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Uncertainty propagation for the coulometric measurement of the plutonium concentration in CRM126 solution provided by JAEA

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This GUM Workbench[TM] propagation of uncertainty is for the coulometric measurement of the plutonium concentration in a Pu standard material (C126) supplied as individual aliquots that were prepared by mass.

The C126 solution had been prepared and as aliquoted as standard material. Samples are aliquoted into glass vials and heated to dryness for distribution as dried nitrate. The individual plutonium aliquots were not separated chemically or otherwise purified prior to measurement by coulometry in the F/H Laboratory. Hydrogen peroxide was used for valence adjustment.

The Pu assay measurement results were corrected for the interference from trace iron in the solution measured for assay. Aliquot mass measurements were corrected for air buoyancy. The relative atomic mass (atomic weight) of the plutonium from X126 certoficate was used. The isotopic composition was determined by thermal ionization mass spectrometry (TIMS) for comparison but not used in calculations.

Individual results were calculated using the equation:

$$Pu_{Conc} = (Q_s - Q_{bp}) * C_{ecf} * A_{rPu} / F / f_{Pu} / w - (Fe * (f_{Fe} / f_{Pu}) * (A_{rPu}/ A_{rFe}))$$

Where:

-- Pu_{Conc} is the measurand, mg Pu / mg sample, i.e., g/g, corrected for Fe, in nitric acid supporting electrolyte, mg/mg

-- Q_s is the integrated current signal from sample (plus background current), total pulses, pulse

-- Q_{bp} is the integrated current signal, $Q_{b,}$ from coulometer measurement of the supporting electrolyte blank, corrected to match sample measurement parameters, i.e., corrected total pulses, pulse

-- C_{ecf} is the electrical calibration factor for the digital integrator (coulometer instrumentation), millicoulombs per pulse, mC/pulse

-- A_{rPu} is the relative atomic mass (atomic weight) of Pu, grams Pu/mol or mg Pu/mmol

-- F is the Faraday Constant, C/mol or mC/mmol

-- f_{Pu} is the fraction of Pu electrolyzed, quantity of dimension 1, (dimensionless)

-- w is the mass of the sample aliquot, mg

-- Fe is the trace Fe content in the sample plus laboratory dissolution reagents. Assuming measurement by ICP-MS or ICP-AES the u(Fe) = ± 5% of the measured value, mg/mg

-- f_{Fe} is the fraction of Fe electrolyzed, quantity of dimension 1, (dimensionless)

-- A_{rFe} is the relative atomic mass (atomic weight) of Fe, grams Fe/mol or mg Fe/mmol

The Pu concentration equation above can be applied as the model equation for the propagation of an ideal case measurement uncertainty for the measurement of plutonium concentration by controlled-potential coulometry using ISO 12183. When calculating an ideal case uncertainty, it is generally desirable not to tie the evaluation to a single population of data from an individual set of measurement or to limit the data collection to just one laboratory. Instead for an ideal case calculation the recommended practice is to use collections of data from multiple sources where possible to assign uncertainties to each of the individual error source individually. This practice sometimes requires making some assumptions based on scientific judgement and experience. The outcome of the ideal case model is a benchmark for measurement uncertainty that can be applied for self-assessment of actual performance at an individual location. The ideal case budget also helps to focus attention on the parameters/variables that are the most important to overall quality, and to avoid unnecessary attention to less important parameters/variables when the individual laboratory has similar performance on a variable that has a small budget consideration.

For the C126 plutonium standard solutions, this GUM propagation is designed to express uncertainty in the characterization measurements for a specific plutonium solution. The actual, replicate measurement data are handled in a Type A evaluation. Other parameters that have the potential for impacting the combined standard uncertainty were addressed as Type B evaluations. The model equations that are developed herein combine the Type A variance (primarily random error) for the measurement of aliquots from the solution provided by PFDC for concentration measurement with the other source of uncertainty. For simplicity, the "other" sources are handled at Type B evaluations. The input information is either from: the F/H Laboratory; from JAEA where the C126 solution and aliquots of the C126 solution were prepared as QCs; from the F/H Laboratory where iron by ICP-MS was performed; or to a small extent from scientific judgement.

The variable Q_{sample} (Q_s) and $Q_{blankprime}$ (Q_{bp}) are used in the ideal case calculation of the measurement result (mg Pu) and they have an impact on the combined standard uncertainty for the measurement. Having the actual replicate data for the measurements handled as a Type A evaluation include all the variance from several sources, such as Q_s and $Q_{bp.}$ Thus, eliminating the minor challenges within the ideal case model to provide a Type A analysis of Q_{bp} based on a large population of actual blank measurement, and the need for the Type B evaluation of $Q_{s,}$ and the scientific judgement to decide on the extent of correlation between these two variables during the measurement of the aliquots. The exact circumstances of the F/H Laboratory coulometric measurements, including the aliquot preparation at PFDC, and the supporting iron by ICP-MS used for iron correction are included in the model equations being applied.

************** Text for "Results" section (at end of document):

The expanded uncertainty calculated using GUM Workbench[TM] agrees with values cited in ISO 12183 and the 2010 International Target Values. The expanded uncertainty cited in ISO 12183, "Controlled-potential coulometric assay of plutonium," for measurements performed in accordance with this standard is ± 0.1 to ± 0.2% at the 95% confidence interval. The performance expectations cited in the 2010 International Target Values for plutonium assay by controlled-potential coulometry are:

o $U_{systematic}$ = ± 0.1%

o U_{random} = ± 0.1%

o $U_{combined\ standard}$ = ± 0.14% (K=1)

o $U_{expanded}$ = ± 0.28% (K=2)

Model Equation:

$$Pu\_Conc_{propagation} = Pu\_Conc_{mg\_per\_g} * \Delta C_{ISO12183} * \Delta_{mass} * \Delta f_{Pu} ;$$

$$Pu\_Conc_{mg\_per\_g} = Pu\_Conc_{AB} - Fe_{correction};$$

$$Fe_{correction} = Fe\_Conc_{mg\_per\_g} * (f_{Fe} / f_{Pu}) * (Pu_{At\_Wt} / Fe_{At\_Wt});$$

$$\Delta_{mass} = \Delta_{mass\_systematic} * \Delta_{mass\_random};$$

$$\Delta_{mass\_random} = (\Delta m_{KK629} + \Delta m_{KK630} + \Delta m_{KK631} + \Delta m_{KK632} + \Delta m_{KK633} + \Delta m_{KK634} + \Delta m_{KK635} + \Delta m_{KK636}) / 8;$$

List of Quantities:

Quantity	Unit	Definition
$Pu\_Conc_{propagation}$	mg/g	Combined average of Pu concentration results, corrected, corrected for iron in the C126 solution with Δ-terms for the other sources of relative uncertainty. Calculated value.
$Pu\_Conc_{mg\_per\_g}$	mg/g	Combined average of Pu concentration measurement results, corrected for iron in the C126 standard solution. Calculated value.
$\Delta C_{ISO12183}$		Uncertainty associated with electrical calibration using Ohm's Law and the Faraday Constant. This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty source.
Δ_{mass}		Uncertainty in masses from balance calibration, solution handling, and residual uncertainty after buoyancy corrections. This Δ variable is calculated from $\Delta_{mass\_systematic}$ and $\Delta_{mass\_random.}$ Type B uncertainty source.
Δf_{Pu}		Uncertainty in fraction of plutonium electrolyzed, caused by fossilized uncertainty from periodic measurement of formal potential, $E_{Pu}^{o'}$. This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty source.
Pu_Conc_{AB}		Pu concentration results for sample analysis before iron corrections. This varialbe is "Type A direct" with CPC method variance from multiple sources of uncertainty.
$Fe_{correction}$	mg/g	Contribution from iron in the original C126 solution converted determined in units of equivalent mg of Pu per g of solution. This value is subtracted from the Pu concentration measure by coulometry. Calculated value.
$Fe\_Conc_{mg\_per\_g}$	mg/g	Iron impurity concentration by ICP-MS performed by F/H Laboratory on the aliquot solutions, after analysis by CPC aliquots
f_{Fe}		Fraction of iron electrolyzed, f_{Fe}, during Pu oxidation. Using average value from sample. ~0.5 with rectangular distribution. Type B uncertainty based on evaluation of measurement data and parameters impacting $f_{Fe.}$
f_{Pu}		Fraction of plutonium electrolyzed, f_{Pu}, during Pu oxidation. Using average value from samples. ~0.999 with rectangular distribution. Type B uncertainty based on evaluation of measurement data and parameters impacting $f_{Fe.}$
Pu_{At_Wt}	g/mol	Atomic weight of Pu calculated from Pu isotope amount ratios from certificate, decayed to analysis date average of Sept. 24, 2017. Type B uncertainty.
Fe_{At_Wt}	g/mol	Atomic Weight of Fe, 55.845 g mol^{-1} +/- 0.002 rectangular. Type B uncertainty.
$\Delta_{mass\_systematic}$		Systematic uncertainty in masses from balance calibration, residual uncertainty after buoyancy corrections, and related systematic sources, This Δ variable was assigned a value of 1, with a rectangular distribution. Type B uncertainty.
Δ_{mass_random}		Random uncertainty in masses from solution handling, balance readability, and related random sources of uncertainty, This Δ-variable was calculated from the variables Δ_{m1} through $\Delta_{mB.}$ Calculated value.

Quantity	Unit	Definition
Δm_{KK629}		Random uncertainty in the mass of aliquot KK629 from solution handling, balance readability, and related random sources of uncertainty, This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty.
Δm_{KK630}		Random uncertainty in the mass of aliquot KK630 from solution handling, balance readability, and related random sources of uncertainty, This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty.
Δm_{KK631}		Random uncertainty in the mass of aliquot KK631 from solution handling, balance readability, and related random sources of uncertainty, This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty.
Δm_{KK632}		Random uncertainty in the mass of aliquot KK632 from solution handling, balance readability, and related random sources of uncertainty, This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty.
Δm_{KK633}		Random uncertainty in the mass of aliquot KK633 from solution handling, balance readability, and related random sources of uncertainty, This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty.
Δm_{KK634}		Random uncertainty in the mass of aliquot KK634 from solution handling, balance readability, and related random sources of uncertainty, This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty.
Δm_{KK635}		Random uncertainty in the mass of aliquot KK635 from solution handling, balance readability, and related random sources of uncertainty, This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty.
Δm_{KK636}		Random uncertainty in the mass of aliquot KK636 from solution handling, balance readability, and related random sources of uncertainty, This Δ variable is assigned a value of 1, with a rectangular distribution. Type B uncertainty.

$Pu\_Conc_{mg\_per\_g}$: Interim Result

Plutonium concentration corrected for iron in the plutonium solution.

$\Delta C_{ISO12183}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0004

This estimate is based upon evaluation of instrument design and performance, uncertainty estimates for the electrical calibration process as well as historical recoveries on Pu standards, routine Pu QC method performance, and participation in external exchange programs. [This estimate involves scientific judgment as well as numeric analysis.]

It is typical at the Laboratory that average of multiple measurements on Pu working standard generate recovery values that agree with the decay corrected reference value within ± 0.01%.

This value of 1 ± 0.0001 halfwidth rectangular is ± 0.01 %. This value corresponds to a Gaussian uncertainty of ± 0.01 % / SQRT(3) = ± 0.005% 1-σ.

Δ_{mass}: Interim Result

Aliquot weights were provided by JAEA. Aliquots are on average 9 g of solution. A 0.0004 g uncetainty was estimated for this measurement. This value corresponds to a Δ_{mass} of 1.00000 with an r = 0.00023 (rectangular distribution).

However,eight (8) replicate aliquots were measured by controlled-potential coulometry and their average included in this GUM Workbench^{TM} uncertainty propagation. The random uncertainty component of the Δ be reduced by replicate measurements, while the systematic uncertainty component of the Δ_{mass} term will not be reduced by replicate measurements.

For this GUM Workbench^{TM} uncertainty propagation, the Δ_{mass} term has been divided into random uncertainty and systematic uncertainty components for an individual mass measurement based on scientific judgement that the random component of an individual mass is larger than the systematic component.

The $\Delta_{mass\_systematic}$ component was assigned a value of 1.00 with r = 0.000087 (rectangular distribution). (See discussion for this variable.)

The Δ_{mass_random} was assigned the remaining uncertainty: r = (0.00023^2 - 0.000087^2) $^{0.5}$ = ± 0.00026 (rectangular distribution).

Δf_{Pu}: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0001

This source of uncertainty is dependent on the current at which the CP-adjustment is initiated. i_0 / 750 or i_0 / 1000 are typical values; with i_0 / 1000 have a lower $\Delta f_{Pu,}$ but the uncertainty in the measurement of the background current increases at 1000 vs. 750.

These measurements were performed with the CP-adjustment set to initiate at i_0/1000.

Pu_Conc$_{AB}$: Type A
Method of observation: Direct
Number of observations: 8

No.	Observation
1	1.64345
2	1.64292
3	1.64066
4	1.64257
5	1.64185
6	1.64243
7	1.63851
8	1.64310

Arithmetic Mean: 1.641936
Standard Deviation: $1.6 \cdot 10^{-3}$
Standard Uncertainty: $577 \cdot 10^{-6}$

Fe$_{correction}$: Interim Result

Iron is measured by ICP-MS at AMU-57, with a total uncertainty of 7.5%. FeAve x (ArPu / ArFe) x (fFe / fPu)

Fe_Conc$_{mg_per_g}$: Type B rectangular distribution
Value: 0.000097 mg/g
Halfwidth of Limits: 0.00013 mg/g

Fe concentration value was measured by the F/H 0Laboratory by ICP-MS. The value of 0.000097 mg Fe / g of solution with with a total uncertainty of 7.5% an uncertainty . For this GUM Workbench™ propagation, a conservative value of r = 0.00013 mg /g (± 5 % 1-σ, relative) was assigned.

Iron is measured by ICP-MS at AMU-57, with a total uncertainty of 7.5%.

Calculation of Halfwidth: FeAve x (ArPu / ArFe) x (fFe / fPu) x 7.5% x SQRT(3), i.e., 0.000097 x 7.5% x 1.73 = 0.000013

f_{Fe}: Type B rectangular distribution
Value: 0.99753
Halfwidth of Limits: 0.0003

Average of the measured f_{Fe} values from sample aliquots was used. A Halfwidth of Limts estimated from the uncertainty in the input varialbes $S_{OX,}$ $S_{RED,}$ $E_{0,}$ Temperature yields . A Halfwidth calculated as s * $3^{0.5}$ yields a more conservative value of 0.0003

KK629 0.997428 KK630 0.997693 KK631 0.997266 KK632 0.997064 KK633 0.997758 KK634 0.997795 KK635 0.997582 KK636 0.997677

average 0.99753 s 0.00026 r 0.00045

The uncertainty in fFe is negligible in H2SO4 supporting electrolyte. This source of uncertainty is more important in HNO3 supporting electrolyte, but depends upon the quantity of Fe present in the aliquot versus the quantity of plutonium present in the aliquot. The actual value for fFe and its uncertainty, fFe , are dependent on measurement cell kinetics and should be calculated from Sox, Sred, T, and EFeo' on each Pu measurement.

f_{Pu}: Type B rectangular distribution
Value: 0.99920
Halfwidth of Limits: 0.000005

Average of the measured f_{Pu} values from sample aliquots A Halfwidth calculated as s * $3^{0.5}$ yields a more conservative value of 0.000005

KK629 0.999179 KK630 0.999228 KK631 0.999140 KK632 0.999124 KK633 0.999242 KK634 0.999253 KK635 0.999203 KK636 0.999240 average 0.99920 s 0.00005 r 0.00008

Uncertainty estimated from the variance in the input variables used to calculate $f_{Pu,}$ i.e., Eo_{Pu}, S_{OX}, S_{RED}, and T.

Pu_{At_Wt}: Type B rectangular distribution
Value: 239.0728 g/mol
Halfwidth of Limits: 0.005 g/mol

Calculated from isotope amount ratios from certificate decay corrected to the date of the individual coulometric measurements.

239.0728

Assigned a conservative uncertainty r = 0.005 rectangular.

Fe_{At_Wt}: Type B rectangular distribution
Value: 55.845 g/mol
Halfwidth of Limits: 0.002 g/mol

IUPAC 2010 value and uncertainty for the iron atomic weight was used.

$\Delta_{mass\_systematic}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.000087

Balance calibration (and quality control monitoring of balance performance using test weights with well know reference masses) are assumed to demonstrate that the systematic uncertainty associated with this Type B (relative uncertainty) term should be better than 0.005 % (1-σ, i.e., 1 ± 0.00005. (Gaussian distribution)

This value was multiplied by $3^{0.5}$ (SQRT(3)) to convert to a rectangular distribution with r = 0.000087.

Δm$_{KK629}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0026

Δm$_{KK630}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0026

Δm$_{KK631}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0026

Δm$_{KK632}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0026

Δm$_{KK633}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0026

Δm$_{KK634}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0026

Δm$_{KK635}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0026

Δm$_{KK636}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0026

Interim Results:

Quantity	Value	Standard Uncertainty
Pu_Conc$_{mg_per_g}$	1.641522 mg/g	$660 \cdot 10^{-6}$ mg/g
Δ_{mass}	1.000000	$533 \cdot 10^{-6}$
Fe$_{correction}$	$415 \cdot 10^{-6}$ mg/g	$321 \cdot 10^{-6}$ mg/g
Δ_{mass_random}	1.000000	$531 \cdot 10^{-6}$

Uncertainty Budgets:

Pu_Conc$_{propagation}$: Combined average of Pu concentration results, corrected, corrected for iron in the C126 solution with Δ-terms for the other sources of relative uncertainty. Calculated value.

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
Pu_Conc$_{mg_per_g}$	1.641522 mg/g	$660 \cdot 10^{-6}$ mg/g				
$\Delta C_{ISO12183}$	1.000000	$231 \cdot 10^{-6}$	rectangular	1.6	$380 \cdot 10^{-6}$ mg/g	10.6 %
Δ_{mass}	1.000000	$533 \cdot 10^{-6}$				
Δf_{Pu}	1.0000000	$57.7 \cdot 10^{-6}$	rectangular	1.6	$95 \cdot 10^{-6}$ mg/g	0.7 %
Pu_Conc$_{AB}$	1.641936	$577 \cdot 10^{-6}$	normal	1.0	$580 \cdot 10^{-6}$ mg/g	24.6 %
$Fe_{correction}$	$415 \cdot 10^{-6}$ mg/g	$321 \cdot 10^{-6}$ mg/g				
Fe_Conc$_{mg_per_g}$	$97.0 \cdot 10^{-6}$ mg/g	$75.1 \cdot 10^{-6}$ mg/g	rectangular	-4.3	$-320 \cdot 10^{-6}$ mg/g	7.6 %
f_{Fe}	0.997530	$173 \cdot 10^{-6}$	rectangular	$-420 \cdot 10^{-6}$	$-72 \cdot 10^{-9}$ mg/g	0.0 %
f_{Pu}	0.99920000	$2.89 \cdot 10^{-6}$	rectangular	$410 \cdot 10^{-6}$	$1.2 \cdot 10^{-9}$ mg/g	0.0 %
Pu_{At_Wt}	239.07280 g/mol	$2.89 \cdot 10^{-3}$ g/mol	rectangular	$-1.7 \cdot 10^{-6}$	$-5.0 \cdot 10^{-9}$ mg/g	0.0 %
Fe_{At_Wt}	55.84500 g/mol	$1.15 \cdot 10^{-3}$ g/mol	rectangular	$7.4 \cdot 10^{-6}$	$8.6 \cdot 10^{-9}$ mg/g	0.0 %
$\Delta_{mass\_systematic}$	1.0000000	$50.2 \cdot 10^{-6}$	rectangular	1.6	$82 \cdot 10^{-6}$ mg/g	0.5 %
Δ_{mass_random}	1.000000	$531 \cdot 10^{-6}$				
Δm_{KK629}	1.00000	$1.50 \cdot 10^{-3}$	rectangular	0.21	$310 \cdot 10^{-6}$ mg/g	7.0 %
Δm_{KK630}	1.00000	$1.50 \cdot 10^{-3}$	rectangular	0.21	$310 \cdot 10^{-6}$ mg/g	7.0 %
Δm_{KK631}	1.00000	$1.50 \cdot 10^{-3}$	rectangular	0.21	$310 \cdot 10^{-6}$ mg/g	7.0 %
Δm_{KK632}	1.00000	$1.50 \cdot 10^{-3}$	rectangular	0.21	$310 \cdot 10^{-6}$ mg/g	7.0 %
Δm_{KK633}	1.00000	$1.50 \cdot 10^{-3}$	rectangular	0.21	$310 \cdot 10^{-6}$ mg/g	7.0 %
Δm_{KK634}	1.00000	$1.50 \cdot 10^{-3}$	rectangular	0.21	$310 \cdot 10^{-6}$ mg/g	7.0 %
Δm_{KK635}	1.00000	$1.50 \cdot 10^{-3}$	rectangular	0.21	$310 \cdot 10^{-6}$ mg/g	7.0 %
Δm_{KK636}	1.00000	$1.50 \cdot 10^{-3}$	rectangular	0.21	$310 \cdot 10^{-6}$ mg/g	7.0 %
Pu_Conc$_{propagation}$	1.64152 mg/g	$1.16 \cdot 10^{-3}$ mg/g				

The propagated concentration has not been decay corrected

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
Pu_Conc$_{propagation}$	1.6415 mg/g	$2.3 \cdot 10^{-3}$ mg/g	2.00	95% (normal)