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Mass measurement uncertainty for plutonium aliquots assayed by controlled-potential coulometry

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Abstract Minimizing plutonium measurement uncertainty is essential to nuclear material control and international safeguards. In 2005, the International Organization for Standardization (ISO) published ISO 12183 "Controlled-potential coulometric assay of plutonium," 2nd edition. ISO 12183:2005 recommends a target of ±0.01% for the mass of original sample in the aliquot because it is a critical assay variable. Mass measurements in radiological containment were evaluated and uncertainties estimated. The uncertainty estimate for the mass measurement also includes uncertainty in correcting for buoyancy effects from air acting as a fluid and from decreased pressure of heated air from the specific heat of the plutonium isotopes.

Keywords Coulometry · Coulometric assay · Plutonium · Mass · Buoyancy · Uncertainty · Propagation · GUM

Introduction

Measurement uncertainty is of particular interest when performing accurate and precise measurements of plutonium in support of national defense programs and international safeguards. The intrinsic value of this radioactive and fissionable element and its attractiveness to diversion for non-peace time applications necessitate that for some measurement applications, the total uncertainty of the plutonium assay or concentration measurement should be 0.1%, or less. The international atomic energy agency endorses international target values of 0.15% for both random and systematic uncertainty of plutonium assay and concentration measurements by controlled-potential coulometry [1, 2]. In addition to being small qualitatively, the uncertainty of the plutonium measurement must be quantified so that its impact on the inventory process used to safeguard this special nuclear material can be modeled and limits on inventory differences can be calculated to satisfy regulatory requirements [3–5]. Controlled-potential coulometry is also applicable for the characterization of plutonium-bearing materials of suitable purity and for the certification of candidate plutonium assay reference materials [6, 7].

ISO standard 12183 "Controlled-potential coulometric assay of plutonium," [8] is based upon the measurement methodology [9] and control-potential coulometer measurement systems [10] used at the Savannah River Site's Analytical Laboratory, Aiken, SC (a contractor operated facility of U.S. Department of Energy), the U.S. Department of Energy's New Brunswick Laboratory, Argonne, IL, and the International Atomic Energy Agency's Safeguards Analytical Laboratory, Seibersdorf, Austria. This methodology and instrumentation is being implemented by the Japan Atomic Energy Agency's laboratory at the Tokai Reprocessing Plant in Tokai-mura, Japan. The coulometer

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cell assemblies and automated coulometric instrumentation used by these laboratories were designed, fabricated, and installed by the Savannah River National Laboratory's Engineered Equipment and Systems division.

ISO standard 12183:2005 provides a definitive measurement methodology for the coulometric assay of plutonium. A claim that a procedure or methodology is a definitive measurement method [11] based upon its adherence to first principles does not infer a claim that a procedure or methodology will have zero systematic uncertainty. An effective application of first principles does not eliminate all sources of random and systematic uncertainty. However, systematic uncertainty should be minimized before the claim of first principles can become important. The uncertainty from systematic error sources should be reduced to a distribution where the identification of new sources of significant systematic error is not likely, given the total uncertainty associated with the measurement and the validation process used to demonstrate method performance and reliability.

To estimate the uncertainty in plutonium assay measurements in accordance with International Standard, JCGM 100:2008 "Guide to the expression of uncertainty in measurement," [12] the systematic and random error sources in mass measurements used to calculate the plutonium assay are identified and quantified. Control of systematic and random uncertainty in the mass value used in plutonium assay requires that analytical balances are selected for proven performance in radiological containment. Users ensure that balances are calibrated and that the apparent mass of the sample is corrected for air buoyancy using a well established protocol [13, 14]. The uncertainty in the air buoyancy correction has been evaluated. The apparent mass of a radioactive object should also be corrected for a buoyancy effect that is specific-heat (specific power; radioactive heat) induced. Experiments were performed to evaluate this effect and its contribution to uncertainty.

Experimental

Two experiments were performed to quantify the change in apparent mass of a radioactive solid sample and bulk material that is thermal heating by its own radioactive decay. In the first experiment, a 0.75 cm^3 stainless steel cube with an imbedded 1500-Ω electrical resistor was fabricated. Current was passed through the electrical resistor to simulate different wattage values, calculated from the measured voltage drop, V, across the resistance, R, as indicated in Table 1. The mass was measured after the object came to thermal equilibrium at each of the desired wattage levels and then again after the object cooled. The volume of the object corresponded to a 15-g sample of plutonium metal that was heated as a low specific heat radioactive material. (The volume of the text object also corresponded to a 5-g samples of plutonium oxide. The test object was also heated to simulate plutonium oxides with higher specific heat materials. However, the metallic form of the object did not simulate all the properties of an oxide material.)

Equation 1 was derived from the first row of data in Table 1, which simulated 15 g of metal that is 5–7% ^{240}Pu and thus generates 2 mW/g. These data were extrapolated to predict the effect on 0.5–15 g of this plutonium metal, based on the assumption that the change in ratio of surface-to-volume correlates with surface temperature and that this buoyancy effect is directly proportional to the surface temperature of the metal sample.

$$B_{heat}@\,Pu_{heat}\text{ of }2\text{ mW/g} = 1 + (\Delta m) \times (m_{solid}/1000)^{-2/3}/(15^{1/3}) \quad (1)$$

where Δm is $-0.00016(6)$. The uncertainty was estimated based on a rectangular distribution with a conservative range, r, of ±0.0001 g. The estimated standard deviation is $r/\sqrt{3} = 0.00006$.

In the second experiment, voltages between 12 and 24.5 V were applied to a 24-Ω resistor (rated for 25 W) sealed in a stainless steel storage can that can hold 1.2 kg of plutonium dioxide, to simulate 1 kg of plutonium of different isotopic distributions. The mass of the stainless steel storage container was measured at room temperature and after it reached thermal equilibrium at each applied voltage, and again after it returned to room temperature. The experiment required 2 days elapsed time. The different types of plutonium materials simulated and the test results are summarized in Table 2.

Table 1 Change in apparent mass from specific-heat of plutonium solid samples, Δm

Simulated Pu material type, burn-up, and specific heat 10^3 MWD/t, mW/g [15, 16]	Calculated power, mW ($V^2 \div R = W$)	Observed change in mass, Δm, g	Calculated change for 15 g Pu metal (%)	Calculated change for 5 g PuO_2 (%)
Pu metal, low, 2.0–2.4	30	−0.00016	−0.001	
PuO_2, 30, 10–20	100	−0.00025		−0.005
PuO_2, 50, 20–30	170	−0.00030		−0.006

The uncertainty in the calculated power was greater than the uncertainty in the mass measurements, but the magnitude of the effect was capture with adequate reliability, given its size and impact on the coulometric assay measurement of plutonium. Further testing would be required to refine these estimates

Table 2 Change in apparent mass from specific-heat of plutonium for bulk materials, Δm

Simulated Pu material type and burn-up, 10^3 MWD/t [15, 16]	Day	Measured power (W) (V × I = W)	Observed change in mass, Δm, g	Calculated change for 1 kg of Pu (%)	Mass change per Watt (%), Δm, % ÷ W
Pu metal or PuO_2, low	A	3.0	−0.04	−0.004	−0.0013
PuO_2, 5–10	A	6.0	−0.07	−0.008	−0.0013
PuO_2, 10–20	A	10.0	−0.13	−0.013	−0.0013
PuO_2, 10–20 repeat	B	10.0	−0.11	−0.011	0.0011
PuO_2, 20–30	B	18.5	−0.19	−0.019	−0.0010
PuO_2, 30–50	B	25.0	−0.22	−0.022	−0.0009

Discussion

Reliability of mass measurements using analytical balances

Accurately measuring the mass of an object is a well understood and characterized process. Reliable analytical balances are available from several manufacturers. Table 7 provided uncertainties for mass measurements for aliquots of plutonium metal samples. If significantly smaller sample masses, total solution masses, or aliquot masses are taken, the relative standard deviation will increase significantly and the propagated uncertainty can become the largest contributor to variance in the plutonium assay measurement.

The physical challenges associated with plutonium mass measurements are a direct result of the radioactive nature of this man-made element. Most plutonium isotopes decay by alpha emission. Handling plutonium materials requires radioactive containment units such as gloveboxes, shielded analytical cells, and radiohoods (chemical hoods with higher air volume requirements) for the protection of personnel. Achieving ideal laboratory conditions is not as easily accomplished in a plutonium laboratory because the facility's ventilation system typically has high-volume, once-through air handling, which require more robust heating and cooling systems to achieve room temperature stability and humidity control. Procedures and controls for the mass measurement are implemented so that the following considerations are addressed and the uncertainty values used in the subsequent propagations are achieved on a routine basis:

- Atmospheric pressure in the different types of radiological containment units is 0–3 mmHg lower than the laboratory, but is addressed by in situ balance calibration.
- High air volume exchange in a containment unit is considered when positioning the balance.
- Temperature in the containment unit can be different from the laboratory module by a few Celsius degrees, so that samples, especially solutions should be allowed to equilibrate to the temperature in the containment unit when they are moved to the containment unit where the balance is located.
- When the relative humidity is low, static electricity can accumulate on an object being weighed and seriously affect the apparent mass of an object. This effect is usually easy to identify and avoided by controlling the relative humidity in the laboratory.
- The effect of local gravity is insignificant provided the balance has been calibrated at the location where it will be used.

Buoyancy effect—air as a fluid, based on Archimedes' principle

The actual mass of an object can be calculated from its apparent mass using the density of the object, the density of the air, and the density of the internal reference mass within the balance.

Buoyancy effect—heat transfer from the sample to the surrounding air

In addition to the physical challenges associated with routine weighing of radioactive plutonium, the heat generated from the alpha-decay of the plutonium isotopes (and the alpha decay of the ^{241}Am daughter that grows into plutonium over time) is expected to have small affects on the mass measurement of solid samples and bulk materials. An object that is warmer than the surrounding area heats this air causing it to rise and reduces the objects apparent mass. The isotopic abundance and specific heat of the man-made element plutonium depends upon the degree of irradiation conditions during reactor production and its age (time since chemical separation).

The higher the specific activity of the plutonium material and the smaller the surface area of the sample (or bulk material package), the greater the equilibrium temperature at the surface will be. As the density of the solid material increases, the surface area of the sample decreases, resulting in higher surface temperatures. Pure plutonium metal has the highest density, and if all other factors were equal, the metal form would have the highest surface temperature and greatest ability to heat the air surrounding the sample. However, plutonium metal assay standards and typical metal samples from weapons manufacturing have isotopic abundances corresponding to lower burn-up materials, and thus lower specific heat.

Applying the guide to the expression of uncertainty in measurement (GUM)

Applying the standardized methodology in JCGM 100:2008 requires that a systematic process be used to explain and document the expression of uncertainty in measurement. This process involves the following key steps:

- Explaining the mass measurement process as it related to the assay of plutonium samples and standards performed in accordance with ISO12183:2005;
- Identifying and discussing the individual variables being measured and other sources of mass measurement uncertainty, x_i;
- Categorizing each variables uncertainty as either Type A or B;
- Quantifying the random and systematic mass measurement uncertainties for each error source and then expressing each of these uncertainties as a standard deviation, $u(x_i)$; and
- Propagating the total uncertainty for mass measurement results from the individual uncertainties in the measured variables and other sources of error, with appropriate consideration for covariance, if involved.

Each of theses key steps are address in the sections below, with details provided in the tables that are referenced when each key step is addressed.

Overview of plutonium measurement and mass measurement calculations

The plutonium assay for a solid sample is calculated using Eq. 2. This paper will focus on the uncertainty in the actual mass of original plutonium metal sample that is in the aliquot, w_{mg}, which is an important variable used in calculating the plutonium assay. This mass is calculated using Eq. 3. The air buoyancy correction term is calculated using Eq. 4. The specific-heat buoyancy correction term for plutonium metal is calculated using Eq. 5.

$$\text{Pu Assay, g/g} = (Q_s - Q'_b) C\, A_r F^{-1} f^{-1} w_{mg}{}^{-1} \tag{2}$$

$$w_{mg} = m_{solid}\ m_{aliquot} m_{solution}{}^{-1} B_{air}\ B_{heat} \tag{3}$$

$$B_{air} = (1 - D_{air}/D_{ss})/(1 - D_{air}/D_{sample}) \tag{4}$$

$$B_{heat} = 1 - (\Delta m')(m_{solid}{}^{-2/3})(Pu_{heat}) \tag{5}$$

The definition of terms and partial derivatives for all variables are provided in Tables 3 and 4.

Identify and discuss the sources of uncertainty in mass measurements

The uncertainty in the mass of original sample in an aliquot prepared for the coulometric measurement of plutonium is a function of the uncertainty in the following measurement variables:

- Measuring the apparent mass of the solid sample;
- Measuring the apparent mass of the dissolved sample solution;
- Measuring the apparent mass of the measurement aliquot;
- Correcting the mass of the solid sample for the effect of air buoyancy (note: correcting the dissolved sample solution and the aliquot masses for the effect of air buoyancy is not required as the corrections are equal and cancel when calculating w_{mg});
- Correcting the mass of the solid sample for the effect of specific heat of the plutonium.

Measuring the sample, dissolved sample solution, and solution aliquot masses

The uncertainty estimate for mass measurement derived herein applies to homogeneous metal samples where the mass of original sample taken is 0.5 g, or larger. The information can be applied to calculate the mass measurement uncertainty for stable oxides and solution samples.

Accurately measuring the apparent mass of an object can be accomplished using reliable analytical balances that are available from several manufacturers. Performing reliable measurements in gloveboxes and radiological hoods requires compatible design and validated procedures. Uncertainty estimates for mass measurements provided in this report consider performing the mass measurement in radioactive containment under such conditions. The actual mass of an object can be accurately calculated from its apparent mass using reliable equations that are based upon Archimedes' Principle of buoyancy. In addition to the physical challenges associated with measuring the mass of radioactive plutonium, the heat generated from the alpha-decay of the plutonium isotopes has a small affects on the measured mass of solid samples. However, heat from dissolved radioactive materials does not increase the temperature of a solution sufficiently that it affects the apparent mass of a solution.

Categorize all sources of uncertainty, Type A or B

Table 5 lists the sources of uncertainty that contribute to mass measurement uncertainty and categorizes the

Table 3 Definition of terms in Eqs. 2–5

Q_s	The integrated electrolysis current during oxidation of the plutonium aliquot, pulses
$Q_b^{\prime}$	The integrated electrolysis current during the oxidation of the supporting electrolyte blank, corrected in accordance with ISO 12183:2005, pulses
C	The electrical calibration factor, millicoulombs per pulse
A_r	The relative atomic mass of plutonium calculated from isotopic abundance, g mol^{-1}
F	The Faraday Constant, 96,485.3399(24) coulombs per mole (C mol^{-1})
f	The calculated fraction of plutonium electrolyzed
w_{mg}	The mass of solid sample to be measured, in mg, i.e., mass of original sample that is in the coulometer cell, calculated from the solution aliquot mass, the final dissolved sample solution mass, and the solid sample mass corrected for buoyancy effects
m_{solid}	The apparent measured mass of the solid sample, mg
$m_{aliquot}$	The apparent measured mass of the solution aliquot taken, g
$m_{solution}$	The apparent measured mass of the dissolved sample solution, g
B_{air}	The buoyancy correction for the fluid properties of air acting on objects during mass measurements
B_{heat}	The buoyancy correction for the reduced pressure of warm air rising above the surface of a solid, radioactive sample, caused by the transfer of thermal energy generated by radioactive decay particles
D_{air}	The density of air
D_{ss}	The density of the stainless steel reference weight(s) in the analytical balance, which are adjusted by the manufacturer to 8.0 g/mL
D_{sample}	The density of the sample. It is measured or estimated appropriately based upon its chemical form
$\Delta m'$	+0.003(1), Δm divided by the 3 mW/g and combined with other constants to simplify Eq. 1
Pu_{heat}	The plutonium specific heat calculated from the plutonium isotopic abundance, the ^{241}Am content, and the specific heat of each isotope, in units of mW/g. This term was introduced as a variable in Eq. 5 when $\Delta m'$ was calculated to replace Δm

Table 4 Partial derivatives for all variables in Eqs. 3–5

$$\partial w_{mg}/\partial m_{solid} = +m_{aliquot} m_{solution}{}^{-1} B_{air}\ B_{heat} \tag{6}$$

$$\partial w_{mg}/\partial m_{aliquot} = +m_{solid} m_{solution}{}^{-1} B_{air}\ B_{heat} \tag{7}$$

$$\partial w_{mg}/\partial m_{solution} = -m_{solid} m_{aliquot}\ m_{solution}{}^{-2}\ B_{air}\ B_{heat} \tag{8}$$

$$\partial w_{mg}/\partial B_{air} = +m_{solid} m_{aliquot}\ m_{solution}{}^{-1}\ B_{heat} \tag{9}$$

$$\partial w_{mg}/\partial B_{heat} = +m_{solid} m_{aliquot}\ m_{solution}{}^{-1}\ B_{air} \tag{10}$$

$$\partial B_{air}/\partial D_{air} = +(1 - D_{sample}/D_{ss})/(D_{sample}(-D_{air}/D_{sample})^2) \tag{11}$$

$$\partial B_{air}/\partial D_{ss} = +D_{air}/(D_{ss}{}^2(1 - D_{air}/D_{sample})) \tag{12}$$

$$\partial B_{air}/\partial D_{sample} = +D_{air}(D_{air}/D_{ss} - 1)/(D_{sample} - D_{air})^2 \tag{13}$$

$$\partial B_{heat}/\partial \Delta m' = -(m_{solid}{}^{-2/3})(Pu_{heat}) \tag{14}$$

$$\partial B_{heat}/\partial Pu_{heat} = -(\Delta m')(m_{solid}{}^{-2/3}) \tag{15}$$

$$\partial B_{heat}/\partial m_{solid} = (\Delta m')(m_{solid}{}^{-5/3})(Pu_{heat}) \tag{16}$$

uncertainty estimate for each source. Variables have Type-A uncertainties when based on measured values. Variables have Type-B uncertainties when based on supplier certificates of analysis, manufacturer specifications, applicable literature, or expert judgment or experience.

Quantify the random and systematic measurement uncertainties

Table 6 lists the sources of uncertainty and quantifies the random, systematic, and total measurement uncertainties for each source, expressing each of these uncertainties as a standard deviation (1σ), $u(x_i)$.

Propagate the total uncertainty for mass of plutonium metal sample in the aliquot

Table 7 illustrates how Eqs. 3 and 6–10 are used to calculate the propagated uncertainty in the mass of original plutonium metal sample that is in the aliquot. The calculations use the typical values for each variable and their $1 - \sigma$ uncertainties. This propagation illustrates that provided the corrections for the buoyancy effects from air and specific heat are made, their contribution is small.

Table 8 illustrates how Eqs. 4 and 11–13 are used to calculate the propagated uncertainty in the air buoyancy correction term for plutonium metal samples.

Table 5 Sources and types of mass measurement uncertainties

Measurement variables	Symbol	Type	Comments
Mass of original sample in aliquot, corrected for buoyancy effects	w_{mg}	B	Propagated using variables: m_{solid} $m_{solution}$ $m_{aliquot}$ B_{air} B_{heat} Manufacturer's specification for balances, rectangular; and Scientist knowledge—mass in radioactive containment
Buoyancy—Air, Archimedes' principle	B_{air}	B	Propagated using variables: D_{air}, D_{ss}, D_{sample} Published literature, triangular distribution, conservative range
Buoyancy—Pu Specific heat	B_{heat}	*	Propagated using variables: $\Delta m' m_{solid}$ Pu_{heat} B&A; scientist judgment & limited testing, assume rectangular
Solid sample mass, apparent, measured	m_{solid}	A	Balance specifications and performance in containment
Dissolved sample solution mass, measured	$m_{solution}$	B	Balance specifications and performance in containment. Insignificant contributor to total variance in w_{mg}
Solution aliquot mass, measured			Balance specifications and performance in containment
Density of air	D_{air}	B	Typical values: 0.00116–0.00120 g/mL. May be calculated from atmospheric pressure and dew point measurements at the mass measurement station. Conservative, triangular $r = 0.00005$
Density of stainless steel weights	D_{ss}	B	Manufacturer's specifications and literature, 8.0 g/mL. Assume triangular with conservative $r = 0.25$. Estimated $s = r/\sqrt{6} = 0.1$
Density of sample	D_{sample}	B	For solution measurements, density meter specifications For solid samples, literature or process history for densities and uncertainties of plutonium metals, alloys, oxides, salts, etc. or measure by immersion/displacement density or tap density
Δmass coefficient for B_{heat}, measured for 15 g	Δm,	A	Value measured is a function of sample form simulated (metal vs. oxide) and simulated specific heat values. Uncertainty is based on a rectangular distribution with bounding $r = 0.0001$ g
Δmass coefficient for B_{heat}, calc. 1–15 g	$\Delta m'$	B	Calculated based on model/assumptions. Uncertainty is based on a rectangular distribution with bounding range, $r = 0.002$ g
Specific-heat of plutonium	Pu_{heat}	B	Value is a function of plutonium isotopic abundance. Insignificant contributor to uncertainty in B_{heat}

Table 6 Typical values and estimated standard deviations for sources of mass measurement uncertainty

Measurement variables, x_i	Symbol	Typical values	Units	$u_s(x_i)$	$u_r(x_i)$	$u_T(x_i)$
Mass of original sample in aliquot, corrected for buoyancy effects	w_{mg}	15.0	mg	0.0009	0.0008	0.0012
Buoyancy air—Archimedes' Principle	B_{air}	0.999912	% change	0.0000015	0.0000015	0.000002
Buoyancy specific heat	B_{heat}	0.99990	% change	0.00003	Negligible	0.00003
Solid sample mass, apparent, measured	m_{solid}	500.00	mg	0.01	0.02	0.02*
Dissolved sample solution mass	$m_{solution}$	200.000	g	0.0002	0.001	0.001**
Solution aliquot mass	$m_{aliquot}$	6.00000	g	0.0001	0.0002	0.0002*
Density of air	D_{air}	0.00118	g/mL	0.00002	Negligible	0.00002
Density of stainless steel weights	D_{ss}	8.0	g/mL	0.1	Negligible	0.1
Density of alpha-phase metal sample	D_{sample}	19.84	g/mL	0.2	Negligible	0.2
Δmass coefficient for B_{heat}, measured for 15 g	Δm	0.00016	g	0.00006	Negligible	0.00006
Δmass coefficient for B_{heat}, calc. 1–15 g	$\Delta m'$	0.003	g^2/mW	0.001	Negligible	0.001
Specific-heat of plutonium	Pu_{heat}	2	mW/g	0.1	Negligible	0.1

* Estimated u_T is about twice the typical balance manufacturers' specifications, when operated in radiological containment

** Conservative estimate applied to demonstrate that this source of mass measurement uncertainty is not significant

Table 9 illustrates how Eqs. 5 and 14–16 are used to calculate the propagated uncertainty in the specific-heat buoyancy correction term for plutonium metal samples.

Results

The total propagated uncertainty in mass for aliquot containing 15 mg of original sample (plutonium metal) was

Table 7 Propagating measurement uncertainty for mass of metal sample in the aliquot, w_{mg}

Variables, X (units)	m_{solid} (mg)	$m_{aliquot}$ (g)	$m_{solution}$ (g)	B_{air} (none)	B_{heat} (none)
Typical values	500.00	6.0036	200.000	0.999912	0.99990
Uncertainty, U_T, $1-\sigma$	0.02	0.0002	0.001	0.000002	0.00003
$\partial w_{mg}/\partial X$	3.00E-2	2.50E+0	−7.50E-2	1.50E+1	1.50E+1
$(\partial w_{mg}/\partial X)^2 \times U^2$	3.6E-7	2.5E-7	5.6E-9	1.3E-9	2.3E-7
Variance, %	42	29	<1	<1	27

Mass of original sample in aliquot calculated from typical values: 15.0062 mg of original sample

Propagated uncertainty, absolute: $\surd$ of $\sum$ $(\partial Pu/\partial X)^2 \times U^2$): 0.0009 mg ($1-\sigma$); relative: 0.006% ($1-\sigma$)

Table 8 Propagated uncertainty for air buoyancy term, B_{air} for plutonium metal

Variables, X (units)	D_{air} (g/mL)	D_{ss} (g/mL)	D_{sample} (g/mL)
Typical values	0.00118	8.0	19.84
Uncertainty, U_T, $1-\sigma$	0.00002	0.1	0.2
$(\partial(M_c/M_a)/\partial X)^2 \times U^2$	2.2E-12	3.4E-12	3.6E-13
Variance, %	37	57	6

The buoyancy correction, B_{air}, calculated from the typical values: 0.999912

Propagated uncertainty, absolute: $\surd$ of $\sum$ $(\partial B_{air}/\partial X)^2 \times U^2$): 0.000002 ($1-\sigma$); relative: 0.0002% ($1-\sigma$)

Table 9 Propagated uncertainty for specific-heat buoyancy term, B_{heat} for plutonium metal

Variables, X (units)	$\Delta m'$	m_{solid} (mg)	Pu_{heat} (mW/g)
Typical values	0.003	500.00	2
Uncertainty, U_T, $1-\sigma$	0.001	0.02	0.1
$(\partial(M_c/M_a)/\partial X)^2 \times U^2$	1.0E-9	1.5E-17	2.3E-11
Variance, %	98	0	2

The buoyancy correction, B_{heat}, calculated from the typical values: 0.99990

Propagated uncertainty, absolute: $\surd$ of $\sum$ $(\partial B_{air}/\partial X)^2 \times U^2$): 0.00003 ($1-\sigma$); relative: 0.003% ($1-\sigma$)

estimated as 0.9 µg at $1-\sigma$ (0.006%). This estimate included the propagated uncertainty in the air buoyancy correction, B_{air}, of 0.036 µg, at $1-\sigma$ (0.0002%), which was insignificant. The estimate also included the propagated uncertainty in the specific heat correction factor, B_{heat}, of 0.45 µg, at $1-\sigma$ (0.003%).

The correction of the apparent mass of a sample for air buoyancy varies from –0.009% for a plutonium metal sample with a density of >19 g/mL to a much larger correction of +0.10% for a plutonium solution sample with a density of 1.01 g/mL. Failure to perform the appropriate air buoyancy correct will dominate the propagated uncertainty for solution samples and is important when optimizing the measurement accuracy for solid samples.

Results in Table 1 indicated that a systematic mass measurement error of −0.16 mg was observed for a simulated 15-g piece of plutonium metal with a specific heat of 2 mW/g. For a change in sample size from 15 to 1 g, the surface area versus mass of the item will increase by a factor of 2.5. The ΔT at the surface (and the effect that it causes) should also decreased by a factor of 2.5. Based on Eq. 5, the apparent mass of 1 g of plutonium metal with a 2.0–2.4 mW/g specific heat would have an estimated error of −0.06 to −0.07 mg (0.006–0.007%). A 0.5-g piece of metal would have an estimated error of −0.05 mg (0.01%).

For a simulated 5-g plutonium oxide sample with a specific heat of 20 mW/g, the systematic mass measurement error is 0.25 mg. The data in Table 1, row 2 were used to derive Eqs. 17 and 18 in the same manner that Eqs. 1 and 5 were derived. Equation 18 applies to plutonium dioxide materials with a specific heat of 10–30 mW/g and a nominal purity of 88%.

$$B_{heat}\ @\ Pu_{heat}\ \text{of}\ 20\,\text{mW/g} = 1 + (\Delta m) \times (m_{solid}/1000)^{-2/3}(5^{-1/3})(0.88) \quad \Delta m = -0.00025(10) \tag{17}$$

$$B_{heat}\ \text{for oxides} = 1 - (\Delta m')(m_{solid}{}^{-2/3})(Pu_{heat}) \quad \Delta m' = +0.0006(3) \tag{18}$$

Based on Eq. 18, the apparent mass of 1 g of plutonium oxide with a 15–30 mW/g specific heat would have an estimated error of −0.1 to −0.2 mg (0.01–0.02%).

The results in Table 2 illustrates that the specific-heat buoyancy effect also contributes a small but somewhat larger uncertainty to bulk measurements of plutonium-bearing materials, which generate heat in proportion to the quantity of plutonium present, the isotopic abundance of the plutonium, and the quantity of ^{241}Am that has grown into the bulk material. The uncertainty in the calculation of the specific heat is dominated by relatively small increases in the abundance of the ^{238}Pu isotope when the burn-up ≥20,000 MWD/t [15]. Reactor design also affects this calculation. A package containing 1 kg of plutonium in oxide form will generate 2–25 W of heat [15, 16]. For a typical stainless steel can capable of holding 1 kg of plutonium in oxide form, the bias associated with the apparent mass is approximately $-0.0012\%\ \mathrm{W}^{-1}$ of heat generated by the package; i.e., 0.002–0.03% systematic error, when the can is at thermal equilibrium with the environment. The systematic error is directly proportional to the surface temperature of the object being measured. At equilibrium, a high-wattage package can have a surface temperature that approach 80–100 °C. However, if the object was recently removed from an outer packaging, the surface temperature of the insulated object will be significantly higher. The resulting effect on the apparent mass will be greater than that observed for the same package at thermal equilibrium. In this case the systematic error could exceed −0.05% for high-wattage packages. These potential systematic uncertainties should be considered when developing procedures for performing bulk material mass measurements and when calculating a limit of error on inventory difference (LEID) to control a manufacturing process or vault operation.

Controlled-potential coulometric assay is normally not applied to high-enriched ^{238}Pu heat sources materials. These space program materials have specific-heat values twelve times greater than the maximum wattage material simulated by the test data in Tables 1 and 2. The mass measurement error for a ^{238}Pu oxide sample may be −0.1%. The effect on ^{238}Pu bulk material mass measurements at thermal equilibrium are likely −0.3%, or larger. Even greater mass measurement errors should be anticipated for bulk materials if the package was recently removed from another container and has not reached thermal equilibrium before its mass was measured.

Placing a thermally heated bulk material into a tared outer container that is at room temperature, closing the outer container to restrict air movement, and promptly measuring the total mass may eliminated the buoyancy effect from specific heat, but this corrective action was not evaluated. If effective and applied, the added uncertainty from the tared outer container would need to be including in the total uncertainty in the mass measurement of the bulk material.

Conclusion

Performing controlled-potential coulometric assay of plutonium in accordance with ISO standard 12183:2005 requires a definitive measurement methodology based upon electrical calibration and application of first principles for each component of the measurement protocol in order to control and minimize systematic and random uncertainty. To achieve the ISO 12183 target of 0.01% uncertainty in the aliquot preparation, appropriate attention must be given to measuring the apparent mass of the solid sample, the dissolved sample solution, and the solution aliquot in radiological containment. Appropriate corrects for buoyancy effects from air and from specific heat must also be applied. Under the conditions details in this report, a total uncertainty of 0.006%, $1-\sigma$ in the aliquot preparation for assay measurement is achievable. The buoyancy effect from air is a well understood and defined process with insignificant uncertainty when properly applied as described herein and in the cited literature. This report documents the importance of the buoyancy effect from specific heat of the radioactive decay of the plutonium and daughter isotopes, and provides quantitative data at the 15-g sample size. The uncertainty estimates developed from the model proposed herein for extrapolating this buoyancy effect to the 1-g range and the underlying assumption of this model are important to the uncertainty estimate provided. Further validation of the extrapolation model is required to refine and ultimately reduce the estimated uncertainty that was calculated.

Accurate measurement of mass for bulk quantities of plutonium-bearing materials is important to material control and accountability. This report provides test results indicated that mass measurements for bulk plutonium-bearing items, could be improved provided attention is given to applying the buoyancy effects from air and for specific heat, and also to refining the correction for the specific heat effect.

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