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APPLICATION OF CONTROLLED-POTENTIAL COULOMETRY AS A PRIMARY METHOD FOR THE CHARACTERIZATION OF PLUTONIUM NITRATE SOLUTIONS BEING USED FOR LARGE-SIZE DRY SPIKE REFERENCE MATERIALS; COLLABORATION BETWEEN JAEA AND SRNL

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ABSTRACT

Since November 2007, the laboratory at the Japan Atomic Energy Agency's (JAEA) Tokai Reprocessing Technology Development Center (TRTDC) and Savannah River National Laboratory (SRNL) have collaborated on a new mission to apply controlled-potential coulometry as a primary method for characterizing plutonium master solutions. Measurement results are being used to prepare traceable and certifiable large-size dry (LSD) spike standards for safeguards measurements by isotope dilution mass spectrometry. Activities included: returning to service two previously installed 1998-vintage SRNL Coulometers; upgrading them to the 2006 SRNL-design; performing periodic component and system calibration; pursuing sustainability and human capital development; and ensuring effective application of a measurement service that is fit-for-purpose. Ensuring analytical fitness included: compliance with ISO 12183 (Pu coulometry assay); qualification versus appropriate acceptance criteria; traceability to the International system of units (SI); application of appropriate measurement controls; and uncertainty propagation in accordance with JCGM 100:2008 (ISO-GUM, current version). The collaboration on upgrades, calibration services, human capital development, and the analytical fitness activities performed by JAEA and SRNL were authorized and funded under the JAEA & United States NNSA/DOE Permanent Coordinating Group. This report will chronicle the collaboration activities of JAEA and SRNL, and provide the detail on the periodic coulometer component calibrations, the coulometric plutonium measures and measure practices, including the uncertainty propagation for the most recent plutonium master solution used for LSD Spike preparation.

INTRODUCTION

In 1998, scientists and engineers from SRNL began collaborating with JAEA under the auspices of the Joint NNSA&DOE/Japan Permanent Coordinating Group. Under this collaboration project, JAEA and SRNL build, test, deliver, and install two SRNL Coulometers in TRTDC Lab.

The SRNL Coulometers were fabricated, assembled, and tested at SRNL. During October 1998, the final phase of the acceptance testing at SRNL was witnessed by TRTDC staff. The system was then delivered and installed at the TRTDC Lab in February 1999 and functionality was demonstrated. Initial training on instrument operation was performed concurrently during and immediately following the demonstration of functionality. The plutonium measurement results from the acceptance testing at SRNL are provided in Table 1. These results meet the uncertainty requirements in the International Target Values 2010 (ITV-2010).[1] JAEA accepted the instrument at the end of the installation visit and began operating the system successfully.[2,3] During this period SRNL provided technical support and information exchange. SRNL staff traveled to the TRTDC Lab to perform component calibration and preventive maintenance activities in 2001 and 2002. The SRNL Coulometers were maintained in standby mode from 2003-2008.

Table 1. Acceptance Testing of SRNL Coulometers for JAEA, at SRNL

Electrolyte / Working Electrode	System #1 Recovery	System #2 Recovery	Average & RSD,%
H_2SO_4 / Platinum	99.99 % 100.01 % 99.97 % 99.99 % 99.98 % 100.04 %	100.01 % 100.01 % 99.95 % 99.95 % 99.96 % 100.00 %	99.99 % 0.03 %
HNO_3 / Gold	99.96 % 100.08 %	99.95 %	100.00 % 0.07 %
HNO_3 / Platinum {Non-routine for SRS}	99.98 %		
H_2SO_4 / Gold {Non-Routine for SRS}	99.85 %		

Starting in 1989, Japan began evaluating large-size dry (LSD) spikes for isotope dilution mass spectrometry (IDMS) and applied LSD-IDMS for routine safeguards measurements.[4,5] During method development and evaluation at the TRTDC, the spikes were prepared by the Nuclear Material Laboratory (NML, formerly the Safeguards Analytical Laboratory) of the International Atomic Energy Agency (IAEA) and by the Institute of Reference Material and Measurements (IRMM). The LSD spikes were prepared using primary uranium metal supplied by the U. S. Department of Energy's New Brunswick Laboratory (DOE-NBL) and primary plutonium metal supplied by DOE-NBL or by Commission d'Établissement des Méthodes d'Analyse (CETAMA) in France. However, neither the United States nor France could support the large increase in the number of units of primary plutonium metal that would be required for the routine operation of two large commercial nuclear facilities in Japan.

In 2007, an LSD Spike review and planning meeting was held in Tokai-mura, Japan. At this meeting it was decided Japan would continue planning to use LSD Spike and Thermal Ionization Mass Spectrometry (TIMS) for all key safeguards measurements, but that alternative plutonium source materials would be need. Based upon direction from this meeting, continued collaboration by SRNL and JAEA was authorized and both organizations began planning to resume coulometry in TRTDC Lab to support the characterization of the primary plutonium solution prepared from existing MOX powder in JAEA.[6,7] The services included an upgrade of the SRNL Coulometers' peripheral devices in 2007.[8] In 2008, SRNL fabricated a coulometer measurement cell for the TRTDC Lab and supported its glovebox installation at the TRTDC Lab. Collaboration with JAEA included exchanging of technical and programmatic information on safeguards measurements and measurement control practices. TRTDC staff demonstrated proficiency in performing measurements in using the SRNL coulometer but was dependent upon the SRNL for component-level calibration and maintenance services.

In 2013, JAEA and SRNL expanded the project focusing on human capital development and sustainability by JAEA in the areas of measurement expertise, instrument maintenance, and traceable component calibration while also continuing required maintenance support from SRNL. SRNL support visits to JAEA under this project were conducted in 2014 and 2015.

In this study, SRNL and JAEA present information on: technical collaboration and information exchange; periodic coulometer component calibration with traceability of measurements to SI standards; the successful characterization of the plutonium solutions prepared from existing MOX powder; and a GUM-compliant uncertainty propagation for the most recent plutonium measurements performed by the TRTDC Lab.

MEASUREMENT CONTROL & FITNESS-FOR-PURPOSE

For coulometric measurements, the TRTDC Lab has implemented international standard ISO 12183 for the controlled-potential coulometric determination of plutonium.[10] Measurement control practices comply with the requirements and guidance in this standard and with TRTDC Lab internal programs for quality assurance and quality control. Implementation satisfies the key attributes of being safe to operate, compliant with all rules and regulations, and analytically fit-for-purpose. A review of TRTDC Lab coulometric measurements for analytical fitness is provided below. The TRTDC Lab does not claim compliance with ASTM standard practices, but the process cited below for assessing analytical fitness are consistent with the guidance in ASTM C1068 Annex A1.[11]

- Data quality objectives: The concentration of the purified plutonium working reference solution that will be used to prepare LSD spike aliquots is expected to be known with an expanded uncertainty that meets or exceeds the quality required in the ITV-2010. TRTDC Lab applies international standard ISO 12183 and the SRNL Coulometer for plutonium measurements and meets the expected performance cited in ISO 12183. Sample aliquots from the Pu working reference solution are taken by mass from the reference solution and dried gently to a glassy nitrate salt deposited in sealed vials. The buoyancy-corrected mass of each aliquot is provided.
- Qualified method and staff: Each aspect of the measurement process has been demonstrated uisng traceable reference material, including the quantitative dissolve and transfer of the dried plutonium nitrate, the oxidation state adjustment to reduce any Pu^{6+} (PuO_2^{2+}) using hydrogen peroxide, fuming to dryness in sulfuric acid, and measurement of the supporting electrolyte blank, the plutonium analyte, and the formal potential of the Pu^{4+}/Pu^{3+} redox couple. TRTDC Lab uses internal quality assurance program to ensure that measurement methods and staff are qualified and proficient.
- Traceability of measurements to SI (i.e., metrological traceability to the modern metric system[12]): Traceability of measurements is achieved by component-level calibration of key components within the SRNL Coulometer: digital integrator modules including voltage-to-frequency converts and quartz crystal oscillator for timing, the load resistor in the potentiostat modules, the interal calibration resistors, and the high-precision voltmeter. These calibration services are provided by SRNL staff using traceable test equipment that is calibrated by an ISO 17025 accredited calibration laboratory at the SRNL. The test equipment is calibrated before being transported to the TRTDC Lab and upon return to the SRNL. Traceability of measurements to SI is also provided by appropriate balance calibration at each location where the aliquots are taken by mass. Well vetted procedures are used by both laboratories for the mass measurements, the drying and sealing of the plutonium nitrate, and the packaging for transport between laboratories.
- Uncertainty: Uncertainty associated with measurement method is understood and its propagation is performed in an manner that is well defined, documented, and effective. Calculations are performed using internationally-accepted standards JCGM100.[13,14,15]
- Measurement control program: The practices are implemented effectively based upon internal quality assurance requirements and guidance in ISO 12183. The TRTDC Lab controls all key aspects of the measurement process using traceable CRM 126-series plutonium metal assay reference materials. Aliquots of the quality control standard prepared by the TRTDC for instrument control are processed through the oxidation state adjustment with hydrogen peroxide and fuming to dryness in sulfuric acid before measurement (the same process used to measure samples). Aliquots of the plutonium solution are received as nitrate salt in sealed vials along with several aliquots of CRM 126-series reference material that has also been dried as a nitrate salt in the same type of sealed vials.
- Compliance with an international standard: Applying standardized measurement practices is an important element in demonstrating analytical fitness. When exceptions or deviations to standardized practices are taken, the requirements and riggor increase for method selection, validation, and qualifications. TRTDC coulometric measurements are performend in full compliance with ISO 12183 and uncertainty calculations comply with JCGM 100.

COULOMETER HARDWARE AND SOFTWARE UPGRADES

The 2008 upgrades to the SRNL Coulometers at TRTDC Lab included all hardware and software enhancement performed on the instruments installed at the SRNL and at the IAEA-NML:

- Installed re-designed Agilent 3470 Data Aquasition Modules (Correcting a manufacturer-identified design issue that caused premature failure.)
- Installed isolated DC/DC floating reference power supplies to improve control-potential stability in the potentiostats modules.
- Replaced outdated instrument controller hardware with a new laptop computer and current vintage operating systems and commercial software i.e., Windows™ and HT Basic™ software.
- Upgraded custom SRNL coulometer measurement software program (operating in HT Basic™).
- Provided new SRNL-designed measurement cell, including new cables, connectors and a moisture-conditioner for the argon gas supply.

COULOMETER MAINTENANCE

SRNL Coulometer unit #1 was kept in continuous electrical calibration mode when not being used. Due to limitation in instrument controllers and other configuration considerations only one of the two units could be kept in continuous electrical calibration mode. Unit #2 was maintained in an energized but standby mode. SRNL Coulometer unit #2 experienced most of the observed maintenance problems, which was believe to be correlated with, if not caused by, not being able to maintain this unit in a fully functional configuration. After March 2011, the TRTDC Lab facilities experience serious issue with environment control of temperature and humidity. The laboratory temperature and humidity fluctuated well beyond the capability of the coulometer on both a 24-hour cycle and a seasonal cycle. Unit #1 could only be used during periods when the outside temperature and humidity was moderate and did not fluctuate significant between day and night. The SRNL Coulometer and the commercial peripheral devices were not designed for these extreme environment fluctuations. By the end of 2015, SRNL concluded that both coulometers units at the TRTDC are at or beyond there expected life time and are now plagued with on-going maintenance issues to the extent that they need to be replaced with a newer-design SRNL Coulometer[9] or equivalent system. Refurbishing would not be practical as it would be extensive, expensive, and risky given the current condition of the two units. In addition, SRNL does not have an adequate inventory of spare parts for the older vintage SRNL Coulometers to facilitate refurbishing and subsequent routine maintenance.

COULOMETER COMPONENT CALIBRATION

Component calibration for the SRNL Coulometer is a systematic process of transferring traceability to SI from calibrated test equipment (voltmeters, counters, and standard resistors) to the components and peripheral devices within the SRNL Coulometer. The test equipment used in 2015 is listed in Table 2. The same or equivalent test equipment has been used by SRNL in Japan since 1999.

Table 2. SRNL calibrated test equipment from SRNL's accredited calibration laboratory

Calibrated test equipment	SRNL tracking #	Calibration expires
Automatic Systems Laboratory Standard Resistor Model RR100	M&TE 3-4030	2016-Jun-02
Agilent 34401A Digital Volt Meter	M&TE 3-4492	2016-July-21
Agilent 53131A Universal Counter	M&TE 3-4168	2016-July-22

During component calibration, SRNL measures both the "as found" and the "updated" calibration results. Calibration results for SRNL Coulometer Unit #1 from 2015-Nov-09 are provided as typical data in Tables 3 and 4.

Table 3. Calibration of Potentiostat#1, Load resistor and Unit #1 internal calibration resistor, Ω

Components	Units	Values	Comment
Standard resistor, $\Omega_{Std\text{-}R}$	Ohms	100.00188 @ 24.8 C	SRNL calibration certificate
Voltage-drop across, $V_{Std\text{-}R}$	Volts	1.001250	Measured value
Voltage-drop across, $V_{Load\text{-}R_1}$	Volts	0.500045	1st Measured value of $V_{Load\text{-}R}$
Load Resistor, ($\Omega_{Load\text{-}R}$)	Ohms	**49.9430**	Calculated using Ohm's Law $\Omega_{Load\text{-}R} = \Omega_{Std\text{-}R} \times (V_{Load\text{-}R1} / V_{Std\text{-}R})$
Previous Load-R, 2014-May	Ohms	49.9422	Δ = **+0.002%** (acceptable agreement)
Voltage-drop across Internal $V_{Cal\text{-}R}$	Volts	1.00233	Measured value
Voltage-drop across $V_{Load\text{-}R_2}$	Volts	0.50055	2nd Measured value of $V_{Load\text{-}R}$
Internal Calibration Resistor ($\Omega_{Cal\text{-}R}$)	Ohms	**100.0087**	Calculated using Ohm's Law $\Omega_{Cal\text{-}R} = \Omega_{Load\text{-}R} \times (V_{Cal\text{-}R} / V_{Load\text{-}R_2})$
Previous Cal-R, 2014-May	Ohms	100.0109	Δ = **–0.002 %** (acceptable agreement)

Table 4. Digital integrator module component alignment (verification data after alignment)

Component	Frequency	Unit	RD %	Comment
VFC #1	1600.35 [1]	Hz	--	acceptable value
VFC #2	1600.59 [1]	Hz	--	acceptable value
Quartz Crystal Oscillator	10000.008 [1] VFCs w. Offset Signal	Hz	Δ = **–0.00008 %**	acceptable agreement
VFC #1 Linearity Test:				
VFC #1 Input Voltage / V measured on Agilent 34401A	VFC #1 / Hz $V_{input}+V_{offset}$ measured on Agilent 53131A	VFC #1 / Hz	Expected / Hz @ 10K Hz/V	RD % vs. Expected
0.499998	6600.5	5000.1	4999.98	+ 0.003 %
0.999999	11600.7	10000.3	9999.99	+ 0.004 %
1.99997	21600.6	20000.2	19999.7	+ 0.003 %
2.99996	31600.8	30000.4	29999.6	+ 0.003 %
3.99997	41601.1	40000.7	39999.7	+ 0.003 %
4.99997	51601.4	50001.0	49999.7	+ 0.003 %
5.99995	61601.4	60001.0	59999.5	+ 0.003 %
6.99996	71601.7	70001.3	69999.6	+ 0.003 %
7.99997	81601.8	80001.4	79999.7	+ 0.002 %
8.99999	91602.0	90001.6	89999.9	+ 0.002 %
Integrator Non-linearity, 2-σ	2 x standard deviation			**± 0.001 %** acceptable value

HUMAN CAPITAL DEVELOPMENT UNDER COLLABORATION PROJECT

In addition to the on-going training and technical exchanges between SRNL and TRTDC staff during coulometric measurements and during component-level calibrations, SRNL provided briefings and self-study information for the TRTDC staff. The topic areas from human capital development were taken from the SRNL Knowledge Preservation Project for Controlled-Potential Coulometry[16] (used by SRNL to train scientists on coulometry and measurement control practices) and from the IAEA Coulometry Workshop conducted by SRNL in Vienna, Austria on May 6-8, 2015. The topic areas included:

- Controlled-potential coulometry – purpose, scope, applications, and limitations
- Control and prevention of interferences
- Measurement control practices
- Methodology for ensuring analytical fitness-for-purpose
- Method qualification practices [ASTM C1068] and accreditation [ISO/IEC 17025]
- Traceability to SI for the SRNL Coulometer and ISO 12183 / ASTM C1008 methodology
- Coulometer calibration methodologies, electrical [ISO 12183] vs. chemical [ASTM C1165]
- Overview of SRNL Calibration Lab capabilities & credentials [NAVLAB & ISO/IEC 17025]

- Coulometric measurement experiences and lessons learned from SRNL, IAEA-NML, and JAEA
- Design considerations for coulometer instrumentation and measurement cells
- Operational amplifier functionality and electrochemical application
- Software design and control, SRNL practices
- Proposed revisions to ISO 12183
- Uncertainty propagations, both GUM and performance-based calculations, and their usage (This segment of human capital development included generating the uncertainty propagation provided in the Uncertainty Propagation section.)

MEASUREMENT PERFORMANCE

The following coulometric measurement results are provided in Table 5 to demonstrate an on-going performance and a high level of proficiency by the staff at the TRTDC Lab to perform plutonium concentration measurements since measurement activities were resumed in 2008.

Table 5. Measuring CRM 126 Pu standards & characterizing Pu solutions for LSD Spike preparation

Year	Purpose	Replicates	Aliquot size (nominal)	Concentration or Recovery	Relative Standard Deviation	CPC vs. IDMS
2008	Characterized 1st Pu solution for LSD Spike preparation	8	15 mg	15.5995 mgPu/g ± 0.053 % [K=2] Analyzed Dec. 2008	0.016 %	-0.064 %
2008	Measured CRM 126 during characterization of 1st Pu solution	9	15 mg	99.977 %	0.025 %	--
2009	Demonstrated measurement precision during SRNL visit	6	16 mg	---	0.03 %	--
2011	Characterized 2nd Pu solution for LSD Spike preparation	12	12 mg	10.0446 mgPu/g Not Corrected for Fe Analyzed Sep. 2011	0.021 %	--
2011	Measured CRM 126 during characterization of 2nd Pu solution	6	14 mg	100.001 %	0.011 %	--
2014-2015	Characterized 3rd Pu solution for LSD Spike preparation	11	13 mg	10.0242 mgPu/g ± 0.067 % [K=2] Decayed to Nov. 2012	0.050 %	+0.08 %
2014	Measured 2011 CRM 126 during characterization of 3rd Pu solution	4	14 mg	99.976 %	0.017 %	--
2015	Measured 2015 CRM 126 during characterization of 3rd Pu solution	5	10 mg	100.012 %	0.043 %	--
2015	Measured 2013 CRM 126 supplied as nitrate salt with 3rd Pu solution	2	10 mg	99.961 %	0.033 %	--

UNCERTAINTY PROPAGATION, using GUM Workbench™ software

Characterization of plutonium concentration by controlled-potential coulometry

Equation for calculating individual plutonium concentration results:

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

- 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

Model equations for uncertainty propagation:

$Pu_Conc_{decayed} = Pu_Conc_{propagation} * Pu_{Decay};$

$Pu_Conc_{propagation} = Pu_Conc_{mg_per_g} * \Delta C_{ISO12183} * \Delta_{mass} * \Delta f_{Pu};$

$Pu_Conc_{mg_per_g} = (Pu_Conc_{013456789AB} - Fe_{correction}) * \Phi Fe_{TRP_Lab_preparation}$

$Fe_{correction} = Fe_Conc_{mg_per_g} * (f_{Fe} / f_{Pu}) * (Pu_{At_Wt} / Fe_{At_Wt});$

$\Delta_{mass} = \Delta_{mass_systematic} * \Delta_{mass_random};$

$\Delta_{mass_random} = (\Delta m_{FF400} + \Delta m_{FF401} + \Delta m_{FF403} + \Delta m_{FF404} + \Delta m_{FF405} + \Delta m_{FF406} + \Delta m_{FF407} + \Delta m_{FF408} + \Delta m_{FF409} + \Delta m_{FF410} + \Delta m_{FF411}) / 11;$

List of quantities, units, definitions, values, and uncertainties:

Quantity	Unit	Definition
$Pu_Conc_{decayed}$	mg/g	Pu concentration result, corrected for radioactive decay, to the date of 2012-Nov-02.
Pu_{Decay}		Correction factor for the decay of plutonium isotopes to 2012-Nov-02.
$Pu_Conc_{propagation}$	mg/g	Pu concentration result, corrected for iron with Δ-terms for the other sources of uncertainty.
$\Delta C_{ISO12183}$		Uncertainty associated with electrical calibration using Ohm's Law and the Faraday Constant.
Δf_{Pu}		Uncertainty in fraction of plutonium electrolyzed.
$Pu_Conc_{mg_per_g}$	mg/g	Pu concentration result (average) corrected for iron in the 3rd Pu standard solution for LSD Spike preparation and for iron added during aliquot preparation steps in the TRTDC Laboratory.
$Fe_{correction}$	mg/g	Correction for iron in 3rd Pu solution, subtracted from Pu concentration measured by coulometry.
$\Phi Fe_{TRP_Lab_preparation}$		Correction for trace iron introduced during TRTDC Lab measurement.
$Pu_Conc_{013456789AB}$	mg/g	Replicate aliquots FF400, FF401, and FF403 through FF411 before iron corrections.
$Fe_Conc_{mg_per_g}$	mg/g	Iron impurity concentration by ICP-AES performed by JAEA's CPF Laboratory.
f_{Fe}		Fraction of iron electrolyzed, f_{Fe}, during Pu oxidation.
f_{Pu}		Fraction of plutonium electrolyzed, f_{Pu}, during Pu oxidation.
Pu_{At_Wt}	g/mol	Atomic weight of Pu calculated from Pu isotope amount ratios by TIMS.
Fe_{At_Wt}	g/mol	Atomic Weight of Fe, 55.845 g mol^{-1} +/- 0.002 rectangular.
Δ_{mass}		Uncertainty in masses from balance calibration, solution handling, and residual uncertainty after buoyancy corrections.

List of quantities, units, definitions, values, and uncertainties:		
Quantity	**Unit**	**Definition**
$\Delta_{mass_systematic}$		Systematic uncertainty in masses from balance calibration, residual uncertainty after buoyancy corrections, and related systematic sources,
Δ_{mass_random}		Random uncertainty in masses from solution handling, balance readability, etc.
Δm_{FF400}		Uncertainty in mass of aliquot FF400 from solution handling, balance readability, etc.
Δm_{FF401}		Uncertainty in mass of aliquot FF401 from solution handling, balance readability, etc.
Δm_{FF403}		Uncertainty in mass of aliquot FF403 from solution handling, balance readability, etc.
Δm_{FF404}		Uncertainty in mass of aliquot FF404 from solution handling, balance readability, etc.
Δm_{FF405}		Uncertainty in mass of aliquot FF405 from solution handling, balance readability, etc.
Δm_{FF406}		Uncertainty in mass of aliquot FF406 from solution handling, balance readability, etc.
Δm_{FF407}		Uncertainty in mass of aliquot FF407 from solution handling, balance readability, etc.
Δm_{FF408}		Uncertainty in mass of aliquot FF408 from solution handling, balance readability, etc.
Δm_{FF409}		Uncertainty in mass of aliquot FF409 from solution handling, balance readability, etc.
Δm_{FF410}		Uncertainty in mass of aliquot FF410 from solution handling, balance readability, etc.
Δm_{FF411}		Uncertainty in mass of aliquot FF411 from solution handling, balance readability, etc.

Quantity	**Value**	**Uncertainty**	**Evaluation type, distribution**
Pu_{Decay}	1.000172	r = 0.000005 [Halfwidth]	Type B, rectangular
$\Delta C_{ISO12183}$	1.0000	r = 0.0004 [Halfwidth]	Type B, rectangular
Δf_{Pu}	1.0000	r = 0.0001 [Halfwidth]	Type B, rectangular
$\Phi Fe_{TRP_Lab_preparation}$	0.9999	r = 0.0002 [Halfwidth]	Type B, U-shaped
$Fe_Conc_{mg_per_g}$	0.00166 mg/g	r = 0.00015 mg/g [Halfwidth]	Type B, rectangular
f_{Fe}	0.54639	r = 0.10400 [Halfwidth]	Type B, rectangular
f_{Pu}	0.99917	r = 0.00010 [Halfwidth]	Type B, rectangular
Pu_{At_Wt}	239.13863 g/mol	r = 0.00500 g/mol [Halfwidth]	Type B, rectangular
Fe_{At_Wt}	55.845 g/mol	r = 0.002 g/mol [Halfwidth]	Type B, rectangular
$\Delta_{mass_systematic}$	1.000000	r = 0.000087 [Halfwidth]	Type B, rectangular
Δm_{FF400}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF401}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF403}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF404}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF405}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF406}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF407}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF408}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF409}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF410}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
Δm_{FF411}	1.00000	r = 0.00026 [Halfwidth]	Type B, rectangular
$Pu_Conc_{013456789AB}$	10.03024 mg/g 10.01604 mg/g 10.02852 mg/g 10.03061 mg/g 10.02165 mg/g 10.03074 mg/g 10.02968 mg/g 10.02880 mg/g 10.02269 mg/g 10.02963 mg/g 10.03231 mg/g	Arithmetic Mean: 10.02736 mg/g Standard Deviation: 5.0×10^{-3} mg/g Standard Uncertainty: 1.69×10^{-3} mg/g	Type A, bayesian Assumed distribution: normal Method of observation: Direct Number of observation: 11

Uncertainty budget: Pu concentration, corrected for radioactive decay to 2012-Nov-02.

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$Pu_Conc_{propagation}$	10.02247 mg/g	3.35×10^{-3} mg/g	∞				
Pu_{Decay}	1.00017200	2.89×10^{-6}	∞	rectangular	10	29×10^{-6} mg/g	0.0 %
$Pu_Conc_{mg_per_g}$	10.02347 mg/g	1.75×10^{-3} mg/g	∞				
$\Delta C_{ISO12183}$	1.000000	231×10^{-6}	∞	rectangular	10	2.3×10^{-3} mg/g	47.7 %
Δ_{mass}	1.0000000	67.6×10^{-6}	∞				
Δf_{Pu}	1.0000000	57.7×10^{-6}	∞	rectangular	10	580×10^{-6} mg/g	3.0 %
$\Phi Fe_{TRP_Lab_preparation}$	0.999900	141×10^{-6}	∞	U-distr.	10	1.4×10^{-3} mg/g	17.9 %
$Pu_Conc_{013456789AB}$	10.02736 mg/g	1.69×10^{-3} mg/g	∞	normal	1.0	1.7×10^{-3} mg/g	25.4 %
$Fe_{correction}$	$3.887\cdot10^{-3}$ mg/g	473×10^{-6} mg/g	∞				
$Fe_Conc_{mg_per_g}$	$1.6600\cdot10^{-3}$ mg/g	86.6×10^{-6} mg/g	∞	rectangular	-2.3	-200×10^{-6} mg/g	0.4 %
f_{Fe}	0.5464	0.0600	∞	rectangular	-7.1×10^{-3}	-430×10^{-6} mg/g	1.6 %
f_{Pu}	0.9991700	57.7×10^{-6}	∞	rectangular	3.9×10^{-3}	220×10^{-9} mg/g	0.0 %
Pu_{At_Wt}	239.13863 g/mol	2.89×10^{-3} g/mol	∞	rectangular	-16×10^{-6}	-47×10^{-9} mg/g	0.0 %
Fe_{At_Wt}	55.84500 g/mol	1.15×10^{-3} g/mol	∞	rectangular	70×10^{-6}	80×10^{-9} mg/g	0.0 %
$\Delta_{mass_systematic}$	1.0000000	50.2×10^{-6}	∞	rectangular	10	500×10^{-6} mg/g	2.3 %
Δ_{mass_random}	1.0000000	45.3×10^{-6}	∞				
Δm_{FF400}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF401}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF403}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF404}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF405}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF406}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF407}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF408}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF409}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF410}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
Δm_{FF411}	1.000000	150×10^{-6}	∞	rectangular	0.91	140×10^{-6} mg/g	0.2 %
$Pu_Conc_{decayed}$	10.02419 mg/g	3.35×10^{-3} mg/g	∞				

Result: Pu concentration, corrected for radioactive decay to 2012-Nov-02.

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$Pu_Conc_{decayed}$	10.0242 mg/g	0.067 % (relative)	2.00	95% (normal)

The expanded uncertainty calculated using GUM Workbench™ complies with expectation cited in ISO 12183 and the International Target Values 2010.

- 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.
- Performance expectations cited in the International Target Values 2010 for plutonium assay by controlled-potential coulometry are:
  - $U_{systematic}$ = ± 0.1%
  - U_{random} = ± 0.1%
  - $U_{combined\ standard}$ = ± 0.14% (K=1)
  - $U_{expanded}$ = ± 0.28% (K=2)

CONCLUSIONS

TRTDC Laboratory and SRNL have collaborated to install, implement, upgrade, and apply controlled-potential coulometry for the characterization of plutonium concentration in purified plutonium solutions that are prepared from existing MOX powder. Plutonium coulometric measurements at the TRTDC Laboratory are fit for the purpose of characterizing reference materials that will be used for safeguards measurements with measurement uncertainties that are well within the requirements of the ITV-2010.

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