ORNL/TM-2023/2854

Measurement of Plutonium Ratios for CRM 137A Recertification

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OAK RIDGE
National Laboratory

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Chemical Sciences Division

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ABBREVIATIONS

CRM	certified reference material
GUM	guide to the expression of uncertainty in measurement
LLNL	Lawrence Livermore National Laboratory
MB	Mass Bias standard
MC-ICP-MS	multiple collector inductively coupled plasma–mass spectrometry
MTE	modified total evaporation
NBL-PO	New Brunswick Laboratory Program Office
NIST	National Institute of Standards and Technology
ORNL	Oak Ridge National Laboratory
QC	quality control
RSD	relative standard deviation
RSE	relative standard error
TE	total evaporation
TIMS	thermal ionization mass spectrometry
WRM	working reference material

1. INTRODUCTION

This report documents the analytical methodologies used by the Chemical and Isotopics Mass Spectrometry (CIMS) Group at the US Department of Energy's Oak Ridge National Laboratory (ORNL) for plutonium isotopic ratio characterizations on purified ~1 mg units prepared by Lawrence Livermore National Laboratory (LLNL) from a mother solution created from an existing 250 mg unit of certified reference material (CRM) 137. The analytical processes described are designed to maintain traceability of the final certified attributes and to eliminate sources of systematic bias for the measurements described. The measurands for certification are the plutonium isotope ratios: ^{238}Pu/^{239}Pu, ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu, and ^{242}Pu/^{239}Pu. The preparation and analytical process included the following activities:

- Preparation of reference materials to be used as calibrants to establish traceability to the SI unit of mass for the isotopic analyses and quality controls. For the plutonium isotopic analyses, CRM 128 (a CRM comprising equal atoms of ^{239}Pu and ^{242}Pu) was used as the primary calibrant.
- Each CRM 137A unit was reconstituted using dilute high-purity HNO_3. From each, seven replicates were distributed for the isotopic characterizations by thermal ionization mass spectrometry (TIMS) using the total evaporation (TE) method for isotope ratio measurements and MC-ICP-MS using a dynamic peak hooping method for secondary isotope ratio measurements.
- Due to time delay in the analyses from the last purification of the original CRM 137 mother solution by LLNL, an aliquot of the three provided plutonium units was purified using Eichrom TEVA separation methods to remove americium in-growth and uranium impurities.
- Minimally corrected data were reported from each analysis using reporting templates provided by the New Brunswick Laboratory Program Office (NBL PO) for the specific methods used for isotopic measurements. In addition, a copy of the instrument exports, Excel templates for isotopic data corrections, and the uncertainty budgets completed with the GUM Workbench software package were submitted to NBL PO.

Table 1. Summary of isotopic data

		^{238}Pu/^{239}Pu		**^{240}Pu/^{239}Pu**		**^{241}Pu/^{239}Pu**		**^{242}Pu/^{239}Pu**	
Instrument	Vial	**Value**	**Uncertainty (2σ)**	**Value**	**Uncertainty (2σ)**	**Value**	**Uncertainty (2σ)**	**Value**	**Uncertainty (2σ)**
TIMS/TE	004	0.0026370	0.0000053	0.240626	0.000077	0.005099	0.000034	0.0155775	0.0000067
MC-ICP-MS	004	—	—	0.240631	0.000072	0.005105	0.000037	0.015573	0.000042
TIMS/TE	052	0.0026440	0.0000095	0.240627	0.000078	0.005111	0.000014	0.0155771	0.0000068
MC-ICP-MS	052	—	—	0.240623	0.000072	0.005105	0.000036	0.015571	0.000043
TIMS/TE	113	0.0026482	0.000019	0.240626	0.000076	0.005121	0.000031	0.015578	0.000067
MC-ICP-MS	113	—	—	0.240635	0.000072	0.005086	0.000040	0.015585	0.000044

2. SAMPLE PREPARATION

2.1 RECEIVED UNITS

ORNL received three units of C137A from LLNL into Lab R139 in Building 4500S (Figure 1). Units received had identifiers of 004, 052, and 113. Each unit contained 1 mg of a plutonium dry nitrate that appeared as a solid light brown residue from the evaporation process that occurred at LLNL (Figure 2). ORNL also received CRM 128 from NBL PO at the Y-12 National Security Complex; the unit identifier was #313.

Figure 1. Three units of C137A in Mylar bags. ORNL received units 004, 052, and 113.

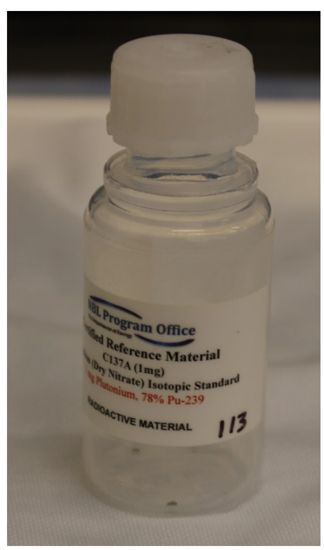


Figure 2. C137A (Unit 113) in 30 mL Teflon bottle with light brown plutonium nitrate residue in the bottom of the vial.

2.2 DISSOLUTION

To dissolve the plutonium nitrate, a 10 mL portion of 4 M HNO_3 + 0.05 M HF was added to each C137A unit, one unit of CRM 128, and a process blank. The acid was prepared from Optima HNO_3 (Lot: 1221120) and Optima HF (Lot: 5217040) purchased from Fisher Scientific, diluted with ASTM Type I water. C137A dissolved after 1 hour on a hot plate set to 60 °C, whereas CRM 128 required 2 hours to dissolve.

2.2.1 Sampling

Each time sampling occurred, a 100 µL aliquot (to provide 10 µg Pu) of each C137A solution and the CRM 128 solution was pipetted into a perfluoroalkoxy vial and transferred to Building 1060 Lab 104 for separation. Triplicate aliquots were pulled from the process blank.

3. SEPARATION

3.1 REAGENTS AND MATERIALS

All acids (HNO_3, HCl, and HF) and H_2O_2 (30%) were Optima grade, purchased from Fisher Scientific and used without further purification. Dilutions of acids were made using ASTM Type I water (>18.0 MΩ·cm) generated using a Thermo Scientific Barnstead GenPure xCAD Plus water purification system. Iron(II) sulfate heptahydrate (Puratronic, 99.999%, metal basis) and sodium nitrite (99.999%, metal basis) were purchased from Alfa Aesar and used without further purification. TEVA cartridges (1 mL, 50–100 µm) were purchased from Eichrom Technologies.

3.2 METHOD

Plutonium was chemically purified from uranium and americium before isotopic analysis to ensure separation from isobaric interference at mass 239 (uranium hydride $^{238}UH^+$) and mass 241 (^{241}Pu decays to ^{241}Am). This purification was accomplished via extraction chromatography with Eichrom TEVA 1 mL cartridges following an established analytical method (CSD-AM-CIMS-IN15[1]) using a vacuum box system inside a radiological hood, as shown in Figure 3. Before separation, samples were dried to remove trace HF and dissolved in 2 mL of 3 M HNO_3. The oxidation state of plutonium in the sample was adjusted to Pu(IV) with ferrous sulfate and sodium nitrite before loading on a preconditioned TEVA cartridge. After loading, the cartridge was rinsed with 38 mL of 3 M HNO_3, converted to the chloride form with 3 mL of 9 M HCl, and plutonium was eluted from the resin with 10 mL of 0.1 M HCl–0.06 M HF. The samples were dried and treated twice with a 1:1 v/v mixture of 8 M HNO_3 and H_2O_2 (30%) to remove any residual column organics. Before the solution were ready for TIMS loading, 20–50 µL 8 M HNO_3 were added to the samples.

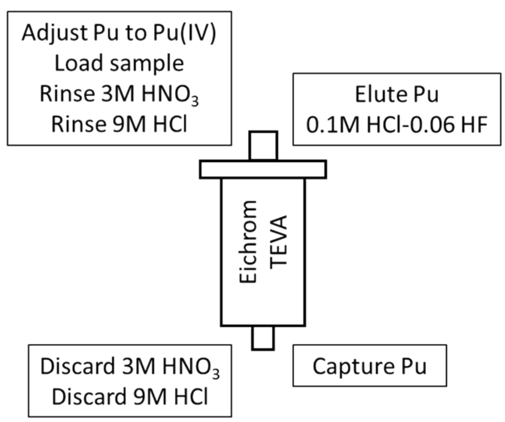


Figure 3. Separation scheme for the purification of plutonium.

4. ANALYSIS

4.1 PLUTONIUM ISOTOPIC COMPOSITION BY TIMS

The isotopic characterizations were performed utilizing the TE method. For this method, approximately 50 ng of plutonium solution was loaded onto a zone-refined double filament. This method is outlined in the following subsections, as described in ASTM 1672[2]. Any method deviation was recorded. Dr. Cole Hexel was previously qualified on the TE method by Dr. K. J. Mathew at the NBL labs on the Argonne National Laboratory campus when the facility was still in operation.

4.1.1 Filament Preparation

High-purity zone-refined rhenium filaments were used for all analyses. The filaments were made by MasCom (Breman, Germany), and purchased from Thermo Fisher Scientific, part number 4062350. The filaments were welded in a double-filament geometry. Before sample loading, the filaments were degassed to condition the filament surface and remove contamination. Table 2 outlines the filament degassing program. No filament background signal was observed from the degassed filament.

Table 2. Filament degassing program

ParameterC	Program	
Limit 1	1.0×10^{-5}	
Limit 2	9.0×10^{-6}	
C1 (Ioni)	Wait 1	1 min
	Slope	+1 A/min
	I1	4.7 A
	Wait 2	30 min
	Slope 2	−10 A/min
C2 (Evap)	Wait 1	40 min
	Slope	+1 A/min
	I1	4.7 A
	Wait 2	30 min
	Slope 2	−10 A/min
C1 + C2	Wait 1	40 min
	Slope	+50 A/min
	I1	5.0 A
	Wait 2	15 s
	Slope 2	−50 A/min

4.1.2 Filament Loading Method

Conditioned filaments were aged for a minimum of 25 days before use. No filaments were aged longer than 30 days. Initially, a filament was heated to 1.6 A, and the edge of a parafilm strip created a hydrophobic dam. This hydrophobic barrier did not perturb the plutonium isotopic analysis but did prevent the sample from skating across the filament surface. After applying the barrier, the filament was cooled to 0 A for loading. Approximately 50 ng of plutonium solution was loaded in 1-0.5 µL application. The droplet was then dried at 0.6 A to evaporate the liquid without causing sample splattering. Once the sample was dry, the amperage was increased to 1 A for 60 s then to 1.5 A for 5 s, and finally to 2 A for 5 s. Next, the filaments were returned to 0 A and loaded onto the turret. Sample filaments and the corresponding ionization filaments were immediately installed on the sample turret along with the extraction plate. All extraction plates were new and placed in the same orientation on the sample turret. Appendix A includes the original filament loading sheets.

4.1.3 Filament Position on Sample Turret

Three turrets were analyzed during a 1 week period. Samples were randomly distributed on each turret. Each sample vial was analyzed using seven replicates. Any sample filament that did not run was added to the third turret to maintain a total of seven replicates. The sample filament distribution can be found in Table 3.

Table 3. TIMS plutonium isotopic composition turret analysis scheme

Turret Position	Turret 1	Turret 2	Turret 3
Position 1	**NBL C128 *(MB)***	**NBL C128 *(MB)***	**NBL C128 *(MB)***
Position 2	*NBL 137 (QC)*	*NBL 137 (QC)*	*NBL 137 (QC)*
Position 3	*NBL 136 (QC)*	*NBL 136 (QC)*	*NBL 136 (QC)*
Position 4	NBL PO 137A-1a	NBL PO 137A-2a	NBL PO 137A-2a
Position 5	NBL PO 137A-2a	NBL PO 137A-3a	NBL PO 137A-2a
Position 6	**NBL C128 *(MB)***	**NBL C128 *(MB)***	**NBL C128 *(MB)***
Position 7	NBL PO 137A-3a	NBL PO 137A-1a	NBL PO 137A-3a
Position 8	**NBL C128 *(MB)***	**NBL C128 *(MB)***	**NBL C128 *(MB)***
Position 9	*NBL 137 (QC)*	*NBL 137 (QC)*	*NBL 137 (QC)*
Position 10	NBL PO 137A-1b	NBL PO 137A-2b	NBL PO 137A-3a
Position 11	NBL PO 137A-2b	NBL PO 137A-1b	ORNL WRM 003
Position 12	**NBL C128 *(MB)***	**NBL C128 *(MB)***	**NBL C128 *(MB)***
Position 13	*NBL 136 (QC)*	*NBL 136 (QC)*	*NBL 136 (QC)*
Position 14	NBL PO 137A-3b	NBL PO 137A-3c	NBL PO 137A-1a
Position 15	NBL PO 137A-1c	NBL PO 137A-1c	ORNL WRM 003
Position 16	NBL PO 137A-2c	NBL PO 137A-1c	ORNL WRM 003
Position 17	**NBL C128 *(MB)***	**NBL C128 *(MB)***	**NBL C128 *(MB)***
Position 18	NBL PO 137A-3c	NBL PO 137A-2c	ORNL WRM 003
Position 19	*NBL 137 (QC)*	*NBL 137 (QC)*	*NBL 137 (QC)*
Position 20	*NBL 136 (QC)*	*NBL 136 (QC)*	*NBL 136 (QC)*
Position 21	**NBL C128 *(MB)***	**NBL C128 *(MB)***	**NBL C128 *(MB)***

Note: QC = quality control; MB = mass bias ; WRM = working reference material

4.1.4 Detector Configuration, Amplifiers, and Calibration

The gain history was used to select the instrument amplifiers that had the lowest standard deviation. The lowest deviation amplifiers were used on mass, *m*/*z*, and the 241 faraday cup. Subsequently the 242, 244, 238, 240, and 239 faraday cup amplifiers were populated in that order (Table 4). The most stable amplifier was used for the least abundant isotope. Only the 10^{11} amplifiers were selected for the TE method. The ORNL WRM 003 sample was used to verify that the detectors were coincident. No amplifier rotation was applied. The faraday detector gain was electronically determined for 3 h using a 0.3333334 gain calibration card. This calibration was performed before the three turrets were analyzed. The results were consistent with the gain history, and the values were within the historical deviation. After the gain calibration, a baseline was conducted for 1,800 s. A baseline was performed before each turret was analyzed. A beam of ^{187}Re was placed on the center faraday cup to verify the faraday mass calibration. A mass calibration filament was loaded, and a full mass calibration was performed at the beginning of the project analysis. The instrument was calibrated at lithium, sodium, strontium, neodymium, rhenium, uranium, plutonium, and UO masses. Before each filament analysis, rhenium and plutonium were recalibrated. No instrument drift was observed.

Table 4. Historical gain from the instrument's history log

Timestamp	Amp 1	Amp 2	Amp 3	Amp 4	Amp 5	Amp 6	Amp 7	Amp 8
10/4/2018 16:40	0.33222	0.33755	0.32926	0.32844	0.32988	0.33407	0.32777	0.33011
3/27/2020 12:55	0.33219	0.33757	0.32926	0.32845	0.32988	0.33408	0.32778	0.33012
8/25/2020 16:44	0.33212	0.33753	0.32921	0.32842	0.32983	0.33403	0.32773	0.33008
11/3/2020 11:28	0.33207	0.33749	0.32916	0.32836	0.32979	0.33399	0.32768	0.33003
1/14/2021 16:32	0.33207	0.33749	0.32915	0.32836	0.32978	0.33398	0.32767	0.33002
1/31/2021 14:57	0.33206	0.33749	0.32915	0.32836	0.32978	0.33397	0.32766	0.33002
2/5/2021 19:08	0.33205	0.33749	0.32915	0.32836	0.32978	0.33398	0.32765	0.33002
2/23/2021 12:04	0.33205	0.33749	0.32914	0.32834	0.32976	0.33397	0.32764	0.33
3/9/2021 16:13	0.33207	0.33751	0.32916	0.32837	0.32978	0.33398	0.32766	0.33003
3/10/2021 17:01	0.33217	0.33744	0.32895	0.3285	0.32978	0.33397	0.32777	0.32968
5/10/2021 22:39	0.33203	0.33746	0.32911	0.32833	0.32974	0.33394	0.32762	0.32998
6/17/2021 23:33	0.33198	0.33743	0.32908	0.3283	0.32972	0.33391	0.32759	0.32996
7/21/2021 22:29	0.332	0.33745	0.32909	0.32831	0.32972	0.33392	0.32759	0.32997
8/1/2021 23:07	0.33207	0.33754	0.32912	0.32837	0.32974	0.33397	0.32759	0.33
10/19/2021 4:43	0.33208	0.33755	0.32912	0.32836	0.32975	0.33396	0.3276	0.32999
11/23/2021 0:13	0.33206	0.33752	0.32912	0.32835	0.32975	0.33395	0.3276	0.32999
12/7/2021 6:00	0.33205	0.33751	0.32911	0.32833	0.32975	0.33395	0.3276	0.32998
1/28/2022 2:55	0.33203	0.33748	0.3291	0.32832	0.32973	0.33394	0.32759	0.32997
6/16/2022 14:22	0.33196	0.33741	0.32905	0.32825	0.32967	0.33388	0.32755	0.32991
8/11/2022 19:11	0.33192	0.33738	0.32902	0.32823	0.32966	0.33385	0.32754	0.3299
10/20/2022 16:48	0.3319	0.33736	0.32901	0.32821	0.32964	0.33384	0.32753	0.32988
10/24/2022 11:16	0.3319	0.33736	0.32901	0.32821	0.32964	0.33384	0.32752	0.32988
Avg	0.33205	0.33748	0.32911	0.32834	0.32975	0.33395	0.32763	0.32998
Std dev	8.4×10^{-5}	6×10^{-5}	7.7×10^{-5}	7.3×10^{-5}	6.5×10^{-5}	6.4×10^{-5}	7.7×10^{-5}	9.3×10^{-5}
% RSD	0.0252%	0.0178%	0.0235%	0.0224%	0.0198%	0.0191%	0.0235%	0.0282%
Mass		241	244	239	240	242	238	

4.1.5 Sample Analysis Method

TIMS startup, tuning, and initial setup was conducted according to the standard operating procedure for the plutonium isotope ratios ($^{238}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$, $^{242}Pu/^{239}Pu$, $^{244}Pu/^{239}Pu$). A sample isotopic survey was performed before the sample turret was analyzed, and no ^{244}Pu was observed via the faraday cup. The instrument optimized the ionization filament to yield a rhenium signal of 160 mA or to a filament current of about 5,100 mA. A filament tune and a mass calibration on ^{187}Re was completed at this heating step. The evaporator current was increased, and the TE analysis started. The filament current was increased to yield a summed total ion current of 3 V and run to exhaustion. The sample mass bias was corrected using an exponential correction model based on the average $^{242}Pu/^{239}Pu$ ratio in the CRM 128 comparator sample filaments. The method and heat profile are shown in Figure 4.

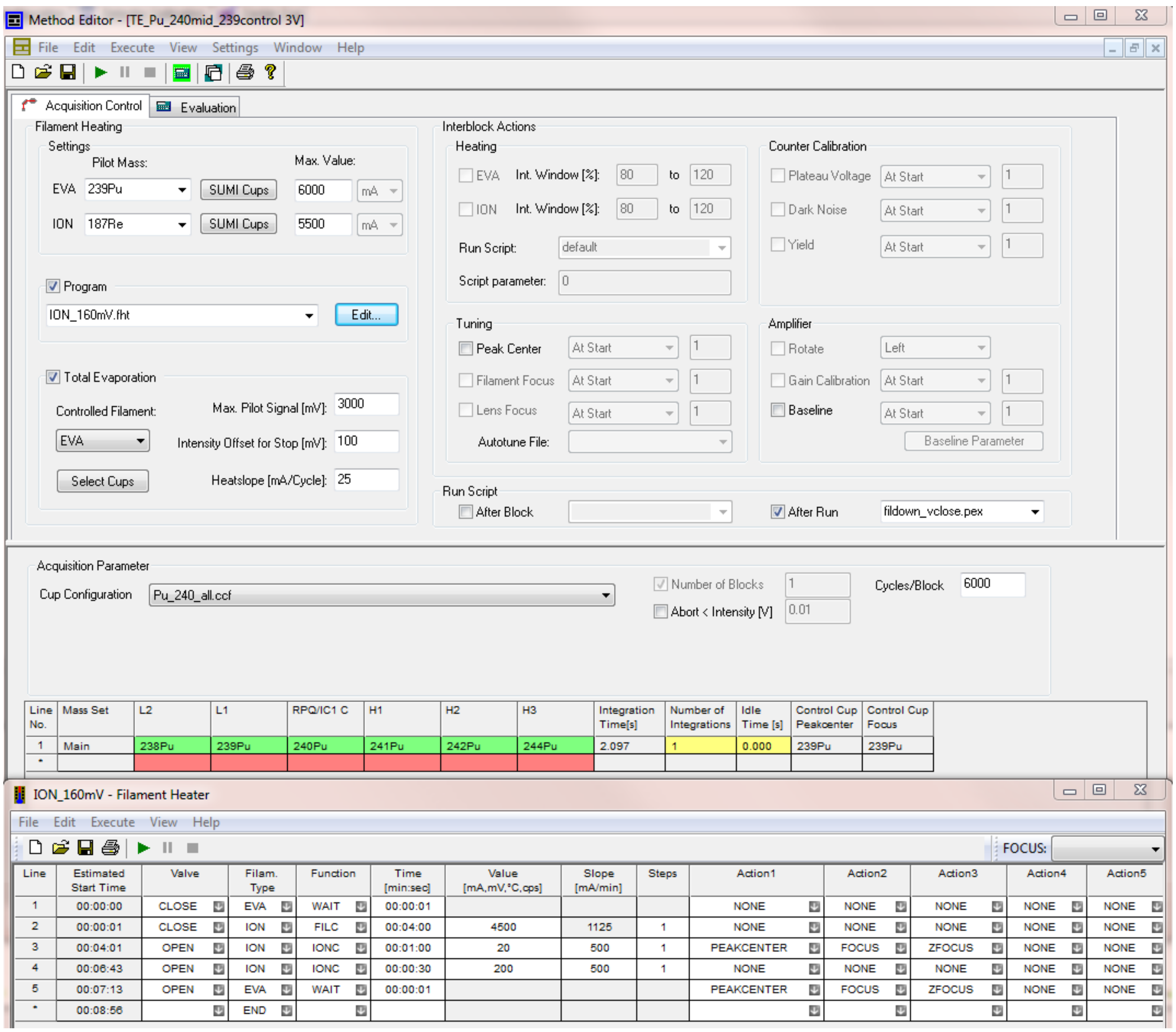
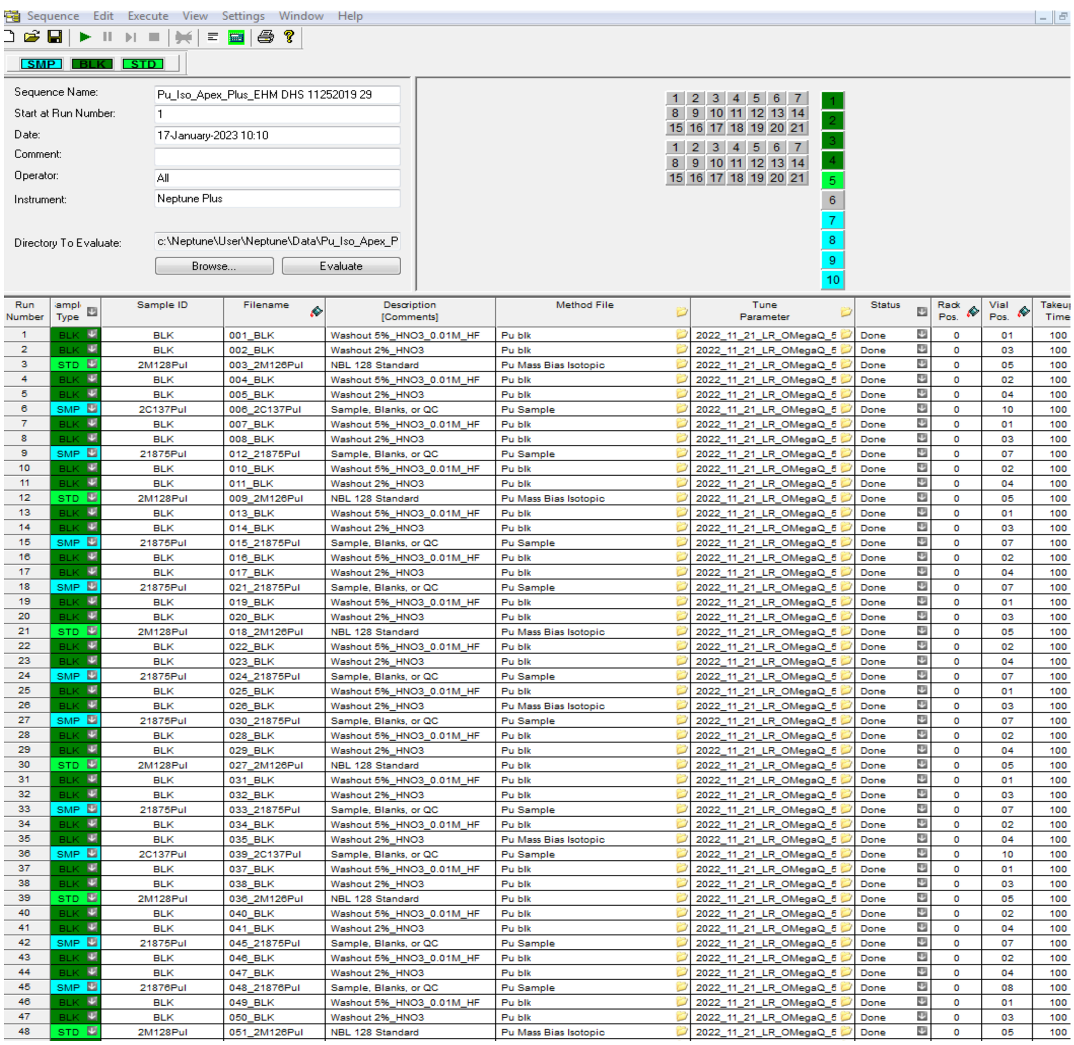


Figure 4. The total evaporation method used for the isotopic analysis by TIMS. The heat profile is included with the method.

4.2 PU ANALYSIS USING MC-ICP-MS

4.2.1 MC-ICP-MS Analysis Sequence

The plutonium isotopic characterizations were performed via multiple collector inductively coupled plasma–mass spectrometry (MC-ICP-MS). The samples were analyzed in a single sequence spanning about 20 h. Within the sample sequence, each vial was analyzed non-sequentially seven times. The sequence was constructed using a standard bracketing method with quality control (QC) samples bracketing the unknown C137A samples (Figure 5). A hydride sample ("H") was analyzed at the beginning and the end of the sequence, and the hydride ratio was averaged across the run. The control samples have the "C" designation, and "M" signifies mass bias or comparator. A wash time of 200 s was used to eliminate washout effects. The washout solutions were 5% HNO_3 + 0.01M HF, and the blank correction 2% HNO_3. The washout and blanks both had an uptake time of 100 s to minimize memory effect before the sample. The samples, QC, and comparator samples had an uptake time of 100 s. This time considers a signal stability time of about 45 s, which is common for standard ICP-MS introduction systems. The method and acquisition parameters can be found in Figure 5.



Run Number	ampl Type	Sample ID	Filename	Description [Comments]	Method File	Tune Parameter	Status	Rack Pos.	Vial Pos.	Takeu Time
1	BLK	BLK	001_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	01	100
2	BLK	BLK	002_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	03	100
3	STD	2M128PuI	003_2M126PuI	NBL 128 Standard	Pu Mass Bias Isotopic	2022_11_21_LR_OMegaQ_5	Done	0	05	100
4	BLK	BLK	004_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	02	100
5	BLK	BLK	005_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	04	100
6	SMP	2C137PuI	006_2C137PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	10	100
7	BLK	BLK	007_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	01	100
8	BLK	BLK	008_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	03	100
9	SMP	21875PuI	012_21875PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	07	100
10	BLK	BLK	010_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	02	100
11	BLK	BLK	011_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	04	100
12	STD	2M128PuI	009_2M126PuI	NBL 128 Standard	Pu Mass Bias Isotopic	2022_11_21_LR_OMegaQ_5	Done	0	05	100
13	BLK	BLK	013_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	01	100
14	BLK	BLK	014_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	03	100
15	SMP	21875PuI	015_21875PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	07	100
16	BLK	BLK	016_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	02	100
17	BLK	BLK	017_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	04	100
18	SMP	21875PuI	021_21875PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	07	100
19	BLK	BLK	019_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	01	100
20	BLK	BLK	020_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	03	100
21	STD	2M128PuI	018_2M126PuI	NBL 128 Standard	Pu Mass Bias Isotopic	2022_11_21_LR_OMegaQ_5	Done	0	05	100
22	BLK	BLK	022_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	02	100
23	BLK	BLK	023_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	04	100
24	SMP	21875PuI	024_21875PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	07	100
25	BLK	BLK	025_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	01	100
26	BLK	BLK	026_BLK	Washout 2%_HNO3	Pu Mass Bias Isotopic	2022_11_21_LR_OMegaQ_5	Done	0	03	100
27	SMP	21875PuI	030_21875PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	07	100
28	BLK	BLK	028_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	02	100
29	BLK	BLK	029_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	04	100
30	STD	2M128PuI	027_2M126PuI	NBL 128 Standard	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	05	100
31	BLK	BLK	031_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	01	100
32	BLK	BLK	032_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	03	100
33	SMP	21875PuI	033_21875PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	07	100
34	BLK	BLK	034_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	02	100
35	BLK	BLK	035_BLK	Washout 2%_HNO3	Pu Mass Bias Isotopic	2022_11_21_LR_OMegaQ_5	Done	0	04	100
36	SMP	2C137PuI	039_2C137PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	10	100
37	BLK	BLK	037_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	01	100
38	BLK	BLK	038_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	03	100
39	STD	2M128PuI	036_2M126PuI	NBL 128 Standard	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	05	100
40	BLK	BLK	040_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	02	100
41	BLK	BLK	041_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	04	100
42	SMP	21875PuI	045_21875PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	07	100
43	BLK	BLK	046_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	02	100
44	BLK	BLK	047_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	04	100
45	SMP	21876PuI	048_21876PuI	Sample, Blanks, or QC	Pu Sample	2022_11_21_LR_OMegaQ_5	Done	0	08	100
46	BLK	BLK	049_BLK	Washout 5%_HNO3_0.01M_HF	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	01	100
47	BLK	BLK	050_BLK	Washout 2%_HNO3	Pu blk	2022_11_21_LR_OMegaQ_5	Done	0	03	100
48	STD	2M128PuI	051_2M126PuI	NBL 128 Standard	Pu Mass Bias Isotopic	2022_11_21_LR_OMegaQ_5	Done	0	05	100

Figure 5. MC-ICP-MS sequence template for plutonium analysis.

4.2.2 Detector Configuration, Amplifiers, and Calibration

The baseline history was used to select the instrument amplifiers with the lowest standard deviation. The lowest deviation amplifier was used on the 241 faraday cup, and then 242, 244, 238, 240, and 239 faraday cup amplifiers were populated in that order. A mix of 10^{11} and 10^{13} amplifiers was selected for the MC-ICP-MS method. No amplifier rotation was applied. The faraday detector gain was electronically determined for 2.5 h using a 0.3333334 gain calibration card. This calibration was performed before the project sequences. The results were compared to the gain history to determine whether the values were within the history deviation. After the gain calibration, a baseline was conducted for 1,800 s. The baseline measurements were completed before each sequence. A mass calibration solution was run to complete a full mass calibration at the beginning of the project analyses (Figure 6). The instrument was calibrated using masses for lithium, sodium, iron, strontium, neodymium, hafnium, lead, uranium, UO, and UO_2. During each sample analysis, plutonium was recalibrated.

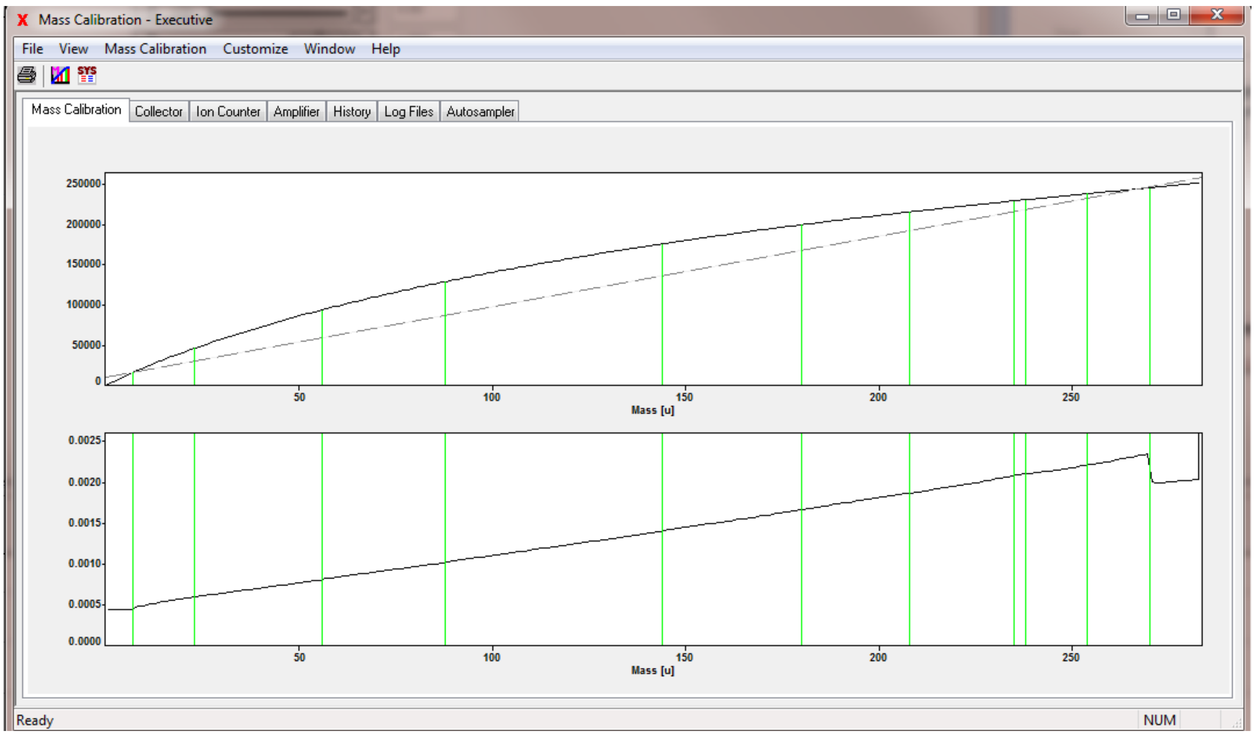


Figure 6. Mass calibration Neptune Plus.

4.2.3 Sample Analysis Method

Plutonium isotope ratios ($^{238}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$, $^{242}Pu/^{239}Pu$, $^{244}Pu/^{239}Pu$) were measured via MC-ICP-MS. An aliquot from the purified stock solution was used to create a 4 ng solution with a volume of 2 mL. Using CRM 137 decay-corrected ratios as an example, total ion current of 4 V should yield 7 mV of mass 238, 1 V of mass 240, 16 mV of mass 241, and 46 mV of mass 242. These signal intensities should all be large enough to be placed on the faraday detector without needing a secondary electron multiplier. A 4 V 239 signal should yield a count rate of 5×10^{-6} V. This correction will be made with the secondary electron multiplier and by measuring ^{241}Pu in two lines using the IC1 B and the center Faraday cup. The analyses were set up in two lines with five integrations on the first line and one integration on the second line. The integration time was set to 16.777 s. Each line was run in an alternating pattern making up one cycle and 10 cycles were run. Outliers were rejected based on two standard deviations of the individual cycles. The sample mass bias was corrected using an exponential correction model based on the average $^{242}Pu/^{239}Pu$ ratio in the CRM 128 comparator sample filaments.

4.3 PLUTONIUM ANALYSIS USING ALPHA SPECTROMETRY

4.3.1 Sample Analysis Method

The activities of ^{238}Pu and $^{239+240}Pu$ were determined in the three units of C137A by means of direct coprecipitation of the plutonium with CeF_3. Because samples were pure plutonium (^{241}Am had recently been separated from ^{241}Pu, as described in Section 3), an additional separation was not required. The CeF_3 precipitation was prepared by spiking 10 mL of a 0.1 M HCl + 0.05 M HF + 0.05 M $TiCl_3$ solution with 100 µL of sample and 0.02 mL of ^{242}Pu standard NIST 4334J-E (used as a tracer to monitor chemical recovery). To this solution, 50 µL of Ce carrier (1000 mg/L) and 2 mL of concentrated HF was added, mixed, and allowed to sit for about 15 min. The precipitate was quantitively transferred and filtered onto an Eichrom Resolve filter (preconditioned with EtOH). The filter was dried under vacuum and transferred to a stainless steel planchette for further drying under a heat lamp for about 15 min. Samples were taken to a count room for counting via alpha spectrometry.

The main purpose of the alpha spectrometry was to provide supporting data for the mass spectrometry measurements. The activity ratio of ^{238}Pu isotope with respect to ^{239}Pu was calculated and used to support the mass spectrometry measurements.

In addition to determining the plutonium isotope activities, the CeF_3 direct precipitation method used precipitated all actinide elements. Thus, any potential actinide impurities present could have been determined. No actinides, other than plutonium, were present in the samples. This information can be used to help assign impurity values in the C137A standard.

4.3.2 Quality Assurance

The alpha spectrometer detectors were calibrated using a mixed-energy alpha source from NIST-certified sources. The energy range was calibrated from 3 to 8 MeV. Efficiency calibrations for the detectors used the same NIST mixed-energy source. The detectors were passivated implanted planar silicon detectors. The counting efficiency of these detectors ranged from approximately 12% to 15%. The detectors are housed in an ORTEC DUO chamber within the ORTEC Ensemble, which is an integrated alpha spectrometer. ORTEC's AlphaVision software performed the data acquisition and analysis. The alpha detectors were checked using a pulsar to ensure proper working conditions, and the backgrounds were performed weekly.

5. RESULTS

5.1 ISOTOPIC DATA

Four turrets were analyzed on four separate days. The first three turrets were analyzed in November. At that time a bias in the $^{241}Pu/^{239}Pu$ ratio was observed between vial 113 and the other two vials. A second sample fraction was pulled and purified to verify the ratio. The second sample solution did not display the same isotopic value. This observation was verified via MC-ICP-MS. The fourth turret was loaded with four additional vial 04 filaments, and eight additional vial 113 filaments along with CRM 128 and CRM 137 served as mass comparator and quality assurance samples. This analysis provided better results for the $^{241}Pu/^{239}Pu$ ratio. No other ratios were perturbed, and all analysis results have been included.

Table 5 displays the 11 replicates TIMS measured for all ratios in vial 004. Table 6 displays the seven replicates MC-ICP-MS measured for all ratios in vial 004. The average $^{240}Pu/^{239}Pu$ TIMS value was

0.240626 ± 0.000077 (2σ), and the average $^{240}Pu/^{239}Pu$ MC-ICP-MS value was 0.240631 ± 0.000072 (2σ). The ratio plots of all replicates for each isotopes system are shown in Figure 7 through Figure 10. The analyzed values are plotted against the decay-corrected values for CRM 137. The guide to the expression of uncertainty in measurement (GUM) models and budgets are given in Appendix B. No $^{238}Pu/^{239}$ Pu ratio was collected with MC-ICP-MS, due to the background of ^{238}U in the system. Replicates 1-7, which corresponds to analysis dates October 25th - October 28th, were separated on October 12th, 2022, and replicates 8 -11 were separated on January 11th, 2023, and subsequently analyzed January 24th, 2023.

Table 5. The isotopic values for vial 004 from all TIMS analyses

TIMS isotopic data							
Replicate	Sample ID	**$^{238}Pu/^{239}Pu$**	**$^{240}Pu/^{239}Pu$**	**$^{241}Pu/^{239}Pu$**	**$^{242}Pu/^{239}Pu$**	**$^{244}Pu/^{239}Pu$**	**Analysis date**
1	202201875	0.0026347	0.240611	0.005108	0.015573	0.0000003	10/25/2022
2	202201875	0.0026353	0.240631	0.005106	0.015578	0.0000047	10/25/2022
3	202201875	0.0026362	0.240662	0.005107	0.015585	0.0000011	10/25/2022
4	202201875	0.0026398	0.240614	0.005180	0.015573	0.0000017	10/26/2022
5	202201875	0.0026369	0.240641	0.005105	0.015577	0.0000011	10/26/2022
6	202201875	0.0026350	0.240576	0.005110	0.015565	0.0000019	10/28/2022
7	202201875	0.0026529	0.240595	0.005194	0.015578	0.0000028	10/28/2022
8	202201875	0.0026342	0.240633	0.005047	0.015579	−0.0000009	1/24/2023
9	202201875	0.0026331	0.240636	0.005054	0.015579	−0.0000044	1/24/2023
10	202201875	0.0026345	0.240640	0.005040	0.015581	−0.0000063	1/24/2023
11	202201875	0.0026346	0.240649	0.005042	0.015586	−0.0000032	1/24/2023
	Average	0.0026370	0.240626	0.005099	0.0155776	−0.0000001	—
	Uncertainty (2σ)	0.0000053	0.000077	0.000034	0.0000067	0.0000033	—

Table 6. The isotopic values for vial 004 from all MC-ICP-MS analyses

MC-ICP-MS isotopic data							
Replicate	Sample ID	**$^{238}Pu/^{239}Pu$**	**$^{240}Pu/^{239}Pu$**	**$^{241}Pu/^{239}Pu$**	**$^{242}Pu/^{239}Pu$**	**$^{244}Pu/^{239}Pu$**	**Analysis date**
12	009_21875PuI	—	0.2406307	0.005071437	0.015596134	-6.6207×10^{-6}	11/22/2022
13	015_21875PuI	—	0.240608131	0.005110372	0.015576855	1.07696×10^{-5}	11/22/2022
14	018_21875PuI	—	0.240640078	0.005089841	0.015556068	-2.3424×10^{-5}	11/22/2022
15	024_21875PuI	—	0.240637052	0.005115536	0.015576865	6.43469×10^{-7}	11/22/2022
16	027_21875PuI	—	0.240630755	0.005117414	0.015552021	1.25449×10^{-8}	11/22/2022
17	033_21875PuI	—	0.240620868	0.005114397	0.015577411	9.1276×10^{-6}	11/22/2022
18	042_21875PuI	—	0.240649037	0.005114528	0.015572375	-3.4938×10^{-7}	11/22/2022
	Average	—	0.240631	0.005105	0.015573	−0.0000014	—
	Uncertainty (2σ)	—	0.000072	0.000037	0.000042	0.0000114	—

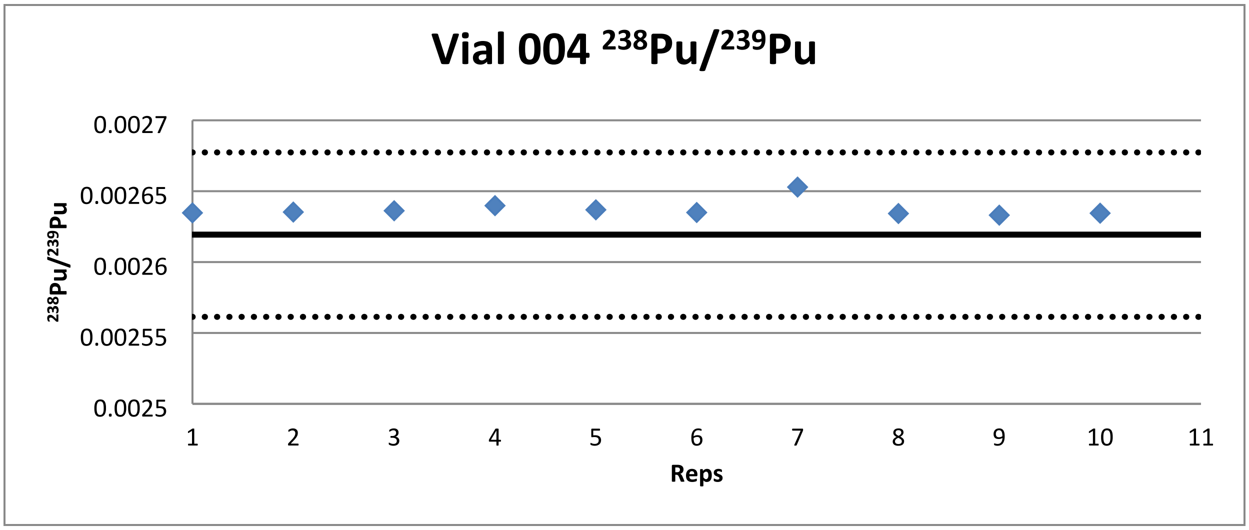


Figure 7. Replicate values of $^{238}Pu/^{239}Pu$ in vial 004 using TIMS, plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

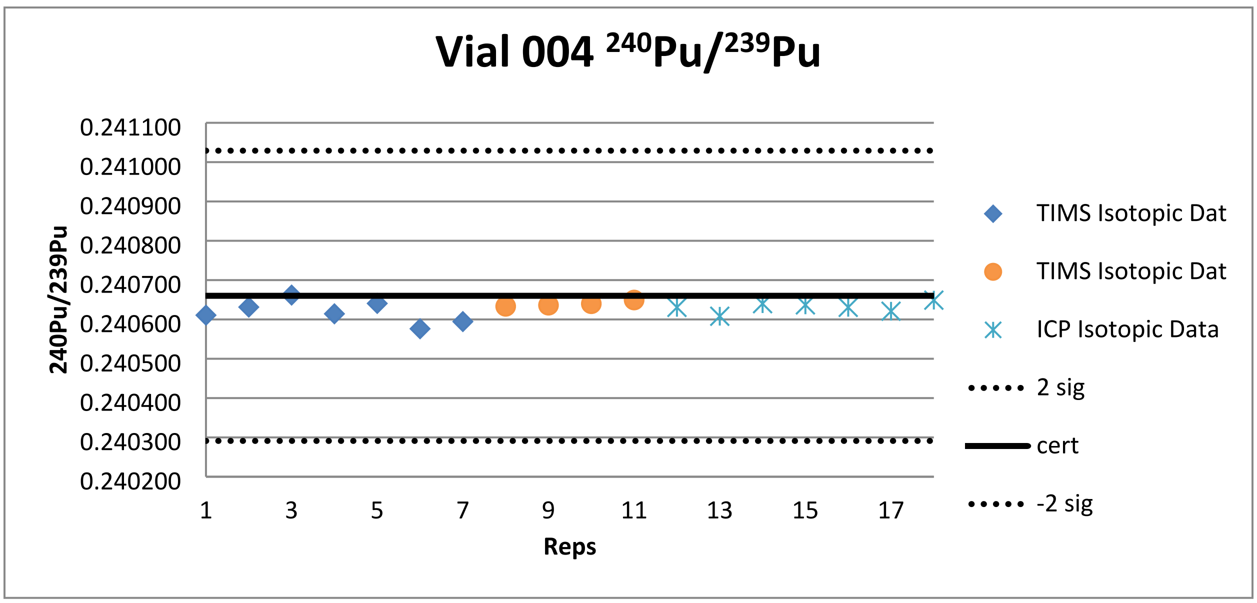


Figure 8. Replicate values of $^{240}Pu/^{239}Pu$ in vial 004 using TIMS and MC-ICP-MS, plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

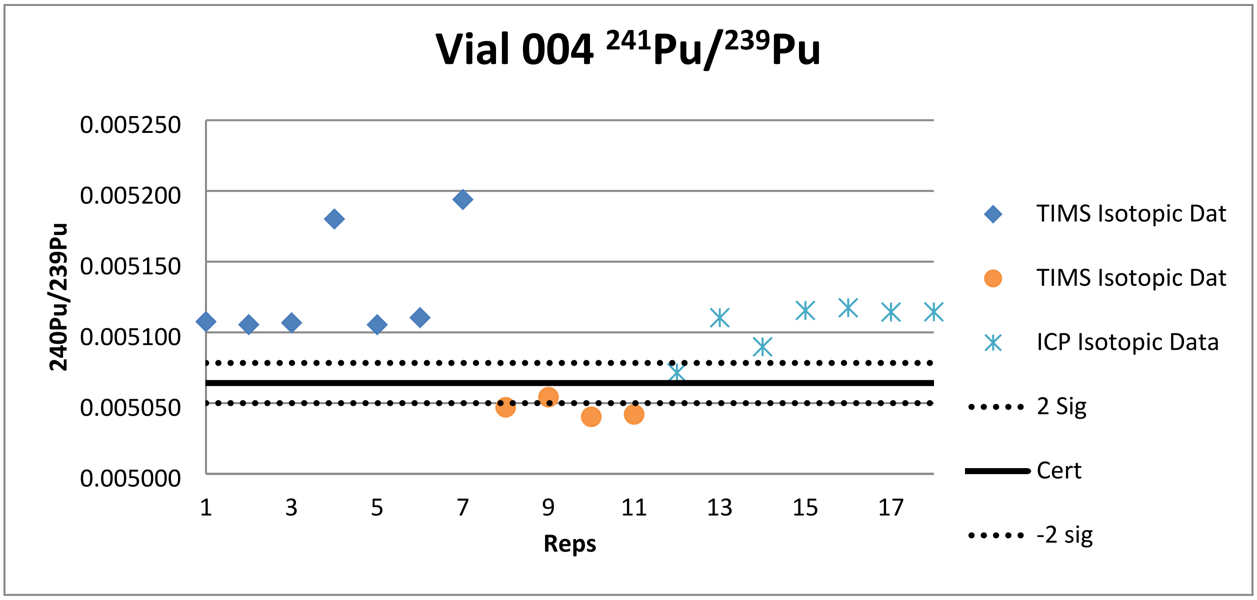


Figure 9. Replicate values of ^{241}Pu/^{239}Pu in vial 004 using TIMS and MC-ICP-MS, plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

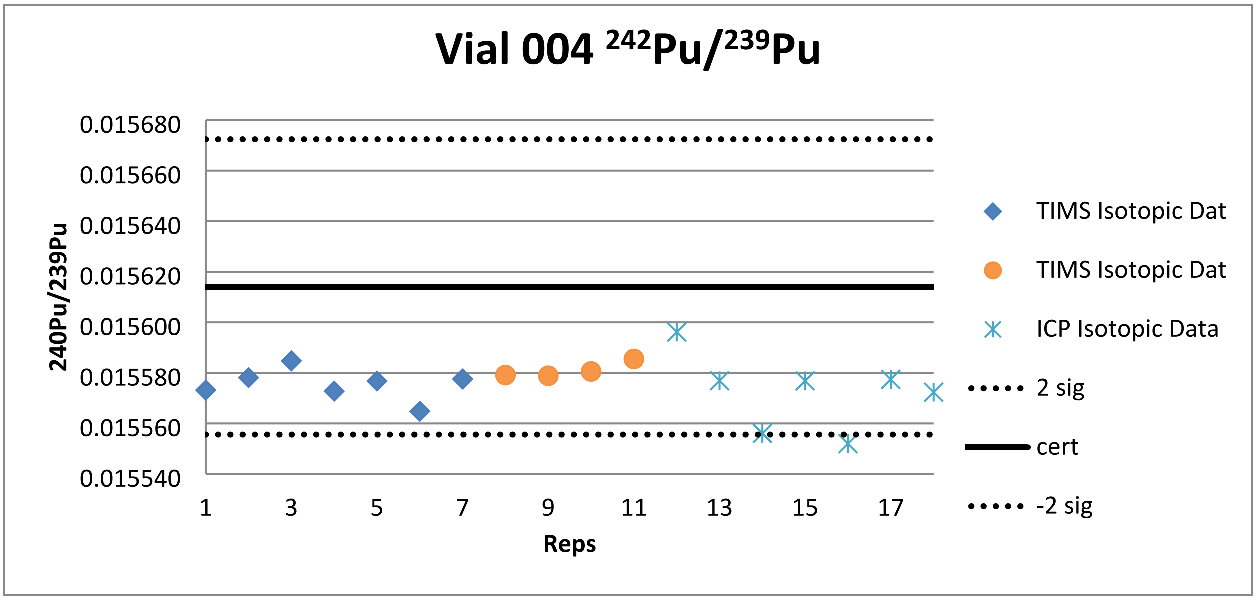


Figure 10. Replicate values of ^{242}Pu/^{239}Pu in vial 004 using TIMS and MC-ICP-MS, plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

Table 7 displays the seven replicates TIMS measured for all ratios in vial 052. Table 8 displays the seven replicates MC-ICP-MS measured for all ratios in vial 052. The average ^{240}Pu/^{239}Pu TIMS value was 0.240627 ± 0.000078 (2σ), and the average ^{240}Pu/^{239}Pu MC-ICP-MS value was 0.240623 ± 0.000072 (2σ). The ratio plots of all replicates for each isotopes system are shown in Figure 11 through Figure 14. The analyzed values are plotted against the decay-corrected values for CRM 137. The GUM models and budgets are given in Appendix C. Replicates 1-7, which corresponds to analysis dates October 25th - October 28th, were separated on October 12th, 2022

Table 7. The isotopic values for vial 052 from all TIMS analyses

TIMS isotopic data							
Replicate	Sample ID	**$^{238}Pu/^{239}Pu$**	**$^{240}Pu/^{239}Pu$**	**$^{241}Pu/^{239}Pu$**	**$^{242}Pu/^{239}Pu$**	**$^{244}Pu/^{239}Pu$**	**Analysis date**
1	202201876	0.0026458	0.240627	0.005113	0.0155755	4.7111×10^{-7}	10/25/2022
2	202201876	0.0026572	0.240621	0.005112	0.0155782	2.17145×10^{-7}	10/25/2022
3	202201876	0.0026337	0.240620	0.005108	0.0155758	4.14565×10^{-7}	10/25/2022
4	202201876	0.0026346	0.240592	0.005110	0.0155684	5.03829×10^{-7}	10/26/2022
5	202201876	0.0026342	0.240677	0.005108	0.0155850	-1.03829×10^{-7}	10/26/2022
6	202201876	0.0026414	0.240631	0.005114	0.0155781	2.00646×10^{-6}	10/28/2022
7	202201876	0.0026611	0.240623	0.005111	0.0155789	1.32822×10^{-6}	10/28/2022
	Average	0.0026440	0.240627	0.005111	0.0155771	0.00000069	—
	Uncertainty (2σ)	0.0000095	0.000078	0.000014	0.0000068	0.00000072	—

Table 8. The isotopic values for vial 052 from all MC-ICP-MS analyses

ICP Isotopic Data							
Replicate	Sample ID	**$^{238}Pu/^{239}Pu$**	**$^{240}Pu/^{239}Pu$**	**$^{241}Pu/^{239}Pu$**	**$^{242}Pu/^{239}Pu$**	**$^{244}Pu/^{239}Pu$**	**Analysis Date**
8	045_21876PuI	—	0.240640	0.005106	0.015564	9.43223×10^{-6}	11/22/2022
9	051_21876PuI	—	0.240596	0.005103	0.015551	-2.27107×10^{-5}	11/22/2022
10	054_21876PuI	—	0.240609	0.005099	0.015570	-6.43841×10^{-8}	11/22/2022
11	060_21876PuI	—	0.240628	0.005118	0.015597	1.40812×10^{-5}	11/22/2022
12	063_21876PuI	—	0.240639	0.005125	0.015585	-2.25803×10^{-5}	11/22/2022
13	072_21876PuI	—	0.240631	0.005091	0.015586	8.79275×10^{-6}	11/22/2022
14	078_21876PuI	—	0.240619	0.005097	0.015546	7.86452×10^{-6}	11/22/2022
	Average	—	0.240623	0.005105	0.015571	−0.000001	—
	Uncertainty (2σ)	—	0.000072	0.000036	0.000043	0.000016	—

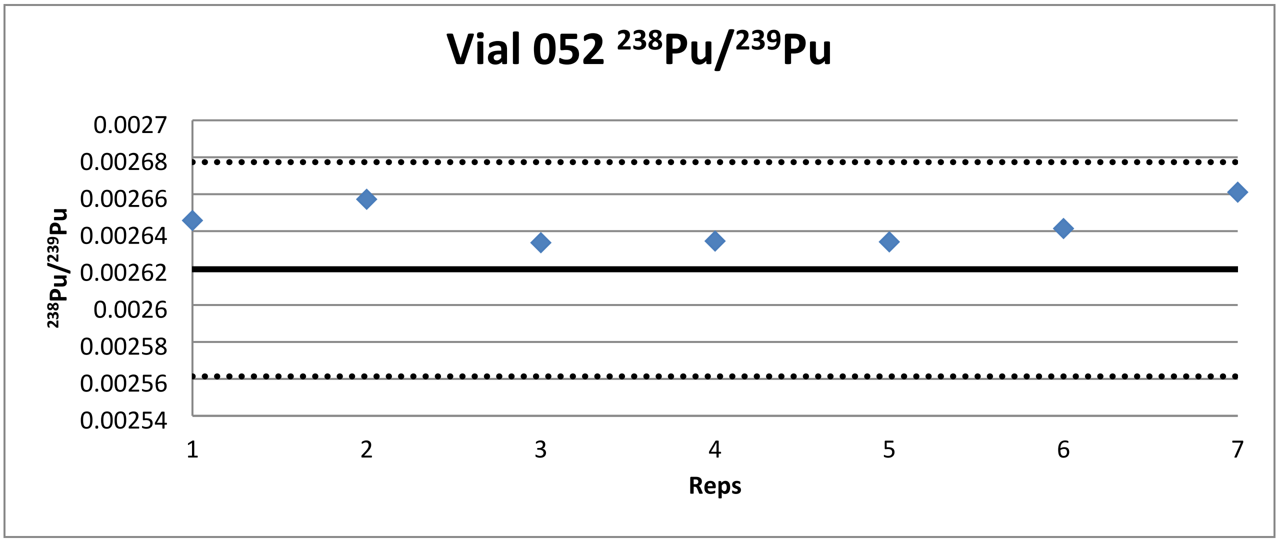


Figure 11. Replicate values of $^{238}Pu/^{239}Pu$ in vial 052 plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

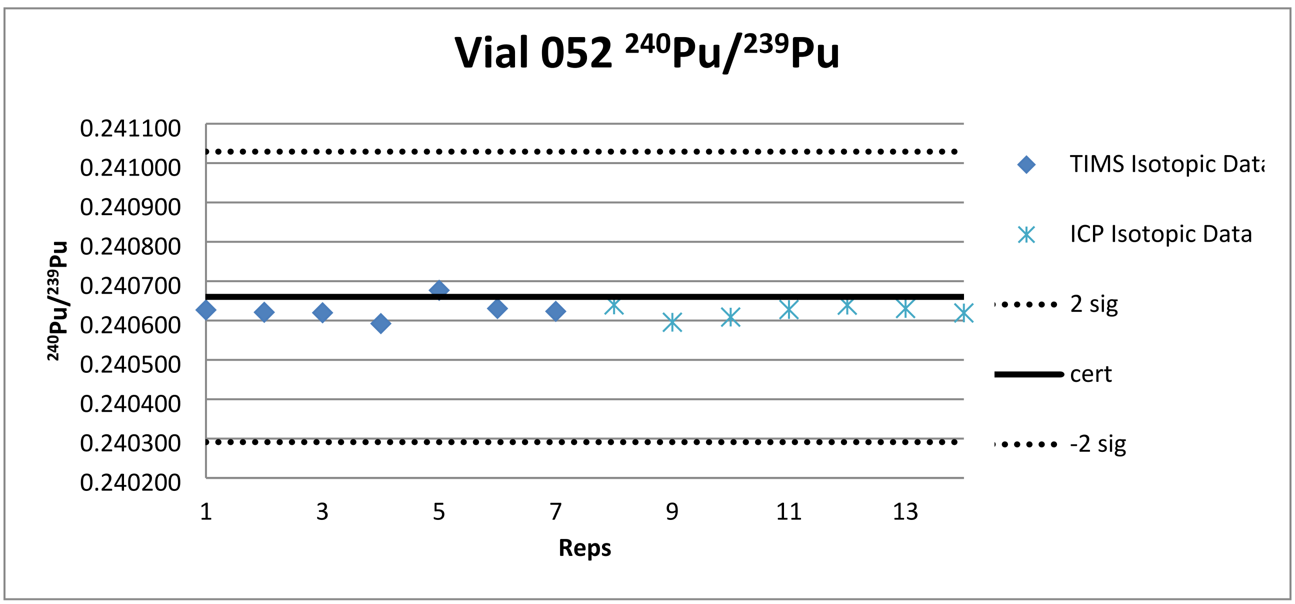


Figure 12. Replicate values of $^{240}Pu/^{239}Pu$ in vial 052 plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

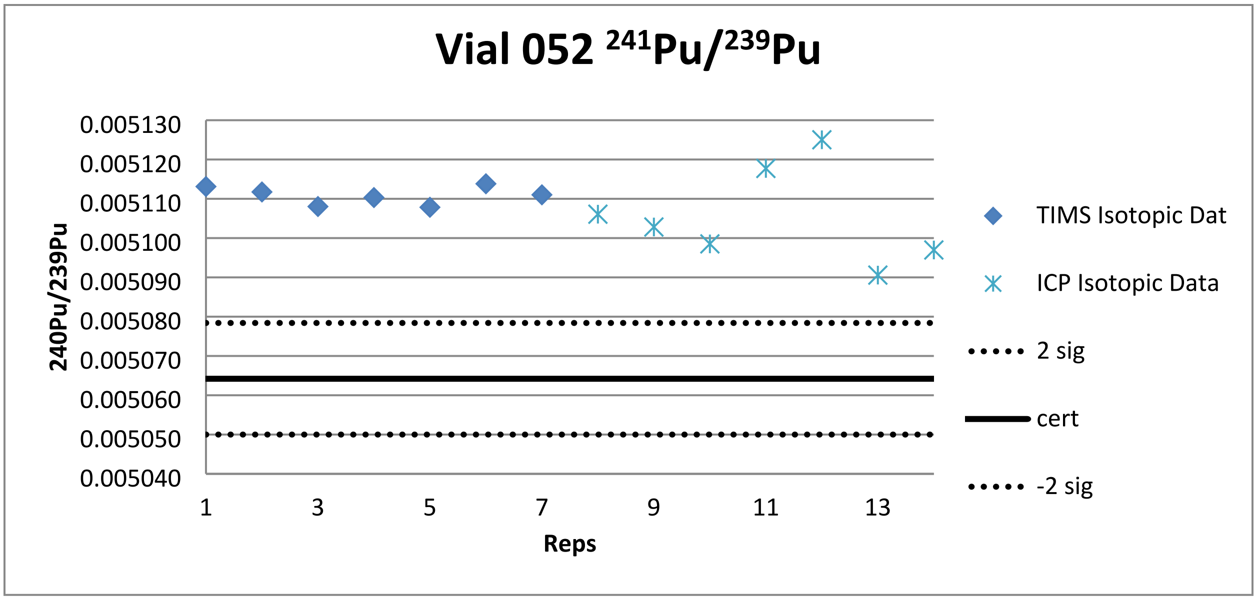


Figure 13. Replicate values of $^{241}Pu/^{239}Pu$ in vial 052 plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

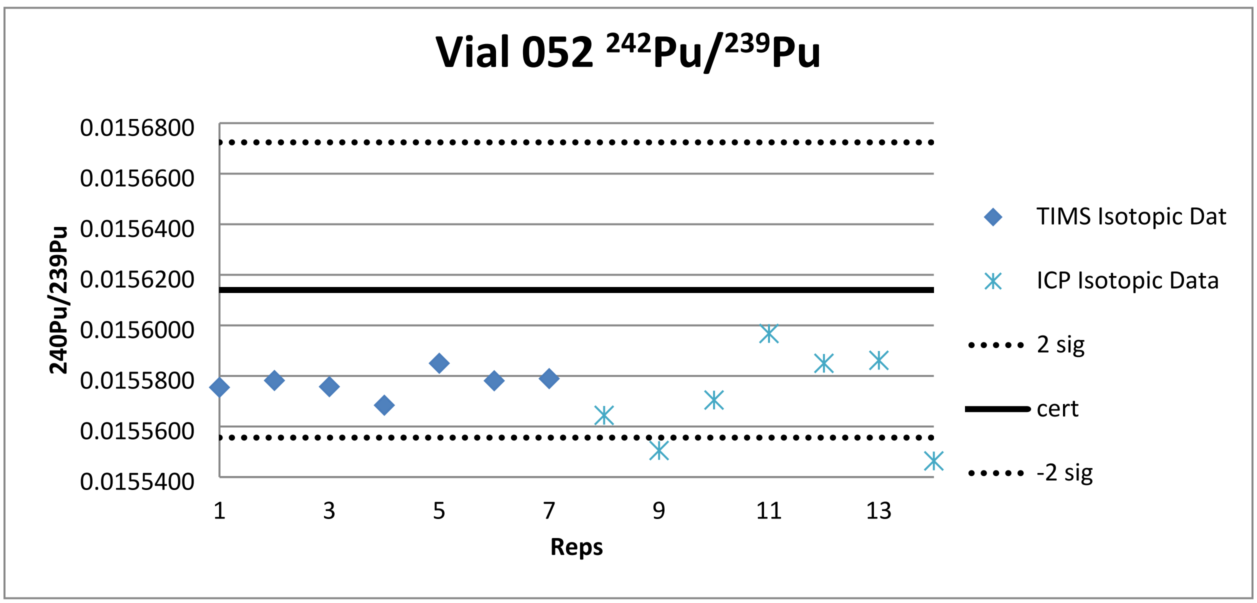


Figure 14. Replicate values of $^{242}Pu/^{239}Pu$ in vial 052 plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

Table 9 displays the 15 replicates TIMS measured for all ratios in vial 113. Table 10 displays the seven replicates MC-ICP-MS measured for all ratios in vial 113. The average $^{240}Pu/^{239}Pu$ TIMS value was 0.240626 ± 0.000076 (2σ), and the average $^{240}Pu/^{239}Pu$ MC-ICP-MS value was 0.240635 ± 0.000072 (2σ). The ratio plots of all replicates for each isotopes system are shown in Figure 15 through Figure 18. The analyzed values are plotted against the decay-corrected values for CRM 137. The GUM models and budgets are given in Appendix D. Replicates 1-7, which corresponds to analysis dates October 25th - October 28th, were separated on October 12th, 2022. While the other replicates were separated on January 11th, 2023, and subsequently analyzed January 24th, 2023.

Table 9. The isotopic values for vial 113 from all TIMS analyses

TIMS isotopic data							
Replicate	Sample ID	**^{238}Pu/^{239}Pu**	**^{240}Pu/^{239}Pu**	**^{241}Pu/^{239}Pu**	**^{242}Pu/^{239}Pu**	**^{244}Pu/^{239}Pu**	**Analysis date**
1	202201877	0.002640	0.240615	0.005180	0.015573	1.65257×10^{-6}	10/25/2022
2	202201877	0.002637	0.240618	0.005170	0.015570	-8.60144×10^{-7}	10/25/2022
3	202201877	0.002634	0.240617	0.005167	0.015573	−8.88115E-07	10/25/2022
4	202201877	0.002644	0.240614	0.005180	0.015573	1.65256×10^{-6}	10/26/2022
5	202201877	0.002660	0.240641	0.005162	0.015578	-8.04512×10^{-7}	10/26/2022
6	202201877	0.002643	0.240620	0.005182	0.015576	5.03829×10^{-7}	10/26/2022
7	202201877	0.002777	0.240612	0.005193	0.015576	2.64673×10^{-6}	10/28/2022
8	202201877	0.002632	0.240589	0.005075	0.015569	1.37884×10^{-6}	1/24/2023
9	202201877	0.002638	0.240639	0.005076	0.015576	-8.59367×10^{-6}	1/24/2023
10	202201877	0.002634	0.240626	0.005075	0.015581	-4.07069×10^{-6}	1/24/2023
11	202201877	0.002634	0.240641	0.005074	0.015580	-1.38997×10^{-5}	1/24/2023
12	202201877	0.002643	0.240632	0.005074	0.015577	-2.24508×10^{-5}	1/24/2023
13	202201877	0.002632	0.240615	0.005070	0.015577	-1.09625×10^{-6}	1/24/2023
14	202201877	0.002641	0.240644	0.005069	0.015595	-4.47132×10^{-6}	1/24/2023
15	202201877	0.002634	0.240660	0.005075	0.015589	-7.03564×10^{-6}	1/24/2023
	Average	0.002648	0.240626	0.005121	0.015578	−0.0000038	—
	Uncertainty (2σ)	0.000019	0.000076	0.000031	0.000067	0.0000069	—

Table 10. The isotopic values for vial 113 from all MC-ICP-MS analyses

ICP isotopic data							
Replicate	Sample ID	**^{238}Pu/^{239}Pu**	**^{240}Pu/^{239}Pu**	**^{241}Pu/^{239}Pu**	**^{242}Pu/^{239}Pu**	**^{244}Pu/^{239}Pu**	**Analysis date**
16	081_21877PuI	—	0.240655	0.005036	0.015617	2.43393×10^{-5}	11/22/2022
17	087_21877PuI	—	0.240638	0.005101	0.015537	2.0161×10^{-5}	11/22/2022
18	090_21877PuI	—	0.240638	0.005106	0.015587	3.63947×10^{-6}	11/22/2022
19	096_21877PuI	—	0.240643	0.005101	0.015600	-1.33184×10^{-5}	11/22/2022
20	099_21877PuI	—	0.240644	0.005069	0.015595	3.80158×10^{-6}	11/22/2022
21	105_21877PuI	—	0.240611	0.005085	0.015571	1.60763×10^{-6}	11/22/2022
22	108_21877PuI	—	0.240617	0.005102	0.015589	-2.21113×10^{-5}	11/22/2022
	Average	—	0.240635	0.005086	0.015585	0.0000026	—
	Uncertainty (2σ)	—	0.000072	0.000040	0.000044	0.0000166	—

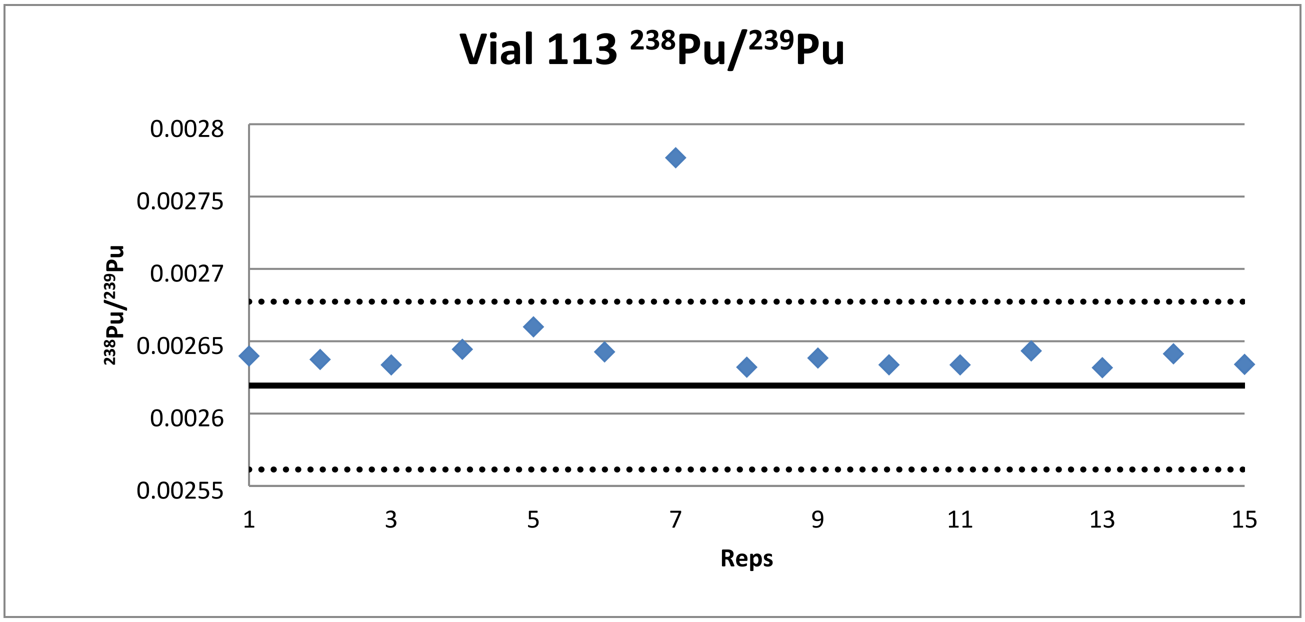


Figure 15. Replicate values of $^{238}Pu/^{239}Pu$ in vial 113 plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

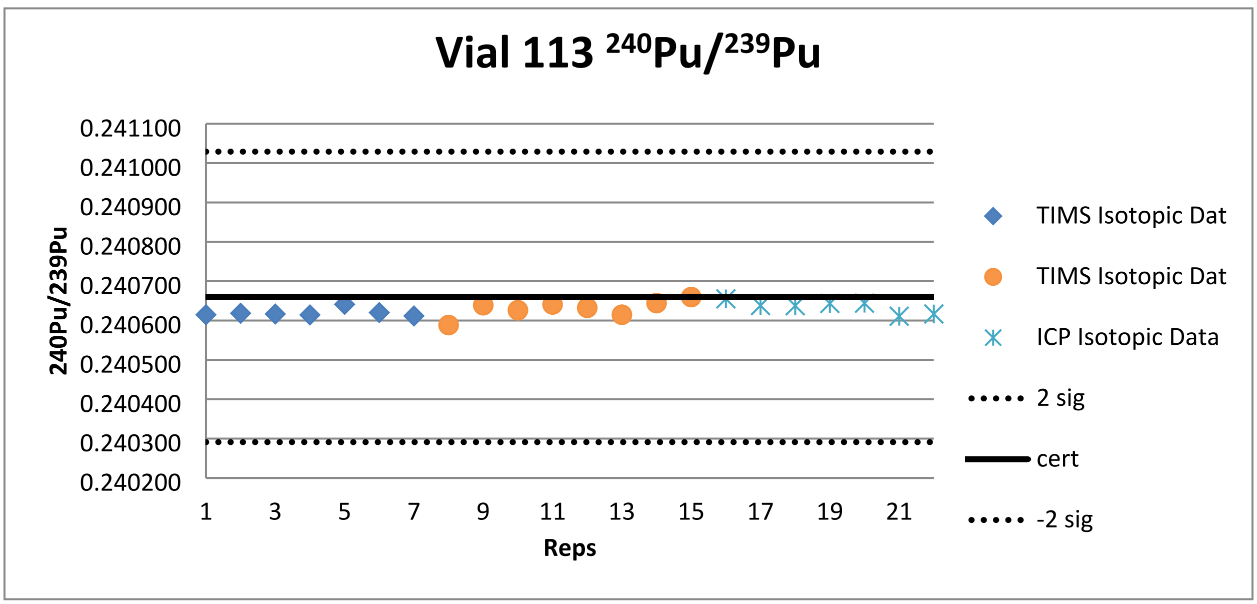


Figure 16. Replicate values of $^{240}Pu/^{239}Pu$ in vial 113 plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

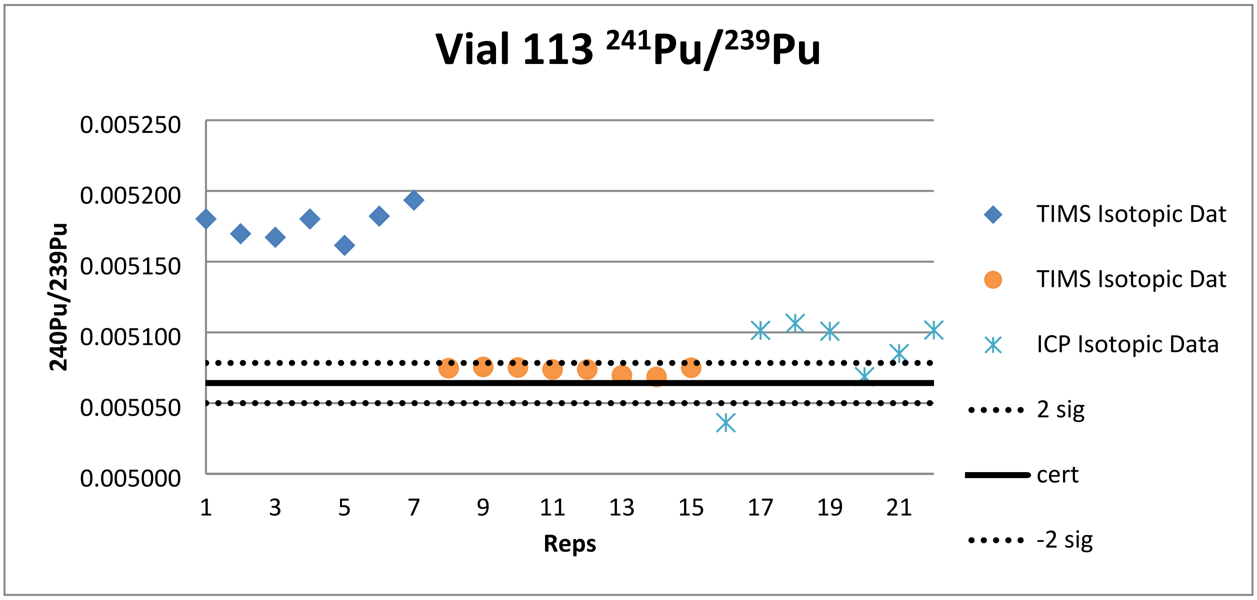


Figure 17. Replicate values of $^{241}Pu/^{239}Pu$ in vial 113 plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

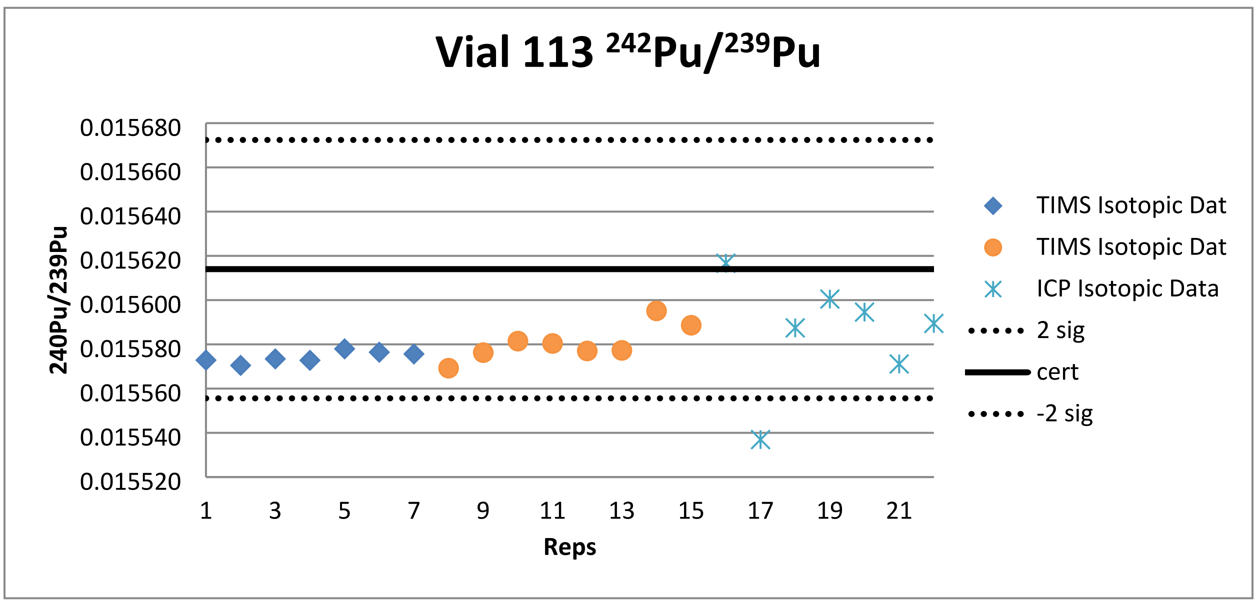


Figure 18. Replicate values of $^{242}Pu/^{239}Pu$ in vial 113 plotted against CRM 137 decay-corrected values. The dashed line represents the expanded uncertainty (k=2) from the original certificate of analysis for CRM 137.

Table 11 displays the all replicates measured by TIMS and MC-ICP-MS. The average $^{240}Pu/^{239}Pu$ value was 0.240628 ± 0.000075 (2σ). The number of replicate measurements was 54. The GUM models and budgets are given in Appendix E.

Table 11. The isotopic values for vials 004, 052, and 113 from all analyses

Replicate analysis for vials 004, 052, and 113							
Replicate	Sample ID	**^{238}Pu/^{239}Pu**	**^{240}Pu/^{239}Pu**	**^{241}Pu/^{239}Pu**	**^{242}Pu/^{239}Pu**	**^{244}Pu/^{239}Pu**	**Analysis date**
1	TIMS vial 04	0.002635	0.240611	0.005108	0.015573	0.000000	10/25/2022
2	TIMS vial 04	0.002635	0.240631	0.005106	0.015578	0.000005	10/25/2022
3	TIMS vial 04	0.002636	0.240662	0.005107	0.015585	0.000001	10/25/2022
4	TIMS vial 04	0.002640	0.240614	0.005180	0.015573	0.000002	10/26/2022
5	TIMS vial 04	0.002637	0.240641	0.005105	0.015577	0.000001	10/26/2022
6	TIMS vial 04	0.002635	0.240576	0.005110	0.015565	0.000002	10/28/2022
7	TIMS vial 04	0.002653	0.240595	0.005194	0.015578	0.000003	10/28/2022
8	TIMS vial 04	0.002634	0.240633	0.005047	0.015579	-0.000001	1/24/2023
9	TIMS vial 04	0.002633	0.240636	0.005054	0.015579	-0.000004	1/24/2023
10	TIMS vial 04	0.002634	0.240640	0.005040	0.015581	-0.000006	1/24/2023
11	TIMS vial 04	0.002635	0.240649	0.005042	0.015586	-0.000003	1/24/2023
12	TIMS vial 52	0.002646	0.240627	0.005113	0.015575	0.000000	10/25/2022
13	TIMS vial 52	0.002657	0.240621	0.005112	0.015578	0.000000	10/25/2022
14	TIMS vial 52	0.002634	0.240620	0.005108	0.015576	0.000000	10/25/2022
15	TIMS vial 52	0.002635	0.240592	0.005110	0.015568	0.000001	10/26/2022
16	TIMS vial 52	0.002634	0.240677	0.005108	0.015585	0.000000	10/26/2022
17	TIMS vial 52	0.002641	0.240631	0.005114	0.015578	0.000002	10/28/2022
18	TIMS vial 52	0.002661	0.240623	0.005111	0.015579	0.000001	10/28/2022
19	TIMS vial 113	0.002640	0.240615	0.005180	0.015573	0.000002	10/25/2022
20	TIMS vial 113	0.002637	0.240618	0.005170	0.015570	-0.000001	10/25/2022
21	TIMS vial 113	0.002634	0.240617	0.005167	0.015573	−0.000001	10/25/2022
22	TIMS vial 113	0.002644	0.240614	0.005180	0.015573	0.000002	10/26/2022
23	TIMS vial 113	0.002660	0.240641	0.005162	0.015578	−0.000001	10/26/2022
24	TIMS vial 113	0.002643	0.240620	0.005182	0.015576	0.000001	10/26/2022
25	TIMS vial 113	0.002777	0.240612	0.005193	0.015576	0.000003	10/28/2022
26	TIMS vial 113	0.002632	0.240589	0.005075	0.015569	0.000001	1/24/2023
27	TIMS vial 113	0.002638	0.240639	0.005076	0.015576	−0.000009	1/24/2023
28	TIMS vial 113	0.002634	0.240626	0.005075	0.015581	−0.000004	1/24/2023
29	TIMS vial 113	0.002634	0.240641	0.005074	0.015580	−0.000014	1/24/2023
30	TIMS vial 113	0.002643	0.240632	0.005074	0.015577	−0.000022	1/24/2023
31	TIMS vial 113	0.002632	0.240615	0.005070	0.015577	−0.000001	1/24/2023
32	TIMS vial 113	0.002641	0.240644	0.005069	0.015595	−0.000004	1/24/2023
33	TIMS vial 113	0.002634	0.240660	0.005075	0.015589	−0.000007	1/24/2023
34	ICP vial 04		0.240631	0.005071	0.015596	−0.000007	11/22/2022

35	ICP vial 04		0.240608	0.005110	0.015577	0.000011	11/22/2022
36	ICP vial 04		0.240640	0.005090	0.015556	−0.000023	11/22/2022
37	ICP vial 04		0.240637	0.005116	0.015577	0.000001	11/22/2022
38	ICP vial 04		0.240631	0.005117	0.015552	0.000000	11/22/2022
39	ICP vial 04		0.240621	0.005114	0.015577	0.000009	11/22/2022
40	ICP vial 04		0.240649	0.005115	0.015572	0.000000	11/22/2022
41	ICP vial 52		0.240640	0.005106	0.015564	0.000009	11/22/2022
42	ICP vial 52		0.240596	0.005103	0.015551	−0.000023	11/22/2022
43	ICP vial 52		0.240609	0.005099	0.015570	0.000000	11/22/2022
44	ICP vial 52		0.240628	0.005118	0.015597	0.000014	11/22/2022
45	ICP vial 52		0.240639	0.005125	0.015585	−0.000023	11/22/2022
46	ICP vial 52		0.240631	0.005091	0.015586	0.000009	11/22/2022
47	ICP vial 52		0.240619	0.005097	0.015546	0.000008	11/22/2022
48	ICP vial 113		0.240655	0.005036	0.015617	0.000024	11/22/2022
49	ICP vial 113		0.240638	0.005101	0.015537	0.000020	11/22/2022
50	ICP vial 113		0.240638	0.005106	0.015587	0.000004	11/22/2022
51	ICP vial 113		0.240643	0.005101	0.015600	−0.000013	11/22/2022
52	ICP vial 113		0.240644	0.005069	0.015595	0.000004	11/22/2022
53	ICP vial 113		0.240611	0.005085	0.015571	0.000002	11/22/2022
54	ICP vial 113		0.240617	0.005102	0.015589	−0.000022	11/22/2022
	Average	*0.002644*	*0.240628*	*0.005107*	*0.0155771*	*−0.000001*	
	Uncertainty (2σ)	*0.000010*	*0.000075*	*0.000017*	*0.0000067*	*0.000010*	

5.2 ALPHA DATA

Alpha Counting was used a secondary verification for the ^{238}Pu/^{239}Pu. The separation and plate produce a clean ^{238}Pu spectrum, measured against a combined 239+240 signal. The ratio data is corrected using the average ^{240}Pu/^{239}Pu for each vial to calculate the ^{238}Pu/^{239}Pu ratio. Table 9 displays the 7 replicates for each vial of the 238/239 ratio. The average ^{238}Pu/^{239}Pu ratio by alpha counting was 0.0260 ± 0.00037 for vial 004, 0.0266 ± 0.00034 for vial 052, and 0.0261 ± 0.00038 for vial 113. The total averaged value for ^{238}Pu/^{239}Pu 0.00262 ± 0.00034. This average was derived with the removal of replicate 7 in vial 113. The ratio plots of all replicates for ^{238}Pu/^{239}Pu are shown in Figure 18. The analyzed values are plotted against the decay-corrected values for CRM 137. The GUM models and budgets are given in Appendix F. While the other replicates were separated on January 11th, 2023,

Alpha Counting Data				
		238Pu/239Pu Value		
Vial	Sample ID	**^{238}Pu/^{239}Pu**	Uncertainty (2σ)	**Analysis date**
Vial004	221278-001A	0.00257	0.00037	2/8/2023
Vial004	221278-001B	0.00259	0.00036	2/8/2023
Vial004	221278-001C	0.00280	0.00041	2/8/2023
Vial004	221278-001D	0.00245	0.00034	2/8/2023
Vial004	221278-001E	0.00248	0.00036	2/8/2023
Vial004	221278-001F	0.00267	0.00038	2/8/2023

Vial004	221278-001G	0.00265	0.00037	2/8/2023
Vial052	221278-002A	0.00250	0.00031	2/8/2023
Vial052	221278-002B	0.00265	0.00034	2/8/2023
Vial052	221278-002C	0.00276	0.00034	2/8/2023
Vial052	221278-002D	0.00268	0.00034	2/8/2023
Vial052	221278-002E	0.00264	0.00035	2/8/2023
Vial052	221278-002F	0.00269	0.00034	2/8/2023
Vial052	221278-002G	0.00271	0.00038	2/8/2023
Vial113	221278-003A	0.00265	0.00039	2/8/2023
Vial113	221278-003B	0.00249	0.00035	2/8/2023
Vial113	221278-003C	0.00261	0.00038	2/8/2023
Vial113	221278-003D	0.00248	0.00036	2/8/2023
Vial113	221278-003E	0.00275	0.00040	2/8/2023
Vial113	221278-003F	0.00270	0.00038	2/8/2023
Vial113	221278-003G	0.00357	0.00038	2/8/2023

Table 12. Displays all replicates measured by alpha counting. The average $^{238}Pu/^{239}Pu$ value was 0.00262 ± 0.00034 (2σ). The number of replicate measurements was 21.

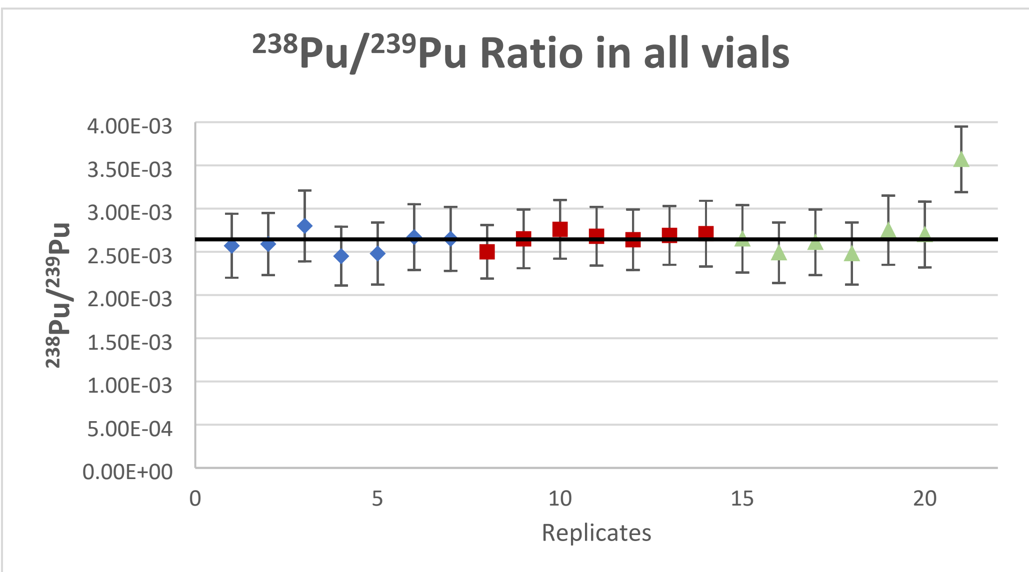


Figure 19. Replicate values of $^{238}Pu/^{239}Pu$ by alpha counts for all the analyzed vials plotted against the average TIMS measured value.

6. REFERENCES

1. CSD-AM-CIMS-IN15, *Purification of U and/or Pu on 1-mL Eichrom UTEVA and/or TEVA Resin for Analysis by Mass Spectrometry*, Oak Ridge National Laboratory, Revision 1.
2. ASTM C1672-17, *Standard Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer,* 2017.

APPENDIX A. TIMS LOADING SHEETS

APPENDIX A. TIMS LOADING SHEETS

Triton Loading Sheet	
Date:	1Ø / 2Ø / 2022
Turret #:	Ø77
Instrument	SN630
Operator:	Hexel

Turret Position	Sample ID	Element	Filament type (Re,W,Ta) (dbl single)	Loading Volume (uL)	Dry@ 0.6 A Filament treatment
1	2M128PuI	Pu	Re, dbl	.9 uL	1A, 60s, 1.5, 5sec 2.0 5sec
2	CRM 137	↓	↓	↓	↓
3	CRM 136				
4	1875				
5	202201876				
6	128				
7	202201877				
8	128				
9	CRM 137				
10	202201875				
11	202201876				Skate/SUS
12	128				
13	CRM 136				
14	202201877				
15	20220 1875				
16	20220 1876				
17	128				
18	20220 1877				
19	CRM 137				
20	CRM 136				
21	128				

√128, 6 → 1, 6, 8, 12, 17, 21
√137, 3 → 2, 9, 19
√136, 3 → 3, 13, 20
√202201875, 3 → ~~5~~ 4, 1Ø, 15
√202201876, 3 → 5, 11, 16
√202201877, 3 → 7, 14, 18

CRM 137A V113 = 3a = 202201877
CRM 137A V052 = 2a = 202201876
CRM 137A V004 = 1a = 202201875

Triton Loading Sheet	
Date:	10/25/2022
Turret #:	Ø77
Instrument	630
Operator:	Hexel

Turret Position	Sample ID	Element	Filament type (Re,W,Ta) (dbl single)	Loading Volume (uL)	Filament treatment
1	2M128 PuI	Pu	Re dbl	1uL	Load @ 0.6A 60@1A, 5@1.5A, 5@2A
2	2C137 PuI	↓	↓	Ø.8Ø	↓
3	2C136 PuI	↓	↓	Ø.9	
4	2022Ø1876			Ø.7ØuL	
5	2022Ø1877			Ø.7ØuL	
6	2M128 PuI			1uL	
7	2022Ø1875			Ø.7uL	
8	2M128 PuI			1uL	
9	2C137 PuI			Ø.8ØuL	
10	2022Ø1876			0.7	
11	2022Ø1875			Ø.7	
12	2M128 PuI			1.Ø	
13	2C136 PuI			Ø.9	
14	2022Ø1877			Ø.7	
15	2022Ø1877			Ø.7	
16	2022Ø1875			Ø.7	
17	2M128 PuI			1.Ø	
18	~~2C137~~ 1876			Ø.7	
19	2C137 PuI			~~1uL~~ Ø.8ØuL	
20	2C136 PuI			~~Ø.85~~ Ø.9	
21	2M128 PuI			1.Ø	

Triton Loading Sheet	
Date:	10 / 27 / 2022
Turret #:	Ø77 Day 3
Instrument	~~Hexel~~ 63Ø
Operator:	Hexel

Turret Position	Sample ID	Element	Filament type (Re,W,Ta) (dbl single)	Loading Volume (uL)	Filament treatment
1	2M128PuI	Pu	Re Dbl	1.Ø uL	Load Ø.6 A 60@1A, 55@1.5A, [illegible]@2A
2	2C137PuI	↓	↓	Ø.6 uL	↓
3	2C136PuI			Ø.9 uL	
4	202201876			~~Ø.7uL~~ Ø.4 uL	
5	202201877			Ø.7	
6	2M128 PuI			1.Ø	
7	202201877			Ø.7	
8	2M128 PuI			1.Ø	
9	2C137 PuI			Ø.6	
10	202201876			Ø.4	
11	WRM003			Ø.8	
12	2M128PuI			1.Ø	
13	2C136 PuI			Ø.9	
14	202201875			Ø.6 uL	
15	2C003 PuI			Ø.8	
16	2C003 PuI			Ø.8	
17	2M128 PuI			1	
18	2C003 PuI			Ø.8	
19	2C137 PuI			Ø.6	
20	2C136 PuI			Ø.9	
21	2M128 PuI			1.Ø	

2M128PuI (6, 1.0uL) : 1, 6, 8, 12, 17, 21
2C137PuI (3, Ø.6uL) : 2, 9, 19
2C136 PuI (3, Ø.9uL) : 3, 13, 2Ø
2C003PuI (4, Ø.8uL) : 11, 15, 16, 18
202201875 (1, Ø.6uL) : 14
202201876 (2, Ø.4uL) : 4, 1Ø
202201877 (2, Ø.7uL) : 5, 7

Triton Loading Sheet	
Date:	01 / 23 / 20
Turret #:	Ø77
Instrument	SN 630
Operator:	Hexel

Turret Position	Sample ID	Element	Filament type (Re,W,Ta) (dbl single)	Loading Volume (uL)	Filament treatment
1	3M128PuI	Pu	Re, dbl, TE	1 uL	Dry @ 0.5 amp, 1A @ 60s, 1.5A @ 5s, 2A @ 5s
2	3M137PuI				
3	21875PuI				
4	21877PuI				
5	21877PuI				
6	3M128PuI				
7	~~3C137PuI~~	21877PuI			
8	3C137PuI				
9	21875PuI				
10	21877PuI				
11	2M128PuI				
12	21875PuI				
13	3C137PuI				
14	21877PuI				
15	21877PuI				
16	3M128PuI				
17	21877PuI				
18	21875PuI				
19	21877PuI				
20	3C137PuI				
21	3M128PuI				

APPENDIX B. VIAL 004 GUM WORKBENCH

Pu Isotopic for recert 137A

Author: Cole R. Hexel

This Workbench is designed to evaluate the uncertainties in the plutonium isotopic abundance data obtained using the multiple collector mass spectrometer.

Model Equation:

{GUM Uncertainty Calculations for Plutonium Isotopic (PuI) Characterization for a single sample.}

{TIMS Data}
{Pu 238/239 Ratio Data}
$R_{89} = R_{89corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq4};$

{Pu 240/239 Ratio Data}
$R_{09} = R_{09corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq};$

{Pu 241/239 Ratio Data}
$R_{19} = R_{19corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq2};$

{Pu 242/239 Ratio Data}
$R_{29} = R_{29corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq3};$

{ICP Data}
{Pu 240/239 Ratio Data}
$ICPR_{09} = ICPR_{09corr} * \delta_{Cert} * \delta_{ICPCFVar} + \delta_{ICPseq};$

{Pu 241/239 Ratio Data}
$ICPR_{19} = ICPR_{19corr} * \delta_{Cert} * \delta_{ICPCFVar} + \delta_{ICPseq2};$

{Pu 242/239 Ratio Data}
$ICPR_{29} = ICPR_{29corr} * \delta_{Cert} * \delta_{ICPCFVar} + \delta_{ICPseq3};$

List of Quantities:

Quantity	Unit	Definition
R_{89corr}		The corrected $^{238}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{09corr}		The corrected $^{240}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{19corr}		The corrected $^{241}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{29corr}		The corrected $^{242}Pu/^{239}Pu$ ratio data from OakLimbs.
δ_{Cert}		Relative uncertainty associated with the decay-corrected certified $^{242}Pu/^{239}Pu$ ratio on the mass bias standard certificate.
δ_{CFVar}		Relative standard error associated with the mass bias measurements before and after the sample for the $^{242}Pu/^{239}Pu$ ratio
δ_{seq}		Daily variability of each sequence run for the $^{240}Pu/^{239}Pu$ ratio
δ_{seq2}		Daily variability of each sequence run for the $^{241}Pu/^{239}Pu$ ratio
δ_{seq3}		Daily variability of each sequence run for the $^{242}Pu/^{239}Pu$ ratio
δ_{seq4}		Daily variability of each sequence run for the $^{238}Pu/^{239}Pu$ ratio
R_{09}		The final $^{240}Pu/^{239}Pu$ ratio and uncertainty
R_{19}		The final $^{241}Pu/^{239}Pu$ ratio and uncertainty
R_{29}		The final $^{242}Pu/^{239}Pu$ ratio and uncertainty
R_{89}		The final $^{238}Pu/^{239}Pu$ ratio and uncertainty
$ICPR_{09corr}$		The corrected $^{240}Pu/^{239}Pu$ ratio data from OakLimbs MC-ICP-MS
$ICPR_{19corr}$		The corrected $^{241}Pu/^{239}Pu$ ratio data from OakLimbs MC-ICP-MS
$ICPR_{29corr}$		The corrected $^{242}Pu/^{239}Pu$ ratio data from OakLimbs MC-ICP-MS
δ_{ICPseq}		Daily variability of each sequence run for the $^{240}Pu/^{239}Pu$ ratio on ICP
$\delta_{ICPseq2}$		Daily variability of each sequence run for the $^{241}Pu/^{239}Pu$ ratio on ICP
$\delta_{ICPseq3}$		Daily variability of each sequence run for the $^{242}Pu/^{239}Pu$ ratio on ICP
$\delta_{ICPCFVar}$		Relative standard error associated with the mass bias measurements before and after the sample for the $^{242}Pu/^{239}Pu$ Ratio
$ICPR_{09}$		The final $^{240}Pu/^{239}Pu$ ratio and uncertainty from ICP
$ICPR_{19}$		The final $^{241}Pu/^{239}Pu$ ratio and uncertainty from ICP
$ICPR_{29}$		The final $^{242}Pu/^{239}Pu$ ratio and uncertainty from ICP

Input Correlation

	R_{89corr}	R_{09corr}	R_{19corr}	R_{29corr}
R_{89corr}	1	−0.4174	0.7846	−0.0471
R_{09corr}	−0.4174	1	−0.5457	0.8651
R_{19corr}	0.7846	−0.5457	1	−0.4151
R_{29corr}	−0.0471	0.8651	−0.4151	1

	$ICPR_{09corr}$	$ICPR_{19corr}$	$ICPR_{29corr}$
$ICPR_{09corr}$	1	−0.0809	−0.2334
$ICPR_{19corr}$	−0.0809	1	−0.4418
$ICPR_{29corr}$	−0.2334	−0.4418	1

Uncertainty Budgets:

R_{09}: The final $^{240}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{09corr}	0.24062618	7.54×10^{-6}	normal	1.0	7.5×10^{-6}	3.9%
δ_{Cert}	1.000000	130×10^{-6}	normal	0.24	31×10^{-6}	66.4%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	0.24	18×10^{-6}	22.9%
δ_{seq}	0.0	10.0×10^{-6}	normal	1.0	10×10^{-6}	6.8%
R_{09}	0.2406262	38.4×10^{-6}				

R_{19}: The final $^{241}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{19corr}	5.0994×10^{-3}	15.8×10^{-6}	normal	1.0	16×10^{-6}	84.2%
δ_{Cert}	1.000000	130×10^{-6}	normal	5.1×10^{-3}	660×10^{-9}	0.1%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	5.1×10^{-3}	390×10^{-9}	0.0%
δ_{seq2}	0.0	6.80×10^{-6}	normal	1.0	6.8×10^{-6}	15.6%
R_{19}	5.0994×10^{-3}	17.2×10^{-6}				

R_{29}: The final $^{242}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{29corr}	0.01557764	1.76×10^{-6}	normal	1.0	1.8×10^{-6}	27.8%
δ_{Cert}	1.000000	130×10^{-6}	normal	0.016	2.0×10^{-6}	36.6%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	0.016	1.2×10^{-6}	12.7%
δ_{seq3}	0.0	1.60×10^{-6}	normal	1.0	1.6×10^{-6}	22.9%
R_{29}	0.01557764	3.35×10^{-6}				

R_{89}: The final $^{238}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{89corr}	2.63702×10^{-3}	1.67×10^{-6}	normal	1.0	1.7×10^{-6}	40.3%
δ_{Cert}	1.000000	130×10^{-6}	normal	2.6×10^{-3}	340×10^{-9}	1.7%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	2.6×10^{-3}	200×10^{-9}	0.6%
δ_{seq4}	0.0	2.00×10^{-6}	normal	1.0	2.0×10^{-6}	57.4%
R_{89}	2.63702×10^{-3}	2.64×10^{-6}				

$ICPR_{09}$: The final $^{240}Pu/^{239}Pu$ ratio and uncertainty from ICP

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
δ_{Cert}	1.000000	130×10^{-6}	normal	0.24	31×10^{-6}	76.3%
$ICPR_{09corr}$	0.24063095	5.05×10^{-6}	normal	1.0	5.0×10^{-6}	2.0%
δ_{ICPseq}	0.0	12.4×10^{-6}	normal	1.0	12×10^{-6}	12.0%
$\delta_{ICPCFVar}$	1.0000000	46.3×10^{-6}	normal	0.24	11×10^{-6}	9.7%
$ICPR_{09}$	0.2406309	35.8×10^{-6}				

$ICPR_{19}$: The final $^{241}Pu/^{239}Pu$ ratio and uncertainty from ICP

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
δ_{Cert}	1.000000	130×10^{-6}	normal	5.1×10^{-3}	660×10^{-9}	0.1%
$ICPR_{19corr}$	5.10479×10^{-3}	6.60×10^{-6}	normal	1.0	6.6×10^{-6}	12.4%
$\delta_{ICPseq2}$	0.0	17.5×10^{-6}	normal	1.0	18×10^{-6}	87.4%
$\delta_{ICPCFVar}$	1.0000000	46.3×10^{-6}	normal	5.1×10^{-3}	240×10^{-9}	0.0%
$ICPR_{19}$	5.1048×10^{-3}	18.7×10^{-6}				

$ICPR_{29}$: The final $^{242}Pu/^{239}Pu$ ratio and uncertainty from ICP

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
δ_{Cert}	1.000000	130×10^{-6}	normal	0.016	2.0×10^{-6}	0.9%
$ICPR_{29corr}$	0.01557253	5.59×10^{-6}	normal	1.0	5.6×10^{-6}	7.2%
$\delta_{ICPseq3}$	0.0	19.9×10^{-6}	normal	1.0	20×10^{-6}	91.7%
$\delta_{ICPCFVar}$	1.0000000	46.3×10^{-6}	normal	0.016	720×10^{-9}	0.1%
$ICPR_{29}$	0.0155725	20.8×10^{-6}				

Results:

Quantity	Value	Expanded uncertainty	Coverage factor	Coverage
R_{09}	0.240626	77×10^{-6}	2.00	95% (normal)
R_{19}	5.099×10^{-3}	34×10^{-6}	2.00	95% (normal)
R_{29}	0.0155776	6.7×10^{-6}	2.00	95% (normal)
R_{89}	2.6370×10^{-3}	5.3×10^{-6}	2.00	95% (normal)
$ICPR_{09}$	0.240631	72×10^{-6}	2.00	95% (normal)
$ICPR_{19}$	5.105×10^{-3}	37×10^{-6}	2.00	95% (normal)
$ICPR_{29}$	0.015573	42×10^{-6}	2.00	95% (normal)

Result Correlation:

	R_{09}	R_{19}	R_{29}	R_{89}	$ICPR_{09}$	$ICPR_{19}$	$ICPR_{29}$
R_{09}	1	−0.0561	0.7533	0.0904	0.7120	0.0289	0.0794
R_{19}	−0.0561	1	−0.1695	0.4636	0.0337	1.4×10^{-3}	3.8×10^{-3}
R_{29}	0.7533	−0.1695	1	0.0900	0.5289	0.0215	0.0590
R_{89}	0.0904	0.4636	0.0900	1	0.1135	4.6×10^{-3}	0.0127
$ICPR_{09}$	0.7120	0.0337	0.5289	0.1135	1	0.0309	0.0871
$ICPR_{19}$	0.0289	1.4×10^{-3}	0.0215	4.6×10^{-3}	0.0309	1	−0.0380
$ICPR_{29}$	0.0794	3.8×10^{-3}	0.0590	0.0127	0.0871	−0.0380	1

APPENDIX C. VIAL 052 GUM WORKBENCH

APPENDIX C. VIAL 052 GUM WORKBENCH

Pu Isotopic for recert 137A

Author: Cole R. Hexel

This Workbench is designed to evaluate the uncertainties in the plutonium isotopic abundance data obtained using the multiple collector mass spectrometer.

Model Equation:

{GUM Uncertainty Calculations for Plutonium Isotopic (PuI) Characterization for a single sample.}

{TIMS Data}
{Pu 238/239 Ratio Data}
$R_{89} = R_{89corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq4};$

{Pu 240/239 Ratio Data}
$R_{09} = R_{09corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq};$

{Pu 241/239 Ratio Data}
$R_{19} = R_{19corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq2};$

{Pu 242/239 Ratio Data}
$R_{29} = R_{29corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq3};$

{ICP Data}
{Pu 240/239 Ratio Data}
$ICPR_{09} = ICPR_{09corr} * \delta_{Cert} * \delta_{ICPCFVar} + \delta_{ICPseq};$

{Pu 241/239 Ratio Data}
$ICPR_{19} = ICPR_{19corr} * \delta_{Cert} * \delta_{ICPCFVar} + \delta_{ICPseq2};$

{Pu 242/239 Ratio Data}
$ICPR_{29} = ICPR_{29corr} * \delta_{Cert} * \delta_{ICPCFVar} + \delta_{ICPseq3};$

List of Quantities:

Quantity	Unit	Definition
R_{89corr}		The corrected $^{238}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{09corr}		The corrected $^{240}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{19corr}		The corrected $^{241}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{29corr}		The corrected $^{242}Pu/^{239}Pu$ ratio data from OakLimbs.
δ_{Cert}		Relative uncertainty associated with the decay-corrected certified $^{242}Pu/^{239}Pu$ ratio on the mass bias standard certificate.
δ_{CFVar}		Relative standard error associated with the mass bias measurements before and after the sample for the $^{242}Pu/^{239}Pu$ ratio
δ_{seq}		day to day variability of each sequence run for the $^{240}Pu/^{239}Pu$ ratio
δ_{seq2}		day to day variability of each sequence run for the $^{241}Pu/^{239}Pu$ ratio
δ_{seq3}		day to day variability of each sequence run for the $^{242}Pu/^{239}Pu$ ratio
δ_{seq4}		day to day variability of each sequence run for the $^{238}Pu/^{239}Pu$ ratio
R_{09}		The final $^{240}Pu/^{239}Pu$ ratio and uncertainty
R_{19}		The final $^{241}Pu/^{239}Pu$ ratio and uncertainty
R_{29}		The final $^{242}Pu/^{239}Pu$ ratio and uncertainty
R_{89}		The final $^{238}Pu/^{239}Pu$ ratio and uncertainty
$ICPR_{09corr}$		The corrected $^{240}Pu/^{239}Pu$ ratio data from OakLimbs MC-ICP-MS
$ICPR_{19corr}$		The corrected $^{241}Pu/^{239}Pu$ ratio data from OakLimbs MC-ICP-MS
$ICPR_{29corr}$		The corrected $^{242}Pu/^{239}Pu$ ratio data from OakLimbs MC-ICP-MS
δ_{ICPseq}		Daily variability of each sequence run for the $^{240}Pu/^{239}Pu$ ratio on ICP
$\delta_{ICPseq2}$		Daily variability of each sequence run for the $^{241}Pu/^{239}Pu$ ratio on ICP
$\delta_{ICPseq3}$		Daily variability of each sequence run for the $^{242}Pu/^{239}Pu$ ratio on ICP
$\delta_{ICPCFVar}$		Relative standard error associated with the mass bias measurements before and after the sample for the $^{242}Pu/^{239}Pu$ ratio
$ICPR_{09}$		The final $^{240}Pu/^{239}Pu$ ratio and uncertainty from ICP
$ICPR_{19}$		The final $^{241}Pu/^{239}Pu$ ratio and uncertainty from ICP
$ICPR_{29}$		The final $^{242}Pu/^{239}Pu$ ratio and uncertainty from ICP

Input Correlation

	R_{89corr}	R_{09corr}	R_{19corr}	R_{29corr}
R_{89corr}	1	−0.4174	0.7846	−0.0471
R_{09corr}	−0.4174	1	−0.5457	0.8651
R_{19corr}	0.7846	−0.5457	1	−0.4151
R_{29corr}	−0.0471	0.8651	−0.4151	1

	$ICPR_{09corr}$	$ICPR_{19corr}$	$ICPR_{29corr}$
$ICPR_{09corr}$	1	−0.0809	−0.2334
$ICPR_{19corr}$	−0.0809	1	−0.4418
$ICPR_{29corr}$	−0.2334	−0.4418	1

Uncertainty Budgets:

R_{09}: The final $^{240}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{09corr}	0.24062720	9.51×10^{-6}	normal	1.0	9.5×10^{-6}	6.0%
δ_{Cert}	1.000000	130×10^{-6}	normal	0.24	31×10^{-6}	64.9%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	0.24	18×10^{-6}	22.4%
δ_{seq}	0.0	10.0×10^{-6}	normal	1.0	10×10^{-6}	6.6%
R_{09}	0.2406272	38.8×10^{-6}				

R_{19}: The final $^{241}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{19corr}	5.110839×10^{-3}	874×10^{-9}	normal	1.0	870×10^{-9}	1.6%
δ_{Cert}	1.000000	130×10^{-6}	normal	5.1×10^{-3}	660×10^{-9}	0.9%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	5.1×10^{-3}	390×10^{-9}	0.3%
δ_{seq2}	0.0	6.80×10^{-6}	normal	1.0	6.8×10^{-6}	97.1%
R_{19}	5.11084×10^{-3}	6.90×10^{-6}				

R_{29}: The final $^{242}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{29corr}	0.01557713	1.88×10^{-6}	normal	1.0	1.9×10^{-6}	30.4%
δ_{Cert}	1.000000	130×10^{-6}	normal	0.016	2.0×10^{-6}	35.3%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	0.016	1.2×10^{-6}	12.2%
δ_{seq3}	0.0	1.60×10^{-6}	normal	1.0	1.6×10^{-6}	22.1%
R_{29}	0.01557713	3.41×10^{-6}				

R_{89}: The final $^{238}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{89corr}	2.64401×10^{-3}	4.27×10^{-6}	normal	1.0	4.3×10^{-6}	81.4%
δ_{Cert}	1.000000	130×10^{-6}	normal	2.6×10^{-3}	340×10^{-9}	0.5%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	2.6×10^{-3}	200×10^{-9}	0.2%
δ_{seq4}	0.0	2.00×10^{-6}	normal	1.0	2.0×10^{-6}	17.8%
R_{89}	2.64401×10^{-3}	4.73×10^{-6}				

$ICPR_{09}$: The final $^{240}Pu/^{239}Pu$ ratio and uncertainty from ICP

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
δ_{Cert}	1.000000	130×10^{-6}	normal	0.24	31×10^{-6}	75.6%
$ICPR_{09corr}$	0.24062296	6.13×10^{-6}	normal	1.0	6.1×10^{-6}	2.9%
δ_{ICPseq}	0.0	12.4×10^{-6}	normal	1.0	12×10^{-6}	11.9%
$\delta_{ICPCFVar}$	1.0000000	46.3×10^{-6}	normal	0.24	11×10^{-6}	9.6%
$ICPR_{09}$	0.2406230	36.0×10^{-6}				

$ICPR_{19}$: The final $^{241}Pu/^{239}Pu$ ratio and uncertainty from ICP

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
δ_{Cert}	1.000000	130×10^{-6}	normal	5.1×10^{-3}	660×10^{-9}	0.1%
$ICPR_{19corr}$	5.10539×10^{-3}	4.58×10^{-6}	normal	1.0	4.6×10^{-6}	6.4%
$\delta_{ICPseq2}$	0.0	17.5×10^{-6}	normal	1.0	18×10^{-6}	93.4%
$\delta_{ICPCFVar}$	1.0000000	46.3×10^{-6}	normal	5.1×10^{-3}	240×10^{-9}	0.0%
$ICPR_{19}$	5.1054×10^{-3}	18.1×10^{-6}				

$ICPR_{29}$: The final $^{242}Pu/^{239}Pu$ ratio and uncertainty from ICP

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
δ_{Cert}	1.000000	130×10^{-6}	normal	0.016	2.0×10^{-6}	0.9%
$ICPR_{29corr}$	0.01557139	7.17×10^{-6}	normal	1.0	7.2×10^{-6}	11.4%
$\delta_{ICPseq3}$	0.0	19.9×10^{-6}	normal	1.0	20×10^{-6}	87.6%
$\delta_{ICPCFVar}$	1.0000000	46.3×10^{-6}	normal	0.016	720×10^{-9}	0.1%
$ICPR_{29}$	0.0155714	21.3×10^{-6}				

Results:

Quantity	Value	Expanded uncertainty	Coverage factor	Coverage
R_{09}	0.240627	78×10^{-6}	2.00	95% (normal)
R_{19}	5.111×10^{-3}	14×10^{-6}	2.00	95% (normal)
R_{29}	0.0155771	6.8×10^{-6}	2.00	95% (normal)
R_{89}	2.6440×10^{-3}	9.5×10^{-6}	2.00	95% (normal)
$ICPR_{09}$	0.240623	72×10^{-6}	2.00	95% (normal)
$ICPR_{19}$	5.105×10^{-3}	36×10^{-6}	2.00	95% (normal)
$ICPR_{29}$	0.015571	43×10^{-6}	2.00	95% (normal)

Result Correlation:

	R_{09}	R_{19}	R_{29}	R_{89}	$ICPR_{09}$	$ICPR_{19}$	$ICPR_{29}$
R_{09}	1	0.0875	0.7614	−0.0136	0.7007	0.0295	0.0767
R_{19}	0.0875	1	0.0480	0.0991	0.0837	3.5×10^{-3}	9.2×10^{-3}
R_{29}	0.7614	0.0480	1	0.0346	0.5170	0.0218	0.0566
R_{89}	−0.0136	0.0991	0.0346	1	0.0631	2.7×10^{-3}	6.9×10^{-3}
$ICPR_{09}$	0.7007	0.0837	0.5170	0.0631	1	0.0324	0.0799
$ICPR_{19}$	0.0295	3.5×10^{-3}	0.0218	2.7×10^{-3}	0.0324	1	−0.0338
$ICPR_{29}$	0.0767	9.2×10^{-3}	0.0566	6.9×10^{-3}	0.0799	−0.0338	1

APPENDIX D. VIAL 113 GUM WORKBENCH

Pu Isotopic for recert 137A

Author: Cole R. Hexel

This Workbench is designed to evaluate the uncertainties in the plutonium isotopic abundance data obtained using the multiple collector mass spectrometer.

Model Equation:

{GUM Uncertainty Calculations for Plutonium Isotopic (PuI) Characterization for a single sample.}

{TIMS Data}
{Pu 238/239 Ratio Data}
$R_{89} = R_{89corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq4};$

{Pu 240/239 Ratio Data}
$R_{09} = R_{09corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq};$

{Pu 241/239 Ratio Data}
$R_{19} = R_{19corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq2};$

{Pu 242/239 Ratio Data}
$R_{29} = R_{29corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq3};$

{ICP Data}
{Pu 240/239 Ratio Data}
$ICPR_{09} = ICPR_{09corr} * \delta_{Cert} * \delta_{ICPCFVar} + \delta_{ICPseq};$

{Pu 241/239 Ratio Data}
$ICPR_{19} = ICPR_{19corr} * \delta_{Cert} * \delta_{ICPCFVar} + \delta_{ICPseq2};$

{Pu 242/239 Ratio Data}
$ICPR_{29} = ICPR_{29corr} * \delta_{Cert} * \delta_{ICPCFVar} + \delta_{ICPseq3};$

List of Quantities:

Quantity	Unit	Definition
R_{89corr}		The corrected $^{238}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{09corr}		The corrected $^{240}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{19corr}		The corrected $^{241}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{29corr}		The corrected $^{242}Pu/^{239}Pu$ ratio data from OakLimbs.
δ_{Cert}		Relative uncertainty associated with the decay-corrected certified $^{242}Pu/^{239}Pu$ ratio on the mass bias standard certificate.
δ_{CFVar}		Relative standard error associated with the mass bias measurements before and after the sample for the $^{242}Pu/^{239}Pu$ ratio
δ_{seq}		Daily variability of each sequence run for the $^{240}Pu/^{239}Pu$ ratio
δ_{seq2}		Daily variability of each sequence run for the $^{241}Pu/^{239}Pu$ ratio
δ_{seq3}		Daily variability of each sequence run for the $^{242}Pu/^{239}Pu$ ratio
δ_{seq4}		Daily variability of each sequence run for the $^{238}Pu/^{239}Pu$ ratio
R_{09}		The final $^{240}Pu/^{239}Pu$ ratio and uncertainty
R_{19}		The final $^{241}Pu/^{239}Pu$ ratio and uncertainty
R_{29}		The final $^{242}Pu/^{239}Pu$ ratio and uncertainty
R_{89}		The final 238Pu/239Pu ratio and uncertainty
$ICPR_{09corr}$		The corrected $^{240}Pu/^{239}Pu$ ratio data from OakLimbs MC-ICP-MS
$ICPR_{19corr}$		The corrected $^{241}Pu/^{239}Pu$ ratio data from OakLimbs MC-ICP-MS
$ICPR_{29corr}$		The corrected $^{242}Pu/^{239}Pu$ ratio data from OakLimbs MC-ICP-MS
δ_{ICPseq}		Daily variability of each sequence run for the $^{240}Pu/^{239}Pu$ ratio on ICP
$\delta_{ICPseq2}$		Daily variability of each sequence run for the $^{241}Pu/^{239}Pu$ ratio on ICP
$\delta_{ICPseq3}$		Daily variability of each sequence run for the $^{242}Pu/^{239}Pu$ ratio on ICP
$\delta_{ICPCFVar}$		Relative standard error associated with the mass bias measurements before and after the sample for the $^{242}Pu/^{239}Pu$ ratio
$ICPR_{09}$		The final $^{240}Pu/^{239}Pu$ ratio and uncertainty from ICP
$ICPR_{19}$		The final $^{241}Pu/^{239}Pu$ ratio and uncertainty from ICP
$ICPR_{29}$		The final $^{242}Pu/^{239}Pu$ ratio and uncertainty from ICP

Input Correlation

	R_{89corr}	R_{09corr}	R_{19corr}	R_{29corr}
R_{89corr}	1	−0.4174	0.7846	−0.0471
R_{09corr}	−0.4174	1	−0.5457	0.8651
R_{19corr}	0.7846	−0.5457	1	−0.4151
R_{29corr}	−0.0471	0.8651	−0.4151	1

	$ICPR_{09corr}$	$ICPR_{19corr}$	$ICPR_{29corr}$
$ICPR_{09corr}$	1	−0.0809	−0.2334
$ICPR_{19corr}$	−0.0809	1	−0.4418
$ICPR_{29corr}$	−0.2334	−0.4418	1

Uncertainty Budgets:

R_{09}: The final $^{240}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{09corr}	0.24062551	4.53×10^{-6}	normal	1.0	4.5×10^{-6}	1.4%
δ_{Cert}	1.000000	130×10^{-6}	normal	0.24	31×10^{-6}	68.1%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	0.24	18×10^{-6}	23.5%
δ_{seq}	0.0	10.0×10^{-6}	normal	1.0	10×10^{-6}	7.0%
R_{09}	0.2406255	37.9×10^{-6}				

R_{19}: The final $^{241}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{19corr}	5.1214×10^{-3}	13.9×10^{-6}	normal	1.0	14×10^{-6}	80.4%
δ_{Cert}	1.000000	130×10^{-6}	normal	5.1×10^{-3}	670×10^{-9}	0.2%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	5.1×10^{-3}	390×10^{-9}	0.0%
δ_{seq2}	0.0	6.80×10^{-6}	normal	1.0	6.8×10^{-6}	19.3%
R_{19}	5.1214×10^{-3}	15.5×10^{-6}				

R_{29}: The final $^{242}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{29corr}	0.01557766	1.75×10^{-6}	normal	1.0	1.8×10^{-6}	27.5%
δ_{Cert}	1.000000	130×10^{-6}	normal	0.016	2.0×10^{-6}	36.8%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	0.016	1.2×10^{-6}	12.7%
δ_{seq3}	0.0	1.60×10^{-6}	normal	1.0	1.6×10^{-6}	23.0%
R_{29}	0.01557766	3.34×10^{-6}				

R_{89}: The final $^{238}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{89corr}	2.64820×10^{-3}	9.37×10^{-6}	normal	1.0	9.4×10^{-6}	95.5%
δ_{Cert}	1.000000	130×10^{-6}	normal	2.6×10^{-3}	340×10^{-9}	0.1%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	2.6×10^{-3}	200×10^{-9}	0.0%
δ_{seq4}	0.0	2.00×10^{-6}	normal	1.0	2.0×10^{-6}	4.3%
R_{89}	2.64820×10^{-3}	9.59×10^{-6}				

$ICPR_{09}$: The final $^{240}Pu/^{239}Pu$ ratio and uncertainty from ICP

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
δ_{Cert}	1.000000	130×10^{-6}	normal	0.24	31×10^{-6}	75.7%
$ICPR_{09corr}$	0.24063514	5.95×10^{-6}	normal	1.0	6.0×10^{-6}	2.7%
δ_{ICPseq}	0.0	12.4×10^{-6}	normal	1.0	12×10^{-6}	11.9%
$\delta_{ICPCFVar}$	1.0000000	46.3×10^{-6}	normal	0.24	11×10^{-6}	9.6%
$ICPR_{09}$	0.2406351	35.9×10^{-6}				

$ICPR_{19}$: The final $^{241}Pu/^{239}Pu$ ratio and uncertainty from ICP

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
δ_{Cert}	1.000000	130×10^{-6}	normal	5.1×10^{-3}	660×10^{-9}	0.1%
$ICPR_{19corr}$	5.08573×10^{-3}	9.64×10^{-6}	normal	1.0	9.6×10^{-6}	23.2%
$\delta_{ICPseq2}$	0.0	17.5×10^{-6}	normal	1.0	18×10^{-6}	76.6%
$\delta_{ICPCFVar}$	1.0000000	46.3×10^{-6}	normal	5.1×10^{-3}	240×10^{-9}	0.0%
$ICPR_{19}$	5.0857×10^{-3}	20.0×10^{-6}				

$ICPR_{29}$: The final $^{242}Pu/^{239}Pu$ ratio and uncertainty from ICP

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
δ_{Cert}	1.000000	130×10^{-6}	normal	0.016	2.0×10^{-6}	0.8%
$ICPR_{29corr}$	0.01558524	9.59×10^{-6}	normal	1.0	9.6×10^{-6}	18.7%
$\delta_{ICPseq3}$	0.0	19.9×10^{-6}	normal	1.0	20×10^{-6}	80.4%
$\delta_{ICPCFVar}$	1.0000000	46.3×10^{-6}	normal	0.016	720×10^{-9}	0.1%
$ICPR_{29}$	0.0155852	22.2×10^{-6}				

Results:

Quantity	Value	Expanded uncertainty	Coverage factor	Coverage
R_{09}	0.240626	76×10^{-6}	2.00	95% (normal)
R_{19}	5.121×10^{-3}	31×10^{-6}	2.00	95% (normal)
R_{29}	0.0155777	6.7×10^{-6}	2.00	95% (normal)
R_{89}	2.648×10^{-3}	19×10^{-6}	2.00	95% (normal)
$ICPR_{09}$	0.240635	72×10^{-6}	2.00	95% (normal)
$ICPR_{19}$	5.086×10^{-3}	40×10^{-6}	2.00	95% (normal)
$ICPR_{29}$	0.015585	44×10^{-6}	2.00	95% (normal)

Result Correlation:

	R_{09}	R_{19}	R_{29}	R_{89}	$ICPR_{09}$	$ICPR_{19}$	$ICPR_{29}$
R_{09}	1	−0.0107	0.7278	-8.9×10^{-3}	0.7182	0.0273	0.0753
R_{19}	−0.0107	1	−0.1601	0.6897	0.0375	1.4×10^{-3}	3.9×10^{-3}
R_{29}	0.7278	−0.1601	1	5.2×10^{-3}	0.5280	0.0201	0.0554
R_{89}	-8.9×10^{-3}	0.6897	5.2×10^{-3}	1	0.0312	1.2×10^{-3}	3.3×10^{-3}
$ICPR_{09}$	0.7182	0.0375	0.5280	0.0312	1	0.0260	0.0728
$ICPR_{19}$	0.0273	1.4×10^{-3}	0.0201	1.2×10^{-3}	0.0260	1	−0.0886
$ICPR_{29}$	0.0753	3.9×10^{-3}	0.0554	3.3×10^{-3}	0.0728	−0.0886	1

APPENDIX E. VIAL 4, 52, 113 COMBINED GUM WORKBENCH

Pu Isotopic for recert 137A

Author: Cole R. Hexel

This Workbench is designed to evaluate the uncertainties in the plutonium isotopic abundance data obtained using the multicollector inductively coupled plasma–mass spectrometer.

Model Equation:

{GUM Uncertainty Calculations for Plutonium Isotopic (PuI) Characterization for a single sample.}

{Pu 238/239 Ratio Data}
$R_{89} = R_{89corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq4};$

{Pu 240/239 Ratio Data}
$R_{09} = R_{09corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq};$

{Pu 241/239 Ratio Data}
$R_{19} = R_{19corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq2};$

{Pu 242/239 Ratio Data}
$R_{29} = R_{29corr} * \delta_{Cert} * \delta_{CFVar} + \delta_{seq3};$

List of Quantities:

Quantity	Unit	Definition
R_{89corr}		The corrected $^{238}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{09corr}		The corrected $^{240}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{19corr}		The corrected $^{241}Pu/^{239}Pu$ ratio data from OakLimbs.
R_{29corr}		The corrected $^{242}Pu/^{239}Pu$ ratio data from OakLimbs.
δ_{Cert}		Relative uncertainty associated with the decay-corrected certified $^{242}Pu/^{239}Pu$ ratio on the mass bias standard certificate.
δ_{CFVar}		Relative standard error associated with the mass bias measurements before and after the sample for the $^{242}Pu/^{239}Pu$ ratio
δ_{seq}		Daily variability of each sequence run for the $^{240}Pu/^{239}Pu$ ratio
δ_{seq2}		Daily variability of each sequence run for the $^{241}Pu/^{239}Pu$ ratio
δ_{seq3}		Daily variability of each sequence run for the $^{242}Pu/^{239}Pu$ ratio
δ_{seq4}		Daily variability of each sequence run for the $^{238}Pu/^{239}Pu$ ratio
R_{09}		The final $^{240}Pu/^{239}Pu$ ratio and uncertainty
R_{19}		The final $^{241}Pu/^{239}Pu$ ratio and uncertainty
R_{29}		The final $^{242}Pu/^{239}Pu$ ratio and uncertainty
R_{89}		The final $^{238}Pu/^{239}Pu$ ratio and uncertainty

R_{89corr}:
Type A
Method of observation: Direct
Number of observations: 33

No.	Observation		No.	Observation		No.	Observation
1	0.002635		12	0.002646		23	0.002660
2	0.002635		13	0.002657		24	0.002643
3	0.002636		14	0.002634		25	0.002777
4	0.002640		15	0.002635		26	0.002632
5	0.002637		16	0.002634		27	0.002638
6	0.002635		17	0.002641		28	0.002634
7	0.002653		18	0.002661		29	0.002634
8	0.002634		19	0.002640		30	0.002643
9	0.002633		20	0.002637		31	0.002632
10	0.002634		21	0.002634		32	0.002641
11	0.002635		22	0.002644		33	0.002634

Arithmetic mean: 2.64358×10^{-3}
Standard deviation: 25×10^{-6}
Standard uncertainty: 4.39×10^{-6}
Degrees of freedom: 32

R_{09corr}:
Type A
Method of observation: Direct
Number of observations: 54

No.	Observation		No.	Observation		No.	Observation
1	0.240611		19	0.240615		37	0.240637
2	0.240631		20	0.240618		38	0.240631
3	0.240662		21	0.240617		39	0.240621
4	0.240614		22	0.240614		40	0.240649
5	0.240641		23	0.240641		41	0.240640
6	0.240576		24	0.240620		42	0.240596
7	0.240595		25	0.240612		43	0.240609
8	0.240633		26	0.240589		44	0.240628
9	0.240636		27	0.240639		45	0.240639
10	0.240640		28	0.240626		46	0.240631
11	0.240649		29	0.240641		47	0.240619
12	0.240627		30	0.240632		48	0.240655
13	0.240621		31	0.240615		49	0.240638
14	0.240620		32	0.240644		50	0.240638
15	0.240592		33	0.240660		51	0.240643
16	0.240677		34	0.240631		52	0.240644
17	0.240631		35	0.240608		53	0.240611
18	0.240623		36	0.240640		54	0.240617

Arithmetic mean: 0.24062754
Standard deviation: 19×10^{-6}
Standard uncertainty: 2.59×10^{-6}
Degrees of freedom: 53

The calculated $^{240}Pu/^{239}Pu$ ratio, Standard Deviation, and number of "Good Points" imported from OakLimbs.

R_{19corr}:
Type A
Method of observation: Direct
Number of observations: 54

No.	Observation		No.	Observation		No.	Observation
1	0.005108		19	0.005180		37	0.005116
2	0.005106		20	0.005170		38	0.005117
3	0.005107		21	0.005167		39	0.005114
4	0.005180		22	0.005180		40	0.005115
5	0.005105		23	0.005162		41	0.005106
6	0.005110		24	0.005182		42	0.005103
7	0.005194		25	0.005193		43	0.005099
8	0.005047		26	0.005075		44	0.005118
9	0.005054		27	0.005076		45	0.005125
10	0.005040		28	0.005075		46	0.005091
11	0.005042		29	0.005074		47	0.005097
12	0.005113		30	0.005074		48	0.005036
13	0.005112		31	0.005070		49	0.005101
14	0.005108		32	0.005069		50	0.005106
15	0.005110		33	0.005075		51	0.005101
16	0.005108		34	0.005071		52	0.005069
17	0.005114		35	0.005110		53	0.005085
18	0.005111		36	0.005090		54	0.005102

Arithmetic mean: 5.10672×10^{-3}
Standard deviation: 39×10^{-6}
Standard uncertainty: 5.33×10^{-6}
Degrees of freedom: 53

The calculated $^{241}Pu/^{239}Pu$ ratio, Standard Deviation, and number of “Good Points” imported from OakLimbs.

R_{29corr}:
Type A
Method of observation: Direct
Number of observations: 54

No.	Observation		No.	Observation		No.	Observation
1	0.015573		19	0.015573		37	0.015577
2	0.015578		20	0.015570		38	0.015552
3	0.015585		21	0.015573		39	0.015577
4	0.015573		22	0.015573		40	0.015572
5	0.015577		23	0.015578		41	0.015564
6	0.015565		24	0.015576		42	0.015551
7	0.015578		25	0.015576		43	0.015570
8	0.015579		26	0.015569		44	0.015597
9	0.015579		27	0.015576		45	0.015585
10	0.015581		28	0.015581		46	0.015586
11	0.015586		29	0.015580		47	0.015546
12	0.015575		30	0.015577		48	0.015617
13	0.015578		31	0.015577		49	0.015537
14	0.015576		32	0.015595		50	0.015587
15	0.015568		33	0.015589		51	0.015600
16	0.015585		34	0.015596		52	0.015595
17	0.015578		35	0.015577		53	0.015571
18	0.015579		36	0.015556		54	0.015589

Arithmetic mean: 0.01557700
Standard deviation: 13×10^{-6}
Standard uncertainty: 1.81×10^{-6}
Degrees of freedom: 53

The calculated $^{242}Pu/^{239}Pu$ ratio, Standard Deviation, and number of "Good Points" imported from OakLimbs.

δ_{Cert}:
Type B normal distribution
Value: 1
Expanded uncertainty: 2.6×10^{-4}
Coverage factor: 2

The uncertainty of the decay-corrected $^{240}Pu/^{239}Pu$ on the certificate used as the mass bias standard. This value will be found in OakLimbs → Common → Support Data → Standards → "look up the $^{240}Pu/^{239}Pu$ ratio" with the ID Code used in the mass bias "M" sample.
Example 3M126PuI "M" equals mass bias ID Code is "126"
The decay-corrected $^{242}Pu/^{239}Pu$ value is 1.00016 ± 0.00026
$0.00026/1.00016 = 2.6 \times 10^{-4}$

δ_{CFVar}:
Type B normal distribution
Value: 1
Expanded uncertainty: 0.0000764
Coverage factor: 1

Uncertainty in the mass bias factor estimated from the variability in the mass bias measurements across the sequences Since each sample is bracket corrected for mass fractionation throughout a run, the multiplicative correction factor is assumed to be 1. However, uncertainties are assigned to this correction factor based on the relative standard uncertainty of the mass bias measurements across a run. The Std Err on the $^{240}Pu/^{239}Pu$ measurements of the comparator in each sequence
Sequence Average R $^{242}Pu/^{239}Pu$ Std Err % RSE (Comparator)
Average %RSE for the fractionation correction factor = $1.66961 \times 10^{-7}/\sqrt{21}$ =
$^{242}Pu/^{239}Pu$ 1 CRM 128 1.0017011 2 CRM 128 1.0017348 3 CRM 128 1.0018845 4 CRM 128 1.0014960 5 CRM 128 1.0015396 6 CRM 128 1.0015440 7 CRM 128 1.0016944 8 CRM 128 1.0017292 9 CRM 128 1.0016014 10 CRM 128 1.0016866 11 CRM 128 1.0015384 12 CRM 128 1.0015404 13 CRM 128 1.0016134 14 CRM 128 1.0015081 15 CRM 128 1.0021248 16 CRM 128 1.0014634 17 CRM 128 1.0016042 18 CRM 128 1.0020550 19 CRM 128 1.0004350 20 CRM 128 1.0019940 21 CRM 128 1.0021628 Average 1.0016501 Std Dev 0.0003503 %RSD 0.035% SE 0.0000764 %RSE 0.008%

δ_{seq}:
Type B normal distribution
Value: 0
Expanded uncertainty: 0.000010
Coverage factor: 1

Normalized sequence variation obtained from first control analyzed for $^{240}Pu/^{239}Pu$ divided by the number of points in the control chart (*N*) . Therefore, normalized sequence variation is sequence variation/sqrt(*N*) = (standard uncertainty)
$^{240}Pu/^{239}Pu$ 0.240659 0.240672 0.240659 0.240692 0.240659 0.240706 0.240641 0.240641 0.240629 0.240632 0.240585 0.240595 0.240648 0.000035 0.015% 0.000010 0.0042%

δ_{seq2}:
Type B normal distribution
Value: 0
Expanded uncertainty: 0.0000068
Coverage factor: 1

Normalized sequence variation obtained from first control analyzed for $^{241}Pu/^{239}Pu$ divided by the number of points in the control chart (*N*) . Therefore, normalized sequence variation is sequence variation/sqrt(*N*) = (standard uncertainty)
$^{241}Pu/^{239}Pu$ 0.0051793 0.0051876 0.0051872 0.0051708 0.0051891 0.0051407 0.0051749 0.0051749 0.0051343 0.0051323 0.0051311 0.0051459 0.0051623 0.0000235 0.45% 0.0000068 0.13%

δ_{seq3}:
Type B normal distribution
Value: 0
Expanded uncertainty: 0.0000016
Coverage factor: 1

Normalized sequence variation obtained from first control analyzed for $^{242}Pu/^{239}Pu$ divided by the number of points in the control chart (*N*) . Therefore, normalized sequence variation is sequence variation/sqrt(*N*) = (standard uncertainty)
$^{242}Pu/^{239}Pu$ 0.0155814 0.0155810 0.0155813 0.0155885 0.0155795 0.0155926 0.0155800 0.0155800 0.0155780 0.0155768 0.0155734 0.0155723 0.0155804 0.0000056 0.036% 0.0000016 0.010%

δ_{seq4}:
Type B normal distribution
Value: 0
Expanded uncertainty: 0.0000020
Coverage factor: 1

Normalized sequence variation obtained from first control analyzed for $^{238}Pu/^{239}Pu$ divided by the number of points in the control chart (*N*) . Therefore, normalized sequence variation is sequence variation/sqrt(*N*) = (standard uncertainty) Rep STD $^{238}Pu/^{239}Pu$ 1 CRM 137 0.0026357 2 CRM 137 0.0026352 3 CRM 137 0.0026575 4 CRM 137 0.0026372 5 CRM 137 0.0026358 6 CRM 137 0.0026432 7 CRM 137 0.0026389 8 CRM 137 0.0026388 9 CRM 137 0.0026323 10 CRM 137 0.0026310 11 CRM 137 0.0026337 12 CRM 137 0.0026344 Average 0.0026378 Std Dev 0.0000070 %RSD 0.27% SE 0.0000020 %RSE 0.077%

Input Correlation

	R_{89corr}	R_{09corr}	R_{19corr}	R_{29corr}
R_{89corr}	1	−0.4174	0.7846	−0.0471
R_{09corr}	−0.4174	1	−0.5457	0.8651
R_{19corr}	0.7846	−0.5457	1	−0.4151
R_{29corr}	−0.0471	0.8651	−0.4151	1

Uncertainty Budgets:

R_{09}: The final $^{240}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{09corr}	0.24062754	2.59×10^{-6}	normal	1.0	2.6×10^{-6}	0.5%
δ_{Cert}	1.000000	130×10^{-6}	normal	0.24	31×10^{-6}	68.8%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	0.24	18×10^{-6}	23.7%
δ_{seq}	0.0	10.0×10^{-6}	normal	1.0	10×10^{-6}	7.0%
R_{09}	0.2406275	37.7×10^{-6}				

R_{19}: The final $^{241}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{19corr}	5.10672×10^{-3}	5.33×10^{-6}	normal	1.0	5.3×10^{-6}	37.8%
δ_{Cert}	1.000000	130×10^{-6}	normal	5.1×10^{-3}	660×10^{-9}	0.6%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	5.1×10^{-3}	390×10^{-9}	0.2%
δ_{seq2}	0.0	6.80×10^{-6}	normal	1.0	6.8×10^{-6}	61.5%
R_{19}	5.10672×10^{-3}	8.67×10^{-6}				

R_{29}: The final $^{242}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{29corr}	0.01557700	1.81×10^{-6}	normal	1.0	1.8×10^{-6}	28.8%
δ_{Cert}	1.000000	130×10^{-6}	normal	0.016	2.0×10^{-6}	36.2%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	0.016	1.2×10^{-6}	12.5%
δ_{seq3}	0.0	1.60×10^{-6}	normal	1.0	1.6×10^{-6}	22.6%
R_{29}	0.01557700	3.37×10^{-6}				

R_{89}: The final $^{238}Pu/^{239}Pu$ ratio and uncertainty

Quantity	Value	Standard uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution	Index
R_{89corr}	2.64358×10^{-3}	4.39×10^{-6}	normal	1.0	4.4×10^{-6}	82.2%
δ_{Cert}	1.000000	130×10^{-6}	normal	2.6×10^{-3}	340×10^{-9}	0.5%
δ_{CFVar}	1.0000000	76.4×10^{-6}	normal	2.6×10^{-3}	200×10^{-9}	0.2%
δ_{seq4}	0.0	2.00×10^{-6}	normal	1.0	2.0×10^{-6}	17.1%
R_{89}	2.64358×10^{-3}	4.84×10^{-6}				

Results:

Quantity	Value	Expanded uncertainty	Coverage factor	Coverage
R_{09}	0.240628	75×10^{-6}	2.00	95% (normal)
R_{19}	5.107×10^{-3}	17×10^{-6}	2.00	95% (normal)
R_{29}	0.0155770	6.7×10^{-6}	2.00	95% (normal)
R_{89}	2.6436×10^{-3}	9.7×10^{-6}	2.00	95% (normal)

Result Correlation:

	R_{09}	R_{19}	R_{29}	R_{89}
R_{09}	1	0.0624	0.7026	0.0532
R_{19}	0.0624	1	−0.0749	0.4445
R_{29}	0.7026	−0.0749	1	0.0345
R_{89}	0.0532	0.4445	0.0345	1

Appendix F. Representative Alpha Counting GUM WORKBENCH

Pu 238/239 Alpha

Author: kt4

Model Equation:

{Ratio}

$R = mol_{238} / mol_{239};$

{Convert back to mol}

$mol_{240} = G_{found240} / AW_{240};$
$mol_{239} = G_{found239} / AW_{239};$
$mol_{238} = G_{found238} / AW_{238};$

{Convert back to grams}

$G_{found240} = A_{meas240} / SA_{240};$
$G_{found239} = A_{meas239} / SA_{239};$
$G_{found238} = A_{meas238} / SA_{238};$

{Activity in measurement}

$A_{meas240} = (AcP_{240} * Ac_{240239})/1000/1000/1000/1000;$
$A_{meas239} = (AcP_{239} * Ac_{240239})/1000/1000/1000/1000;$
$A_{meas238} = Ac_{238}/1000/1000/1000/1000;$

{Activity Percent}

$AcP_{240} = Ci_{240} / Ci_{total};$

$AcP_{239} = Ci_{239} / Ci_{total};$

$Ci_{total} = Ci_{240} + Ci_{239};$

{Ci ratio}

$Ci_{240} = g_{240} * SA_{240};$
$Ci_{239} = g_{239} * SA_{239};$

$g_{240} = AW_{240} * R_{09};$
$g_{239} = AW_{239}$

List of Quantities:

Quantity	Unit	Definition
Ac_{238}	pCi/mL	Alpha spec instrument response intensity of the combined Pu238 peak

Quantity	Unit	Definition
Ac_{240239}	pCi/mL	Alpha spec instrument response intensity of the combined Pu239/240 peak
AW_{238}	g/mol	Atomic weight
AW_{239}	g/mol	Atomic weight
AW_{240}	g/mol	Atomic weight
R_{09}	mol:mol	Ratio of 239:240 from TIMS data
SA_{239}	Ci/g	Specific activity of 239
SA_{240}	Ci/g	Specific activity of 240
SA_{238}	Ci/g	Specific activity of 338
mol_{238}	mol	Conversion to mols for 238
mol_{239}	mol	Conversion to mols for 239
$G_{found240}$	g	Convert back to grams for mass 240
$G_{found239}$	g	Convert back to grams for mass 239
$G_{found238}$	g	Convert back to grams for mass 238
$A_{meas240}$	Ci/mL	240 activity in measured
$A_{meas239}$	Ci/mL	239 activity in measured
$A_{meas238}$	Ci/mL	238 activity in measured
AcP_{240}	%	Ci:Ci activity fraction for 239:240 using TIMS data
AcP_{239}	%	Ci:Ci activity fraction for 239:240 using TIMS data
Ci_{240}	Ci	Curies of 240
Ci_{total}	Ci	Sum of the Ci activity of 238, 239 & 240
Ci_{239}	Ci	Curies of 239
g_{240}	g	Grams of 240
g_{239}	g	Grams of 239
R	mol/mol	Final ratio mol:mol of 238:239
mol_{240}	mol	Conversion to mols for 240

Ac_{238}:
Type B normal distribution
Value: $3.289 \cdot 10^{+3}$ pCi/mL
Expanded Uncertainty: 353.8 pCi/mL
Coverage Factor: 2

Ac_{240239}:
Type B normal distribution
Value: $8.3580 \cdot 10^{+3}$ pCi/mL
Expanded Uncertainty: 780.8 pCi/mL
Coverage Factor: 2

AW_{238}:
Type B normal distribution
Value: 238.049559 g/mol
Expanded Uncertainty: 0.0000019 g/mol
Coverage Factor: 2

AW_{239}:
Type B normal distribution
Value: 239.0521636 g/mol
Expanded Uncertainty: .0000019 g/mol
Coverage Factor: 2

AW_{240}:
Type B normal distribution
Value: 240.0538138 g/mol
Expanded Uncertainty: .0000019 g/mol
Coverage Factor: 2

R_{09}:
Type B normal distribution
Value: 0.240626 mol:mol
Expanded Uncertainty: 0.0000076 mol:mol
Coverage Factor: 2

SA_{239}:
Constant
Value: $6.20400 \cdot 10^{-2}$ Ci/g

SA_{240}:
Constant
Value: 0.22696 Ci/g

SA_{238}:
Constant
Value: $1.7119 \cdot 10^{+1}$ Ci/g

Uncertainty Budgets:

R: Final ratio mol:mol of 238:239

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
Ac_{238}	3289 pCi/mL	177 pCi/mL	normal	$820 \cdot 10^{-9}$	$150 \cdot 10^{-6}$ mol/mol	56.9 %

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
Ac_{240239}	8358 pCi/mL	390 pCi/mL	normal	$-320\cdot10^{-9}$	$-130\cdot10^{-6}$ mol/mol	43.1 %
AW_{238}	238.049559000 g/mol	$950\cdot10^{-9}$ g/mol	normal	$-11\cdot10^{-6}$	$-11\cdot10^{-12}$ mol/mol	0.0 %
AW_{239}	239.052163600 g/mol	$950\cdot10^{-9}$ g/mol	normal	$6.0\cdot10^{-6}$	$5.7\cdot10^{-12}$ mol/mol	0.0 %
AW_{240}	240.053813800 g/mol	$950\cdot10^{-9}$ g/mol	normal	$5.3\cdot10^{-6}$	$5.0\cdot10^{-12}$ mol/mol	0.0 %
R_{09}	0.24062600 mol:mol	$3.80\cdot10^{-6}$ mol:mol	normal	$5.3\cdot10^{-3}$	$20\cdot10^{-9}$ mol/mol	0.0 %
SA_{239}	0.06204 Ci/g					
SA_{240}	0.22696 Ci/g					
SA_{238}	17.119 Ci/g					
mol_{238}	$807.1\cdot10^{-15}$ mol	$43.4\cdot10^{-15}$ mol				
mol_{239}	$299.1\cdot10^{-12}$ mol	$14.0\cdot10^{-12}$ mol				
$G_{found239}$	$71.51\cdot10^{-9}$ g	$3.34\cdot10^{-9}$ g				
$G_{found238}$	$192.1\cdot10^{-12}$ g	$10.3\cdot10^{-12}$ g				
$A_{meas239}$	$4.436\cdot10^{-9}$ Ci/mL	$207\cdot10^{-12}$ Ci/mL				
$A_{meas238}$	$3.289\cdot10^{-9}$ Ci/mL	$177\cdot10^{-12}$ Ci/mL				
AcP_{239}	0.53079488 %	$3.93\cdot10^{-6}$ %				
Ci_{240}	13.109933 Ci	$207\cdot10^{-6}$ Ci				
Ci_{total}	27.940730 Ci	$207\cdot10^{-6}$ Ci				
Ci_{239}	14.8307962297 Ci	$58.9\cdot10^{-9}$ Ci				
g_{240}	57.763189 g	$912\cdot10^{-6}$ g				
g_{239}	239.052163600 g	$950\cdot10^{-9}$ g				
R	$2.698\cdot10^{-3}$ mol/mol	$192\cdot10^{-6}$ mol/mol				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
R	$2.70\cdot10^{-3}$ mol/mol	$380\cdot10^{-6}$ mol/mol	2.00	95% (normal)