have an uncertainty of 0.5%–1.0 % RSD or less to keep the P_{eff} error in the 0.1%–0.15 % RSD range. At this level, the uncertainty of the analytic value for P_{eff} will be several times lower than the typical uncertainty in P_{eff} from FRAM nondestructive gamma-ray isotopic measurements.

Standardized measurement methods and CRMs for the measurement of ^{241}Am in plutonium need to be developed and put into practice to achieve this goal.

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