Safeguards Technology Development Program
FY2023 Mid-Year Report
1-April-2023

WBS # – Project Title: 24.1.3.4 - Development of Analytical Method for Measuring U and Pu particles by Laser Ablation MC-ICP-MS for the NWAL

HQ Team Lead and PM: Arden Dougan and Ning Xu

Summary Statement of Work: This project will develop methodology to analyze the Pu isotope ratio in mixed U-Pu particles by laser ablation MC-ICP-MS. This will involve: 1) testing and validation of the Pu analytical method using mixed U-Pu solutions and Pu doped glasses, 2) isotopic analysis of mixed U-Pu particles by laser ablation MC-ICP-MS, and 3) continued development of the R-based data reduction program. Details regarding the analytical method development and results of QC testing will be output as a deliverable to the IAEA, along with an updated version of the data reduction software.

Report Title: Developing Methodology to Determine Pu Isotopic Composition by Laser Ablation MC-ICP-MS

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Major Highlights: Extensive testing performed with Pu and mixed U-Pu solutions to determine accuracy and precision of Pu measurements using ion counters. Quantified the effect of interferences from U on the Pu mass range. Tested Pu isotopic measurements by laser ablation – obtaining the correct isotopic composition from glass doped with the C128 standard. Synthesized a series of new Pu-bearing glass standards for characterization in Q3-4. Made significant improvements to the LARA reduction software, including ability to handle Pu data.

Progress: See following report.

Lawrence Livermore National Laboratory

Developing Methodology to Determine Pu Isotopic Composition by Laser Ablation MC-ICP-MS

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1. Executive Summary

This project will develop methodology to analyze the Pu isotope ratio in mixed U-Pu particles by laser ablation MC-ICP-MS. This will involve: 1) testing and validation of the Pu analytical method using mixed U-Pu solutions and Pu doped glasses, 2) isotopic analysis of mixed U-Pu particles by laser ablation MC-ICP-MS, and 3) continued development of the R-based data reduction program. Details regarding the analytical method development and results of QC testing will be output as a deliverable to the IAEA, along with an updated version of the LARA data reduction software.

2. Plutonium isotopic analyses by laser ablation ICP-MS

2.1.Introduction

This mid-year report documents the development of new methods to measure Pu isotope ratios by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) by Lawrence Livermore National Laboratory (LLNL). This work builds on a previously methods of characterizing the U isotopic composition of U-bearing glasses and particles funded by the Office of International Nuclear Safeguards. The new focus is on plutonium isotopic analyses by laser ablation. As yet, there are few previous studies that have attempted to utilize laser ablation as a rapid sampling tool for isotopic analyses of Pu, particularly in the micron-scale particles. Early work combined laser ablation ICP-MS with an isotope dilution technique to measure Pu concentrations in mosses and soils (Boulgya et al., 2003; 2004), or performed laser ablation analysis of electroplated purified Pu (Cizdziel et al., 2008). Later work demonstrated the utility of this technique for smaller scale in situ analyses; isotopic analysis of Pu bearing particles from the Chernobyl nuclear power plant (Konegger-Kappel & Prohaska 2016) achieved accurate $^{240}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ ratios with precision of ~10%. However, the particle sizes ranged between 200 and 1000µm, orders of magnitude larger than those relevant to environmental sampling. A more recent study analyzed Pu isotopes in micron scale, Pu-bearing particles and obtained $^{240}Pu/^{239}Pu$ ratios with precisions of <2% (Wang et al., 2017). However, in this case the isotopic compositions were not accurate within the stated precision and minor isotopes were not attempted. Ultimately, previous studies have demonstrated that laser ablation analyses of Pu can be successfully deployed in a range of sample matrices, achieving %-level precision on the $^{240}Pu/^{239}Pu$ ratio in solid samples and Pu-bearing particles. However, here we have more specific requirements to test; the ability to produce accurate Pu isotopic data in U-Pu particles at the micron scale. Constraining Pu detection limits and understanding the effect of high U content on Pu isotope ratios are key requirements. It will also be important to understand whether the two minor Pu isotopes (^{241}Pu and ^{242}Pu) can be measured with any degree of accuracy using this technique.

Here, we present results of Pu isotopic analyses of Pu and U containing solutions and preliminary analyses of Pu bearing glasses (Task-1). We have also made significant modifications to the Laser Ablation Reduction Application (LARA), including enabling the reduction of Pu isotopic data (Task-3). Future work in Q3 and Q4 will continue both tasks, before focusing on characterizing the accuracy and precision of Pu isotopic measurements from micron scale Pu/U particles (Task-2).

Figure 1 – Neptune-Plus MC-ICP-MS (left) and Photon Machines 193nm excimer laser system (right) at LLNL.

2.2.Hardware Description

Laser ablation systems are used as in-situ sample introduction systems for inductively coupled plasma mass spectrometers (ICP-MS). In brief, solid samples are ablated by the laser and the resulting fine aerosol is carried to the plasma source on the mass spectrometer in a stream of helium carrier gas. Analyte atoms in the sample aerosol are ionized in the plasma and the ions that are generated are transmitted through the mass spectrometer where the element of interest is selected based on the ratio of mass to charge. The selected species are detected when they hit the detector array, which on multi-detector ICP-MS instruments are comprised of come combination of ion counters and Faraday cups. The following hardware description focuses on setup of the mass spectrometer and laser ablation system, with specific information pertaining to measurement of Pu isotopes. The hardware setup for Pu isotopic analyses by LA-MC-ICP-MS at LLNL consists of a Photon Machines 193nm excimer laser system that is connected to a Thermo Scientific Neptune-plus MC-ICP-MS (Fig. 1).

2.2.1. Mass Spectrometer – Thermo Scientific Neptune-Plus MC-ICP-MS

The Neptune-Plus MC-ICP-MS at LLNL is equipped with 10 Faraday detectors, 3 full-size secondary electron multipliers (SEMs) and 3 compact discrete dynode detectors (CDD's). This detector configuration is designed for isotopic analyses of uranium, enabling large ion beams of the major uranium isotope (^{238}U) to be measured on a Faraday detector and minor isotopes to be measured using ion counters. This means that measurement of Pu isotopes, in which the major isotope is the lightest species (^{239}Pu) is more challenging. To collect useful data for all isotopes of Pu either requires that large ion beams of all isotopes are detected on Faraday cups, or that trace levels of all Pu isotopes are detected on ion counters (ICs) (Fig. 2). In either case, large differences in abundance between minor isotopes (i.e., ^{241}Pu, ^{242}Pu) and ^{239}Pu mean that uncertainties associated with minor ^{241}Pu and ^{242}Pu measurements will be compromised by low intensities/count rates. It is possible to set up a hybrid Faraday-IC array in which Faraday level ^{239}Pu signals can be measured alongside ^{240}Pu on an ion counter, however, this configuration would not collect useful

data for ^{241}Pu or ^{242}Pu. In Table 1 we present three possible detector arrays for Pu isotopic analysis using the Neptune. Of these, we anticipate that configurations 2 and 3 will be the most useful for laser ablation analyses. Anticipated Pu signals from Pu-bearing glasses and particles are unlikely to be high enough to warrant use of the all-Faraday configuration 1.

2.2.2. Laser ablation system – Photon Machines Analyte 193nm excimer laser

The laser ablation system used for this project is described in full in a previous report (Wimpenny et al., 2021). In brief, this is a Photon Machines Analyte 193nm excimer laser system with a 4ns pulse length and equipped with a two-volume 'Helex' laser cell, shown in Fig. 3.

Table 1 – Detector configuration on the Neptune-Plus MC-ICP-MS for Pu isotope analysis

	H5	H4	H3	H2	H1	C/IC1A	L1	L2	L3	IC6	L4	IC1B	IC2/L5	IC3	IC5
Config.-1				(^{244}Pu)		^{242}Pu	^{241}Pu	^{240}Pu	^{239}Pu						
Config.-2										(^{244}Pu)		^{242}Pu	^{241}Pu	^{240}Pu	^{239}Pu
Config.-3						^{240}Pu	^{239}Pu	^{238}U							

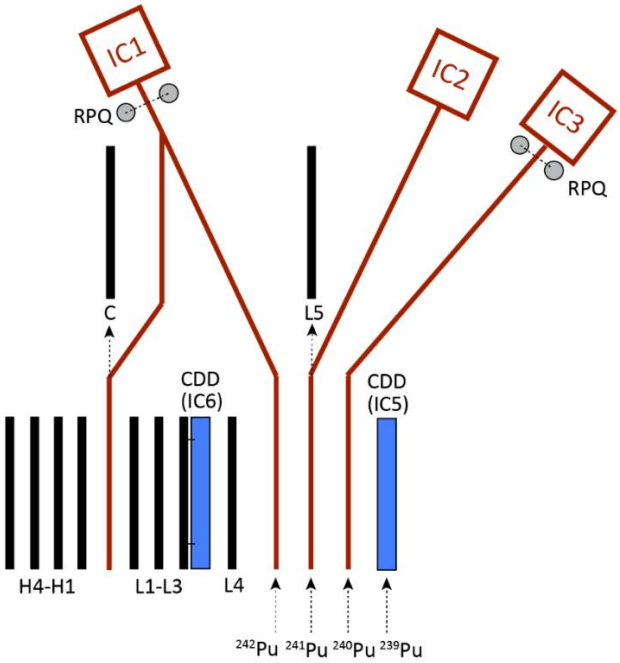

Figure 2 – The detector array on the Neptune-Plus MC-ICP-MS. Faraday detectors are in black, SEM's are in red, and CDD's are in blue. The IC1 and IC3 SEM's are fitted with energy filters (RPQ's). The Pu species and associated detectors in configuration-1 are labeled.

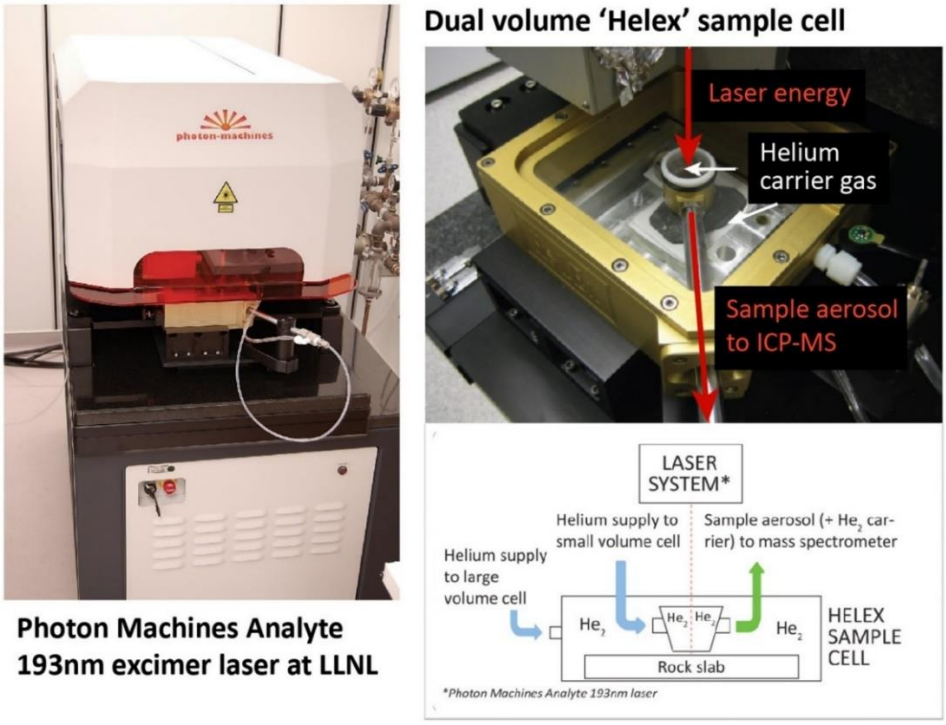

Figure 3 – The dual volume 'Helex' sample cell on the laser ablation system. Helium is supplied to both the main cell and inner cup as a carrier gas for the ablated sample aerosol, which is transported out of the cell to the ICP-MS.

3. Plutonium Isotope Quality Control Testing

Initial development work focused on characterizing the performance of the Neptune MC-ICP-MS during isotopic analyses of pure Pu solutions using the ion counting array. To obtain accurate Pu isotopic data using ICs requires that corrections are made to adjust for performance differences between each individual detector. This correction factor is also called the ion counter gain factor. In addition, a correction must also be applied for instrumental mass bias effects, which preferentially discriminate for the heavy isotopes during transition through the instrument. This is called the mass bias correction factor (MBCF). Thus, the measurement of Pu isotopes by MC-ICP-MS requires a similar analytical setup and calculation of similar correction factors as U isotopic analyses using a mixed Faraday-IC array (Wimpenny et al., 2021). These correction factors could be easily calculated for U by ablating a U-reference glass with known isotopic composition during each analytical session. Unfortunately, the current lack of Pu isotopic reference materials for in situ analyses (i.e. glasses/other solid matrices) means that it may be challenging to calculate these correction factors online during each laser ablation session. Instead, there are two alternatives for Pu; i) establishing a set of correction constants based on previous isotopic measurements in solution mode, or ii) using a U reference glass to calculate correction factors for Pu.

Here, testing was performed to establish the degree of accuracy and precision that can be attained for the isotopic composition of Pu in solution-mode, which will provide an upper limit on the expected precision achievable by laser ablation. The isotopic analysis of Pu CRMs will also enable

us to assess the constancy of the instrumental mass bias and ion counter gain corrections both within and between analytical sessions. In addition to characterizing the behavior of Pu, we ran solutions of uranium CRMs alongside Pu samples and standards to compare correction factors generated by uranium and plutonium. This will allow us to assess whether plutonium behaves similarly to uranium during isotopic analysis on the Neptune, and, if so, whether the use of uranium reference glasses to generate online mass bias and IC gain correction factors is robust for Pu.

3.1.Plutonium isotopic analyses of solutions by MC-ICP-MS

The Neptune was configured as shown in Figure 2 with four isotopes of plutonium measured simultaneously using the IC's 1, 2, 3 and 5. The Neptune was equipped with the 'Jet' sampling cone for extra sensitivity and 'H' skimmer cone which reduces oxide formation. Samples were dissolved in a carrier solution of 2% HNO_3 + 0.005M HF at a nominal concentration of 3 parts per trillion (ppt). Samples were aspirated using a Cetac 100µl/min nebulizer and introduced to a desolvating device to enhance sensitivity and reduce polyatomic species, in this case the Cetac Aridus II. Typical sensitivity of a 3ppt solution of Pu using this introduction system was ~200,000cps ^{239}Pu in the New Brunswick Laboratory (NBL) CRM-138, which has an approximate ^{239}Pu content of 91%. This equates to a sensitivity of ~1200V of Pu per ppm. For performance testing, two plutonium CRMs from NBL (CRM 126-A and CRM 137) were analyzed as unknowns over a six month period in which five separate analytical sessions were performed. During each session, the mass bias and ion counter gains were calculated using CRM 138. The specific collectors used during the Pu peak jumping routine are given below in Table 2.

Table 2 – Pu-jump routine to obtain IC gain factors and average mass bias correction factor.

	IC1B	IC2	IC3	IC5
Static Collection	^{242}Pu	^{241}Pu	^{240}Pu	**^{239}Pu**
Jump-1		^{240}Pu	**^{239}Pu**	
Jump-2	^{240}Pu	**^{239}Pu**		
Jump-3	**^{239}Pu**			

Ion counter gains were calculated by performing a peak jumping routine in which the ^{239}Pu beam was jumped onto each ion counter in turn, in order to calculate ion counter gain factors relative to IC5. The ^{240}Pu beam was measured on ICs 1, 2 and 3, which enabled three separate measurements of the ^{240}Pu/^{239}Pu ratio on each IC during the peak jumping routine. These ^{240}Pu/^{239}Pu ratios were averaged in order to calculate a MBCF from each CRM 138 standard. The Pu isotopic composition of each 'unknown' was measured statically, and corrections were applied to their blank corrected isotope ratios using correction factors from the bracketing CRM 138's.

Using this analytical technique, we can assess the accuracy and precision of Pu isotopic analyses by solution MC-ICP-MS. In addition, these analyses provide a base level assessment of the stability of instrumental mass bias and ion counter gain corrections within and between analytical sessions. A summary of the isotopic data for CRM 126-A (n = 37) and CRM 137 (n = 31) are provided in Table 3 and isotopic data are presented in Fig. 4 and 5.

Table 3 – Pu isotopic data for CRM 126-A and CRM 137. These were measured by solution-mode MC-ICP-MS.

		$^{240}Pu/^{239}Pu$	2σ	% RSD	$^{241}Pu/^{239}Pu$	2σ	% RSD	$^{242}Pu/^{239}Pu$	2σ	% RSD
CRM 126-A	Reference	0.062652	0.000018	0.03%	0.00078913	0.00000038	0.05%	0.00038485	0.00000026	0.07%
(Purified 12/07/2017)	Measured	0.062711	0.000391	0.62%	0.00080050	0.00002449	3.06%	0.00038348	0.00000747	1.95%
CRM-137	Reference	0.24066	0.00029	0.12%	0.005528	0.000015	0.28%	0.015613	0.000052	0.33%
(Purified 2/1/2021)	Measured	0.24132	0.00147	0.61%	0.005570	0.000261	4.69%	0.015586	0.000280	1.80%

As shown, the Pu isotope data for both CRM 126-A and 137 fall within uncertainty of reference values. Internal uncertainties (2σ) for $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ ratios are typically ~0.6%, 1.4% and 1.8% respectively. External precision (2σ), based on the standard deviation of 31-37 replicate analyses from five analytical sessions equate to respective RSDs (relative standard deviation) of 0.6%, 4% and 1.9% on the $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ ratios. Although the data are generally very consistent, it is interesting to note that the $^{240}Pu/^{239}Pu$ ratios for CRM 126-A and CRM 137 became more precise in later analyses. As this change in precision was not observed for the other ratios to ^{239}Pu this could indicate that the performance of the IC3 detector improved over time (i.e. the IC required more 'burn in' time). In addition, there was a clear excursion in the $^{241}Pu/^{239}Pu$ ratios measured for CRM 137 towards higher ratios. This was a temporary offset of ~6%, for which there is no obvious explanation. For this reason, the true uncertainty relating to $^{241}Pu/^{239}Pu$ ratios may be >4%.

Overall, these analyses demonstrate that accurate Pu isotopic data can be obtained by using a Pu reference standard to calculate mass bias and ion counter gain factors during each analytical session. This provides an upper limit on the likely precision that will be achievable during laser ablation analyses of Pu in silicate glasses or U-Pu particles. Given that the expected Pu signals from glasses containing 0.1-10 ppm Pu may be at significantly lower levels and laser signals are inherently less stable, precision of <5% on the $^{240}Pu/^{239}Pu$ ratio may be challenging. Robust constraints on the ^{241}Pu and ^{242}Pu contents of a sample will be dependent on both the Pu concentration, Pu isotopic composition and ablated mass (i.e. glass vs particle). However, given their low abundance it may be challenging to achieve precision of <20%.

As previously discussed, there are two options for performing mass bias and ion counter gain corrections during laser ablation analyses; using constant correction factors or using a U or Pu reference material during each analytical session. Here, we assess the stability of mass bias and ion counter gain factors on the Neptune MC-ICP-MS over several analytical sessions, based on replicate analyses of Pu and U certified reference materials. Although a uranium glass such as CAS53-500 could be used to generate a mass bias correction factor (MBCF) and IC gains, in practice it is not suitable for providing the required gain factors for plutonium analyses. This is because the uranium detector array has ^{235}U on the L5 faraday detector, meaning we cannot obtain a gain factor for IC2 (used to collect ^{241}Pu). Furthermore, the uranium detector configuration has ^{233}U on IC5 (used to collect ^{239}Pu) and most U-glasses do not contain measurable ^{233}U. Hence the utility of a uranium glass standard would be confined to generation of online mass bias factors and IC gain factors would need to be generated by an alternative method, most likely using an assumed constant factor.

In Fig. 6, we present IC gain factors between IC5-IC3, IC5-IC2 and IC5-IC1, measured in solution mode over four separate analytical sessions. There are several interesting observations from these data. First, the spread in IC gain factors over ~6 months of analysis is significant, equating to 3-5% depending on the ion counter. In run variations are more consistent, with IC5-IC3 and IC5-IC2 gain factors varying by ~0.5%. This level of variation is likely to be insignificant if measurement uncertainties on $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ ratios are 10% or greater by laser ablation MC-ICP-MS. The data for IC5-IC1 are far more variable, with gain factors varying by 2-4% within analytical session. This illustrates the difference in performance between individual ion counters and highlights the need for accurate constraints on IC efficiency. It also indicates that precision on $^{242}Pu/^{239}Pu$ ratios of <2-4% will not be possible if a constant IC5-IC1 gain factor is used. Based on these data, we recommend that recent IC gain factors generated during the last 6 months of analyses will have sufficient accuracy and precision to generate %-level precision on Pu isotope ratios measured by laser ablation. However, this recommendation is driven, to a large extent, by estimates of isotopic precision achievable by laser ablation MC-ICP-MS for each isotope ratio. This will be better constrained after the analysis of Pu reference glasses later in Q3.

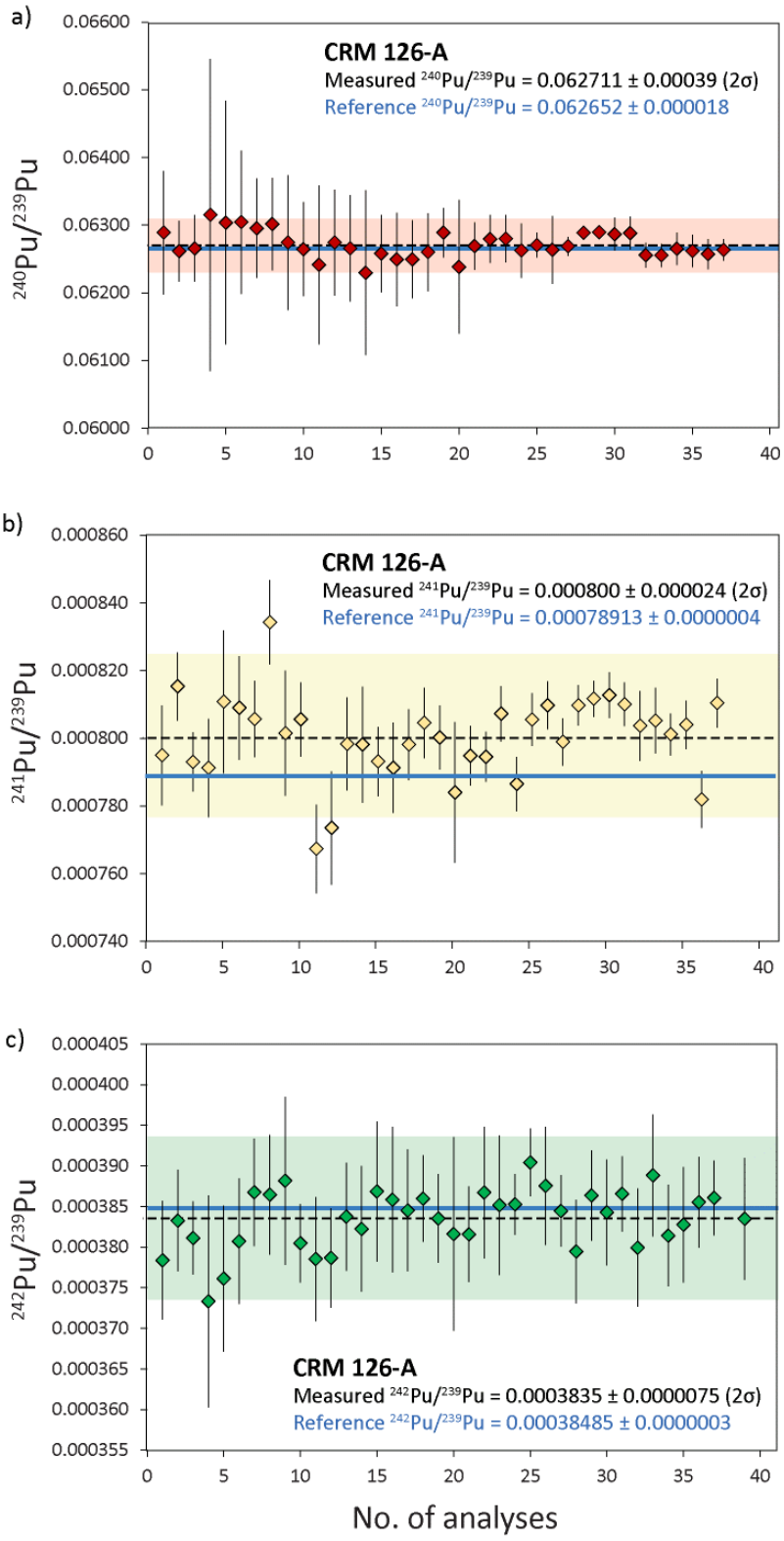

Figure 4 – Plutonium isotopic composition of CRM 126-A, which was last purified on the 1st December 2017. Data were measured over 5 separate analytical sessions. All uncertainties are 2σ.

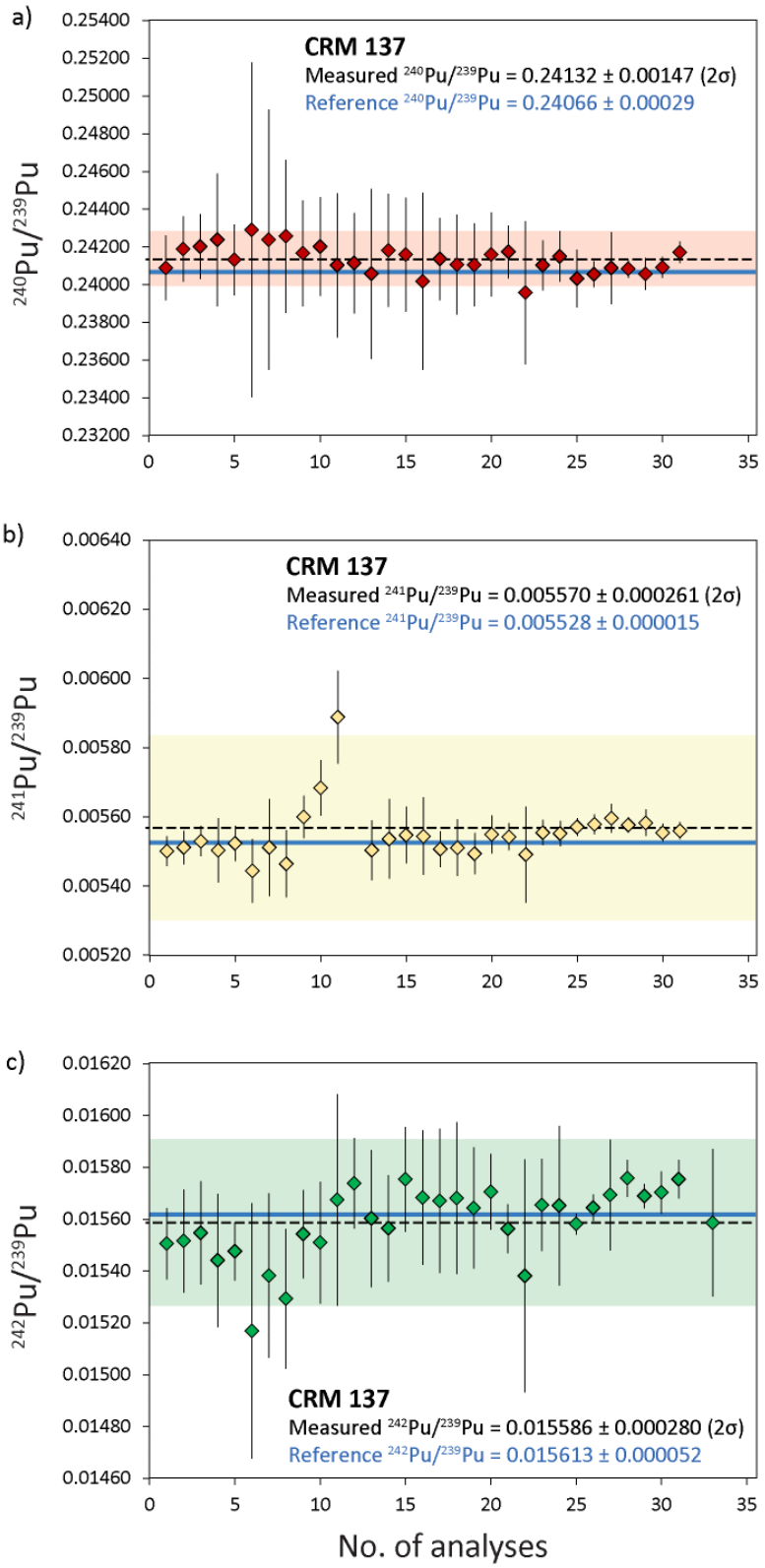

Figure 5 – Plutonium isotopic composition of CRM 137, which was last purified on the 1st February 2021. Data were measured over 5 separate analytical sessions. All uncertainties are 2σ.

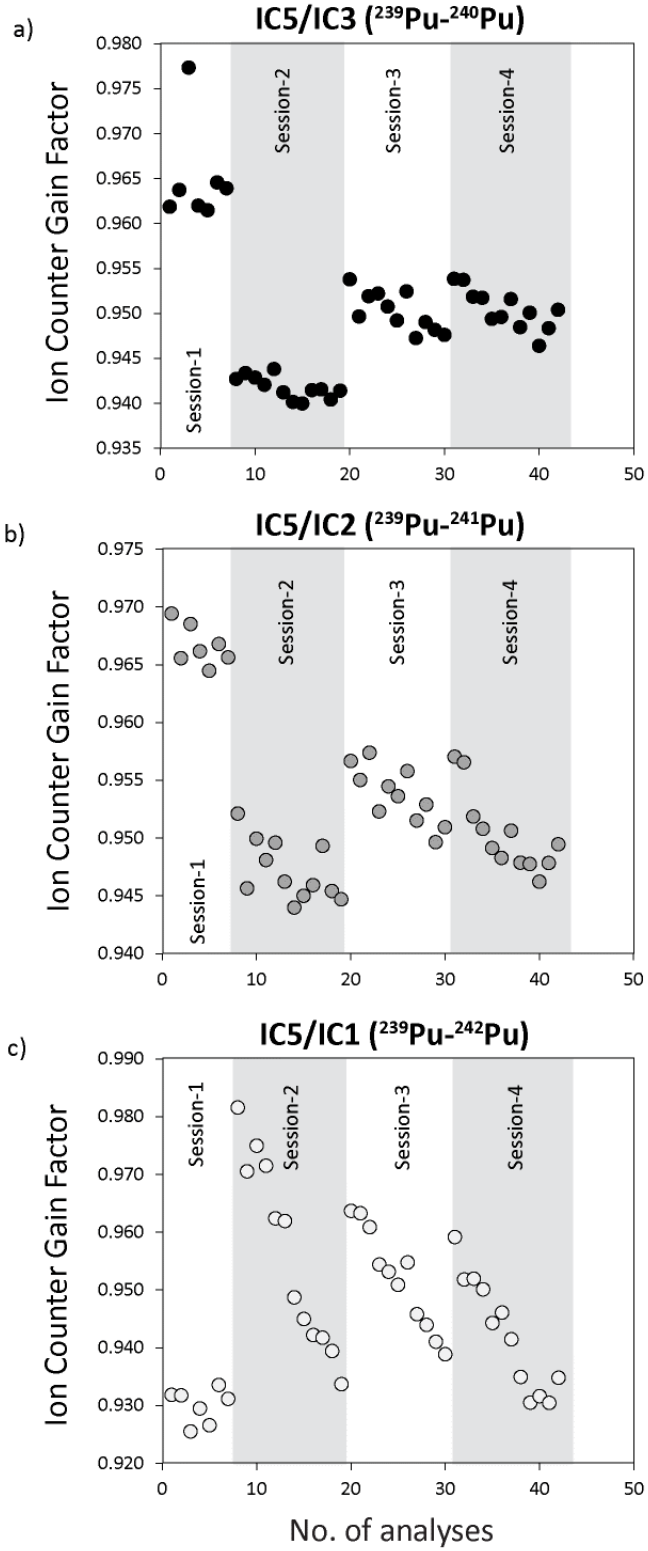

Figure 6 – Ion counter gain factors relative to IC5 (^{239}Pu). Gain factors were measured over four separate analytical sessions and drift is observed within and between analytical sessions.

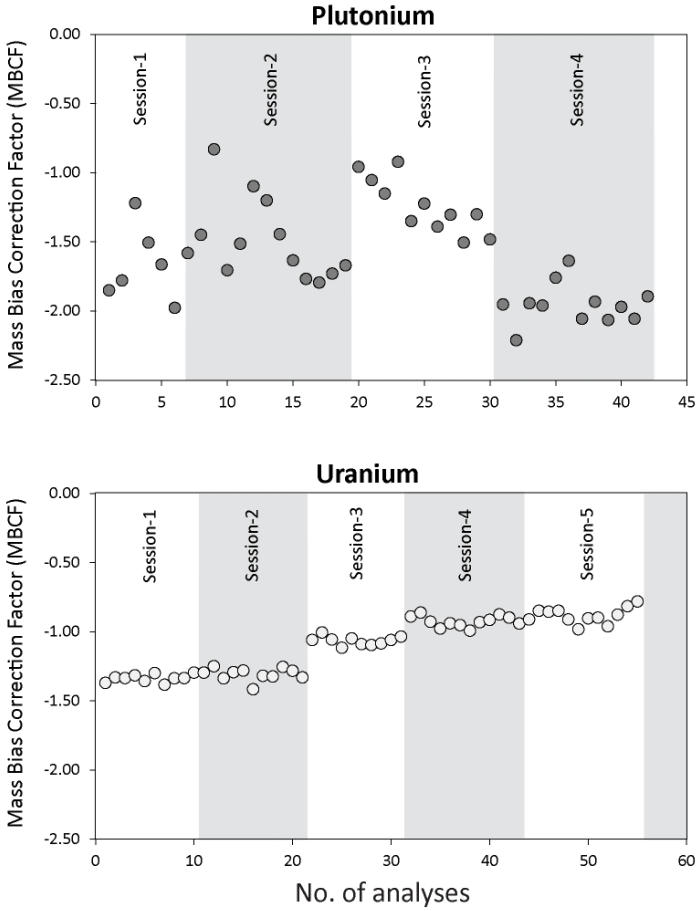

Figure 7 – Mass bias correction factors measured using CRM 138 (Pu) and NBS 960 (U) over 4-5 separate analytical sessions. Average MBCFs from Pu and U are, on average, the same within uncertainty.

In Fig. 7, we present instrumental MBCFs calculated using CRM 138 for Pu and NBS 960 for U. There is a clear difference in stability between the two sets of data, which is not unexpected given that U was run at 20ppb and Pu run at ~3ppt (i.e. a factor of ~10,000 difference in concentration). However, in general, the MBCFs generated by these techniques overlap, with average factors from Pu and U of -1.58 ± 0.70 and -1.09 ± 0.39 respectively, and a total range of MBCFs between -0.8 and -1.9. This level of variance in the MBCF would impart a 0.46%, 0.91% and 1.37% difference in the respective $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ ratios of an unknown. Thus, the importance of using a highly accurate MBCF for the laser ablation analyses is lessened, given the likelihood of %-level precision on the raw isotope ratios. As shown in Fig. 7, the average MBCF calculated from U or Pu are within uncertainty over the last 6 months. Thus, similar to our conclusions from the IC gain determinations, regular monitoring of the MBCF for Pu by solution mode analyses will be useful for ensuring QC standards are maintained. In general, the use of a constant MBCF over a period of 6 months+ is unlikely to perturb the measured Pu isotope ratios produced by laser ablation MC-ICP-MS outside of measurement uncertainties.

3.2.Analysis of Pu isotopes in mixed U-Pu solutions

The ultimate aim of this project is to assess the isotopic composition of Pu in mixed U-Pu particles with Pu concentrations ranging from 10 to 10,000ppm. This equates to Pu/U ratios between 1×10^{-2} to 1×10^{-5}. An important concern when calculating accurate Pu isotopic compositions are peak tailing effects or hydride interferences from the neighbouring ^{238}U peak. During solution based isotopic analyses these analytical artifacts can be negated by performing ion exchange chromatography to purify the Pu fraction by removing U from the sample. However, this is not applicable to isotopic analyses by laser ablation, which is a bulk micro-sampling technique. Peak tailing effects could be diminished by the use of retarding potential quadrupole (RPQ) filters, however on the Neptune at LLNL these are only present on two of the full-sized SEMSs (IC1 and IC3), meaning it cannot help all isotopes of Pu equally. Also, the use of RPQs will not screen out polyatomic interferences. The Neptune is capable of operating at high resolution ($m/\Delta m$ = 4000-10000), which could help to separate the isotopes of Pu from their interfering species. However, this significantly reduces the transmission of ions through the mass spectrometer by >80%, which is problematic if, as we expect, the Pu signal from U-Pu particles is already very low. Thus, it is unlikely that U-generated interferences on Pu can be easily eradicated. For this reason, we have investigated the magnitude of these interferences on Pu isotope systematics in order to quantify their size and whether correction schemes can be generated.

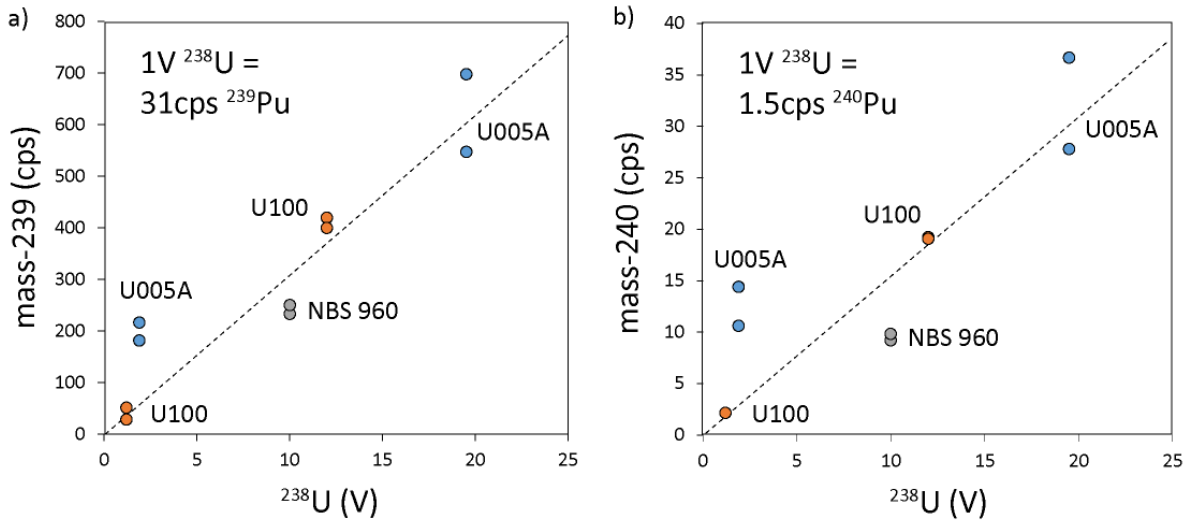

Figure 8 – Interferences on mass-239 and -240 from varying ^{238}U intensities. Linear relationships between interference magnitude and voltage of ^{238}U enable the interference to be quantified.

Two experiments were performed to quantify the magnitude of U interferences on Pu isotopes. The first involved analysis of the Pu mass range when aspirating U solutions at approximately 2 and 20 ppb. Three U solutions were used with different ^{235}U enrichment factors; NBS 960 (natural), U005-A (depleted) and U100 (LEU). Apparent Pu signals were observed at all masses of Pu, with the highest count rates at ^{239}Pu and ^{240}Pu (Fig. 8). Relationships between approximate ^{238}U intensities and count rates of the four Pu isotopes are roughly linear, with correlations lines that define the following count rates per V of ^{238}U; 31 cps ^{239}Pu, 1.5 cps ^{240}Pu, 3 cps ^{241}Pu and 0.2 cps ^{242}Pu. The largest effect is seen at mass-239, consistent with its proximity to ^{238}U. Interestingly, a larger interference is measured at mass-241 than at mass-240. This can be explained by the RPQ

on IC3 (^{240}Pu), which filters out tailing U ions. Given that ^{241}Pu is usually a lower abundance isotope than ^{240}Pu (by ~ 80 times in CRM 126-A), this means that U interferences on Pu are likely to have a far greater effect on the ^{241}Pu/^{239}Pu ratio than the ^{240}Pu/^{239}Pu ratio.

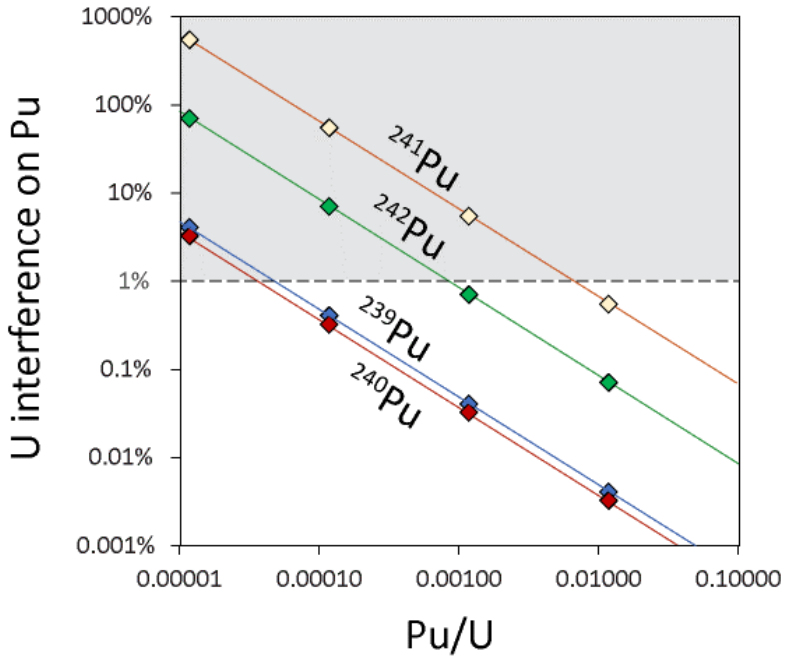

Figure 9 – Estimating the proportion of Pu signal from U interferences (in %) at U/Pu ratios ranging from 0.00001 to 0.1.

It is clear that high levels of U generate significant interferences at the Pu mass range. However, the importance of these interferences will ultimately depend on the U/Pu ratio in the sample of interest. In Fig. 9, we estimate the proportion of the Pu signal that is generated by interferences on ^{238}U in samples with varying U/Pu ratios. Here, we assume that the ionization and mobilization of Pu and U are similar during laser ablation. Previous analyses of U-oxide particles (~850,000 ppm U) by laser ablation produced maximum ^{238}U intensities of ~0.2 V, or 12 × 10^6 cps (Wimpenny et al., 2021). If Pu is present at 10-10,000 ppm in U-Pu particles, then the sensitivity for uranium can be used to estimate count rates for each Pu isotope, assuming a composition similar to CRM 126-A. For example, if ^{239}Pu is the dominant isotope, we estimate that count rates would range between 150 and 150,000 cps, depending on concentration. Based on the linear correlation in Fig. 8, we estimate that a 0.2V ^{238}U signal would generate ~6 cps at the 239-mass range. Thus, U interferences would account for between 0.004 to 4% of the measured ^{239}Pu, being more significant (>0.4%) where Pu contents of <100ppm are present. In Fig. 9, we also perform this calculation for the minor isotopes of Pu. As shown, the effects of U interferences on the two least abundant isotopes of Pu (^{241}Pu and ^{242}Pu) far outweigh effects on ^{239}Pu or ^{240}Pu. In fact, at Pu/U ratios of 1 × 10^{-4} and 1 × 10^{-5} the interference from uranium accounts for up to 500% of the expected ^{241}Pu signal. In both cases, we would expect measured ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu values to be significantly higher than the true ratios. Thus, accurate minor isotopic data for Pu may not be achievable from laser ablation analyses unless the Pu/U ratio is >1 × 10^{-3}.

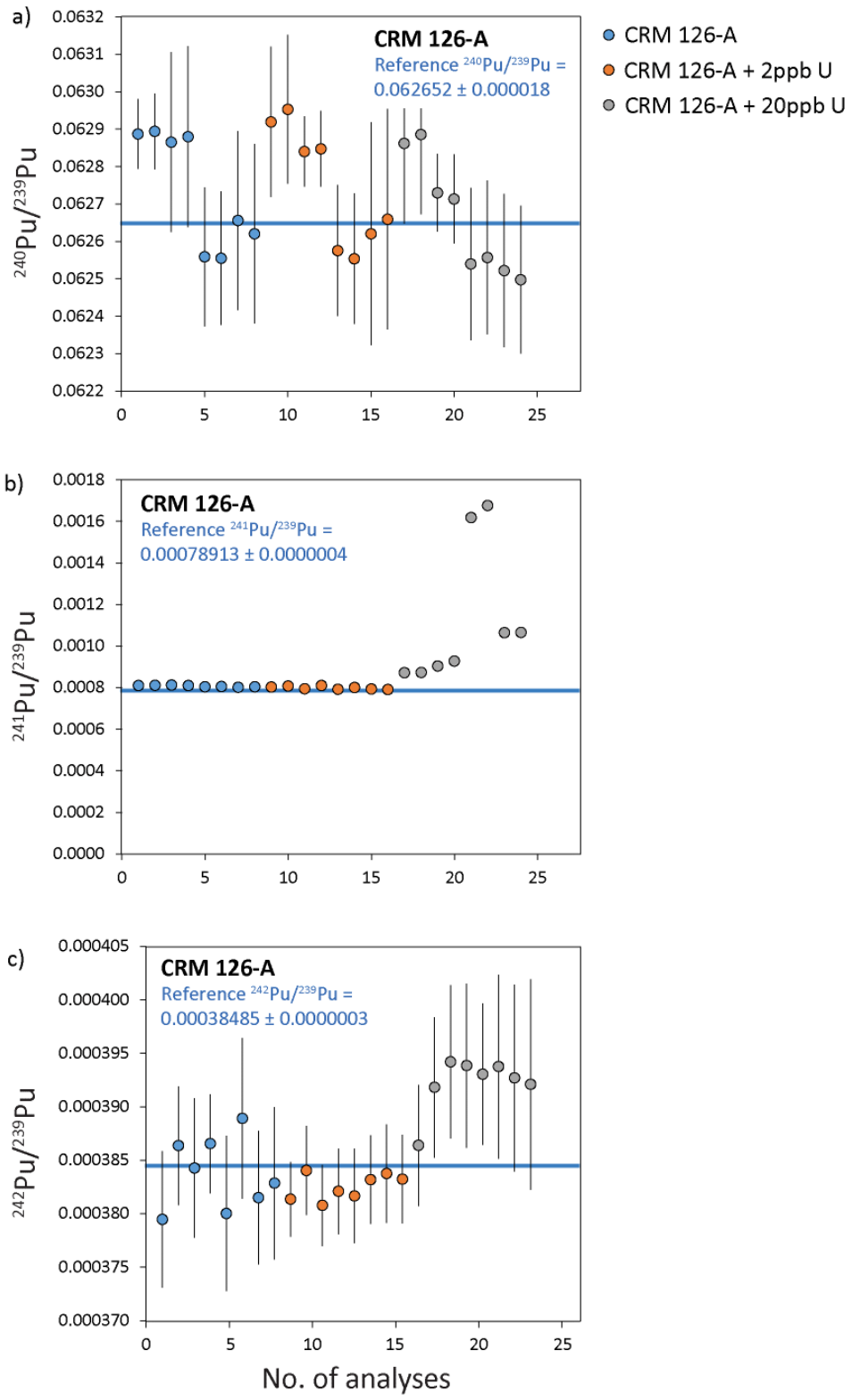

Figure 10 – Plutonium isotopic composition of CRM 126-A after doping with various amounts of NBS 960. Pu concentration is ~3 ppt, U concentrations range from 0-20 ppb. All uncertainties are 2σ.

To test the importance of U interferences further, natural uranium (NBS 960) was added into aliquots of NBL CRM 126-A at concentrations of 2 and 20 ppb and Pu isotope ratios were measured in solution. For each sample, Pu was at a nominal concentration of 3ppt, meaning Pu/U ratios were 1.5×10^{-3} and 1.5×10^{-4}. Based on Fig. 9, at these Pu/U ratios the interferences from U should have little to no effect on the measured $^{240}Pu/^{239}Pu$ ratio (<1%), a moderate effect on the $^{242}Pu/^{239}Pu$ (between 0 and 10% high) and a significant effect on the $^{241}Pu/^{239}Pu$ ratios (between 10 and 100% high). Results of replicate Pu isotopic analyses are fully consistent with these predictions. No systematic offset in the $^{240}Pu/^{239}Pu$ ratio is observed at any U doping level (Fig. 10a). Elevations in the $^{242}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ ratios are elevated outside of uncertainty at Pu/U ratios of $\sim 1.5 \times 10^{-4}$, with perturbations of ~2.5% and ~100% respectively (Fig. 10b, c). This is fully consistent with the assertion that it may not be possible to accurately quantify the distribution of ^{241}Pu and ^{242}Pu by laser ablation MC-ICP-MS.

3.3.Laser ablation analyses of Pu bearing glass materials

3.3.1. Development of Pu reference materials using additive manufacturing methods

To constrain the accuracy and precision of Pu isotopic analyses by laser ablation requires quality control testing using Pu bearing glasses with known isotopic compositions. Such materials are either unavailable or not widely distributed. Thus, an important component of the development work required synthesis of appropriate reference materials. To this end, we synthesized silica glasses that were doped with Pu reference materials using existing additive manufacturing methods at LLNL (e.g. Sio et al, 2020). Monodispersed submicron Pu-doped Stöber particles are used as feedstock materials for electrophoretic deposition (EPD) and subsequent sintering into glasses that are homogenous at micron scales relevant to laser ablation. Briefly, the dopants were added along with doubly distilled (milli-Q) water, ammonium hydroxide, and tetraethylorthosilicate (TEOS) to ethanol and stirred for at least 10 hours at 22 ^{o}C. The volume ratio of EtOH: TEOS: NH_4OH: H_2O was 20:1:1.5:2, giving the reaction mixture a total ammonium hydroxide concentration of 1.15 M. The particles were doped with 10 ppm Nd to ensure some opacity to the final glass; enabling the laser to better couple with the substrate. The Pu dopants were NBL C128 Pu, which contains subequal amounts of ^{239}Pu and ^{242}Pu, and NBL CRM 137. Plutonium was added at 0.1 and 1ppm, together with either 0, 10, or 100 ppm U, equating to Pu/U ratios of 0.1 to 0.001. Particles were washed and suspended in ethanol for electrophoretic deposition (EPD). An in-house designed EPD cell was used with stainless steel anode and layered cathode consisting of stainless steel, copper, and graphite foil with the deposition occurring on the graphite layer. Deposition was performed by applying 200 V across the cell while pumping the particle suspension back-and-forth through the cell twice at a flow rate of 1 mL/min. Final particles were calcined in air with a muffle furnace at 600^{o}C for 1 h, and subsequently sintered in graphite crucibles in an inert argon atmosphere at 1400^{o}C for 10 min. Glass samples were then mounted in epoxy and polished ready for loading into the laser ablation cell.

3.3.2. Laser ablation analytical protocol

The methodology to ablate glasses and U-oxide particles for Pu follows previously described procedures for U (Wimpenny et al., 2021; 2023). In brief, the sample is loaded into the Helex cell on the 193nm laser system. The cell is flushed with He carrier gas and Ar is used to flush the sample lines. Pu bearing glasses are ablated as spots, which bore down through the sample surface,

producing a characteristic decaying laser signal. Pu isotopic data is reduced using the Laser Ablation Reduction Application (LARA); current updates in LARA v2.0 are described in Section 5.

3.3.3. Initial Laser Ablation Data

Preliminary isotopic analyses were performed on synthetic glass doped with 100ppb of the NBL C128 reference standard. In this experiment, constant ion counter gain factors were used, based on previous isotopic analyses of 3ppt CRM 138 solutions. Corrections for the MBCF were made using online analyses of the in-house uranium standard glass CAS53-500, but as previously demonstrated a constant MBCF could have been used from prior solution work and would have generated similar results. As shown in Fig. 11, the measured isotopic composition of C128 using this technique falls within uncertainty of the reference value ($^{242}Pu/^{239}Pu$ = 1.0016 ± 0.0002). Internal uncertainties associated with individual analyses range from 1-1.6%, while the standard deviation of the sample population (n = 12) equates to an RSD of 2.4%. This uncertainty is similar in magnitude to those derived from pure Pu reference solutions in Section 4.1. and demonstrates that accurate Pu isotopic data can be obtained from the ablation of Pu bearing glass with isotopic intensities <1000cps. However, the applicability of this material to operational samples is limited, given that it contains no U and its isotopic composition is significantly different to weapons or reactor grade Pu. Future work in Q3 will expand the testing to include glassy materials with more relevant Pu isotopic compositions (CRM 137) and variable uranium concentrations.

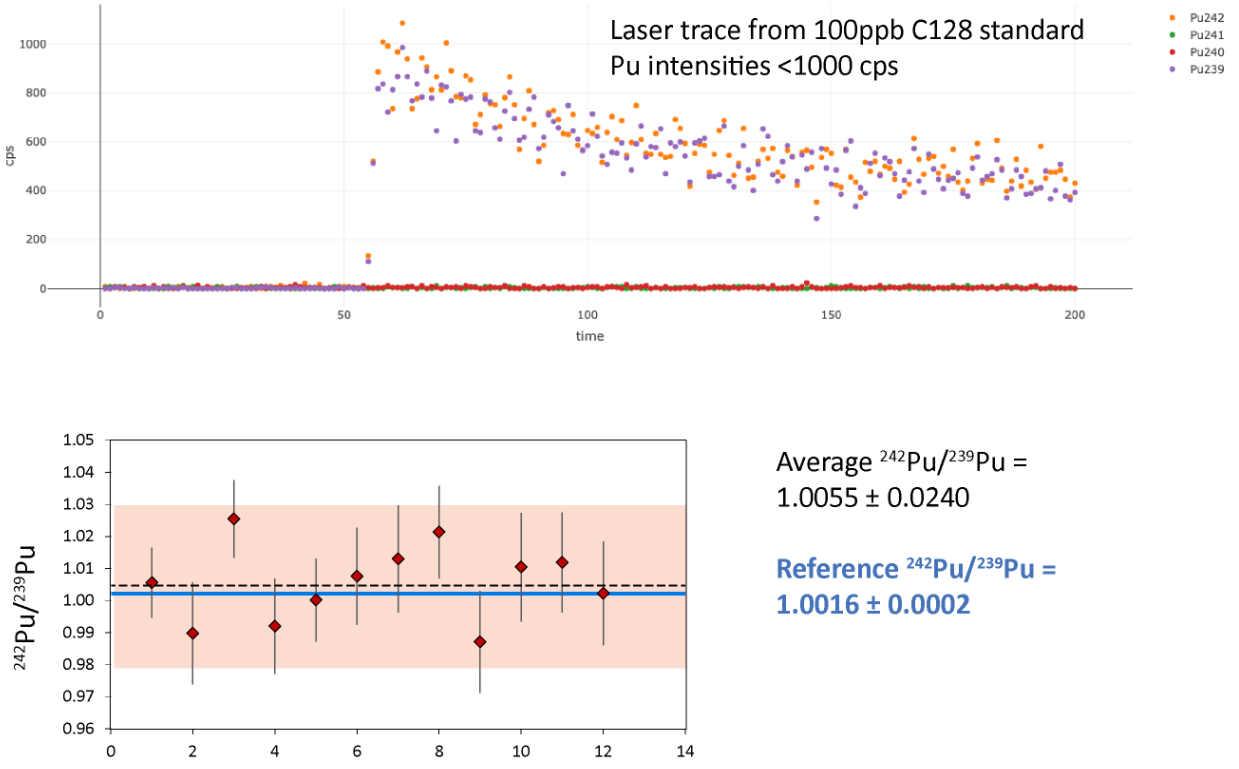

Figure 11 – Laser ablation of glass containing C128 at ~ 100 ppb. A representative laser trace made in LARA v2.0 is shown in (a). In (b), we present the average isotopic composition of the Pu-doped glass from 12 replicate analyses.

4. Development of the Laser Ablation Reduction Application (LARA) – version 2.0

The original version of LARA was designed in the statistical software R to reduce uranium isotopic data obtained from laser ablation analyses of glasses and U-particles. An important component of development was a user friendly interface using the Shiny application in R, which enabled the rapid and robust reduction of isotopic data without the user having prior coding experience. LARA was designed to fully propagate sources of uncertainty in a consistent way, and different data reduction processes were created for solid samples (glass) and U-particles. The main objective of developing LARA v2.0 for the FY23 project was to add the ability to handle Pu data generated by the Neptune MC-ICP-MS. In addition, we wanted to improve the interface design and add user functionality to improve the operating experience. The main changes in LARA v2.0 are listed below:

- Implementation of the Pu reducer to read Pu data and process it following similarly developed code for the reduction of U data.
- Addition of a log axis option for Pu plots given the large disparity in isotopic abundance between ^{239}Pu and minor isotopes (Fig. 12).
- Addition of a Shiny theme for a better looking, and more user friendly, interface (Fig. 13).
- Addition of new and improved notifications to inform the user of processes taking place while the application is busy.
- Reformatting the constants table to show values and uncertainties grouped by row
- Changed the constants table to a modal window to make it easier to read.

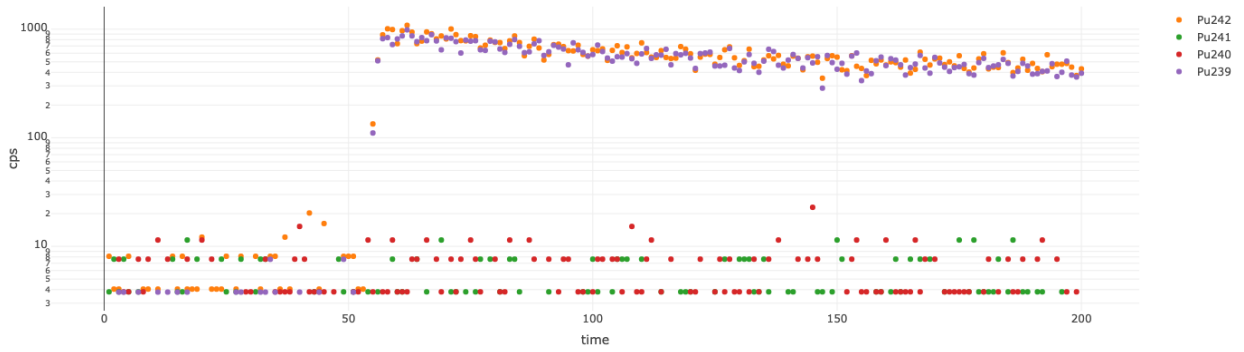

Figure 12 – Plutonium plotting function in LARA v2.0.

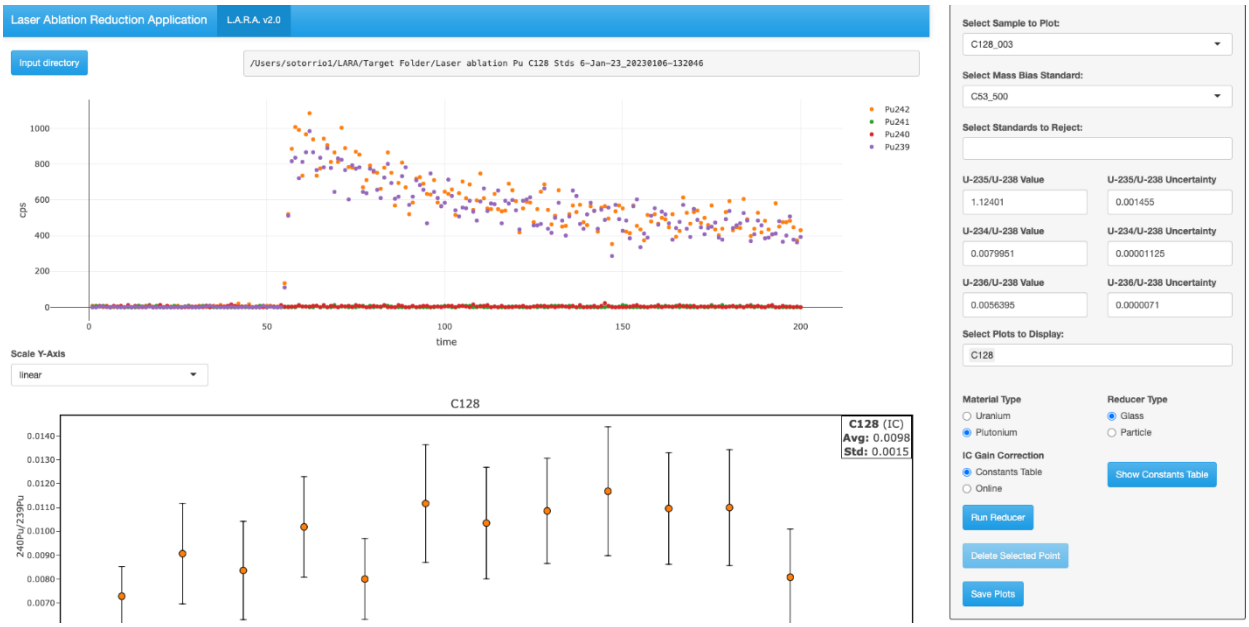

Figure 13 – Updated user interface in LARA v2.0.

Future work in Q3 and 4 will focus on QC testing the newly added Pu data reduction component to ensure it generates accurate results and handles uncertainties appropriately. Separate schemes to reduce data from Pu bearing glasses and U-Pu particles is also essential. Further functionality that could be added is the ability to read in data from other types of mass spectrometer.

Summary

In this mid-year report, we detail the setup and optimization of a Neptune laser ablation MC-ICP-MS system to perform isotopic analyses of plutonium. The results of the solution analyses demonstrate that 0.5-5% level precision can be achieved for the Pu isotopic composition of high purity Pu samples using the ion counting array. Corrections for MBCF and ion counter gain are relatively small (<1%) in the context of the analytical precision. This means that constant correction factors can be used during laser ablation analyses without significant degradation of the final isotopic data. Real world samples are unlikely to be pure Pu, meaning it is also important to test the accuracy and precision of isotopic analyses in samples where Pu is a trace constituent. Interferences from the ^{238}U peak are clearly measurable at the Pu mass range and can have a significant effect on the isotopic composition of Pu, particularly if Pu/U ratios are $< 1 \times 10^{-3}$. In this case, we have demonstrated that it may not be possible to obtain robust isotopic data for ^{241}Pu and ^{242}Pu, but the ^{240}Pu/^{239}Pu is relatively unaffected. We will verify this assertion during further testing of U-Pu glasses and particles in Q3. If ^{241}Pu and ^{242}Pu are not collected, then it potentially opens the detector configuration up to include one or more isotopes of U. This could potentially enable U/Pu ratios to be collected. However, the ideal configuration for a mixed ^{238}U, ^{239}Pu and ^{240}Pu array would be a Faraday detector on the low mass side adjacent to two ion counters. This configuration does not currently exist on the Neptune but could be custom built for future instruments.

Preliminary laser ablation analyses of a glass doped with 100ppb Pu produced accurate ^{242}Pu/^{239}Pu data with precision ~2% from a count rate <1000cps. This demonstrates that accurate Pu isotopic

data can be obtained by laser ablation. However, it is difficult to use this dataset to predict the accuracy and precision of Pu isotope ratios from U-Pu glasses and particles. A first order estimate is that accurate $^{240}Pu/^{239}Pu$ ratios can be produced from these samples with precision of ~5%.

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