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Characterization of U Isotope Ratios by Laser Ablation MC-ICP-MS for IAEA Safeguards

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Disclaimer

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Safeguards Technology Development Program
FY2021 Mid-Year Report
30-April-2021

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 & Ning Xu

Summary Statement of Work: This project will develop methodology to identify and analyze U and Pu containing particles using laser ablation MC-ICP-MS. The proposed work will involve: i) setup and optimization of the LA-MC-ICP-MS system, ii) testing and validation by analysis of QC standards, iii) designing analytical protocols for single particles, and iv) developing a data processing system. Ultimately, this project will output a detailed operating procedure documenting the experimental techniques and data processing routines required to perform particle identification and analysis by laser ablation MC-ICP-MS, that can be shared with IAEA-NWAL laboratories.

Report Title: Characterization of U isotope ratios by laser ablation MC-ICP-MS for IAEA Safeguards

Names of Authors and Affiliations: PI - Josh Wimpenny (LLNL), Kyle Samperton (LLNL).

Major Highlights: 1) Setup and optimization of laser ablation MC-ICP-MS hardware complete at end of Q1. 2) Tests to assess the precision and accuracy of U isotopic analyses complete by end of Q2. 3) R-script to reduce laser ablation data from analysis of U-glass standards is now operational.

Progress: See following report.

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Executive Summary

The aim of this project is to develop a capability to identify and analyze U and Pu containing particles using laser ablation MC-ICP-MS. The developed methodology will ultimately be described in a detailed procedural document that will be shared with IAEA-NWAL laboratories. In this Mid-Year report, we detail efforts to setup and optimize the laser ablation MC-ICP-MS hardware (Task-1) and assess the accuracy and precision of the technique using in house U-glass standards (Task-2). This includes a summary of ongoing efforts to develop a data reduction package to reduce laser ablation data and assign appropriate uncertainties to final isotope ratios.

Mission Relevance

STR 385: T.2.R6 - Develop and implement methods to detect signatures of nuclear activities in environmental samples
STR 393, pg18: SGAS-002 - Environmental Sample Analysis Techniques, "Implementation of the laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) technique to analyze Pu and mixed U/Pu particles in environmental samples"

Laser Ablation Mass Spectrometry

1. Introduction

Laser ablation systems are used as in-situ sample introduction systems for inductively coupled plasma mass spectrometers (ICP-MS). The basic principle is that a solid sample is placed in the laser sampling chamber, the laser energy is focused onto the sample surface and ablates the analyte, generating a fine aerosol that is carried to the ICP-MS plasma in a stream of carrier gas (usually helium). 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 interested is selected for based on the mass to charge ratio. Finally, the selected species is detected when it hits the detector array, usually comprised of ion counters and/or Faraday cups.

For high precision isotopic analyses by ICP-MS the ideal method is to use an instrument with multiple detectors (multi-collector ICP-MS or MC-ICP-MS) to detect different isotopes of an element simultaneously. This overcomes the inherent instability of the plasma source while also negating problems associated with analyzing a transient laser ablation signal. The relative instability of the ablation signal means laser ablation MC-ICP-MS cannot produce isotope ratio data that is as precise as analyses made by traditional methods (i.e. solution). Nevertheless, the ability to make relatively high precision isotope ratio measurements in-situ, with little or no sample preparation time means it could potentially be a powerful analytical technique for actinide isotope determination in nuclear safeguards.

This project is to address the mission needs listed in the IAEA *Development and Implementation Support Programme for Nuclear Verification 2020-2021* STR 393, SGAS-002 - Environmental Sample Analysis Techniques, "Implementation of the laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) technique to analyze Pu and mixed U/Pu particles in environmental samples".

This mid-year report documented the progress of developing a new capability established at Lawrence Livermore National Laboratory (LLNL) using the existing Photon Machines Analyte 193nm excimer laser system, coupled with a Thermo Scientific Neptune-Plus MC-ICP-MS (Figure 1) for U/Pu particles in environmental samples, particularly the initial setup and optimization of the hardware. Future work in quarter 3 and 4 will assess the accuracy and precision of laser ablation using glass reference standards, before focusing on techniques to analyse and process data from the ablation of micron-scale particles.

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

2. Hardware Description

a) 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 (Figure 2). The ability to switch between an ion counter (IC2) and Faraday detector (L5) means that it is also straightforward to handle samples with variable ^{235}U enrichment levels. Energy filters (or RPQ's) on IC1 and IC3 help to reduce scattering of ions and peak tailing that might affect accurate analysis of ^{234}U and ^{236}U.

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

	Detector				
	L4	**IC1B**	**L5/IC2**	**IC3**	**CDD5**
Uranium isotopes	^{238}U	^{236}U	^{235}U	^{234}U	^{233}U
Amplifier Resistor	10^{11}	N/A	$10^{11}/10^{12}$	N/A	N/A
RPQ	N/A	Yes	No	Yes	No

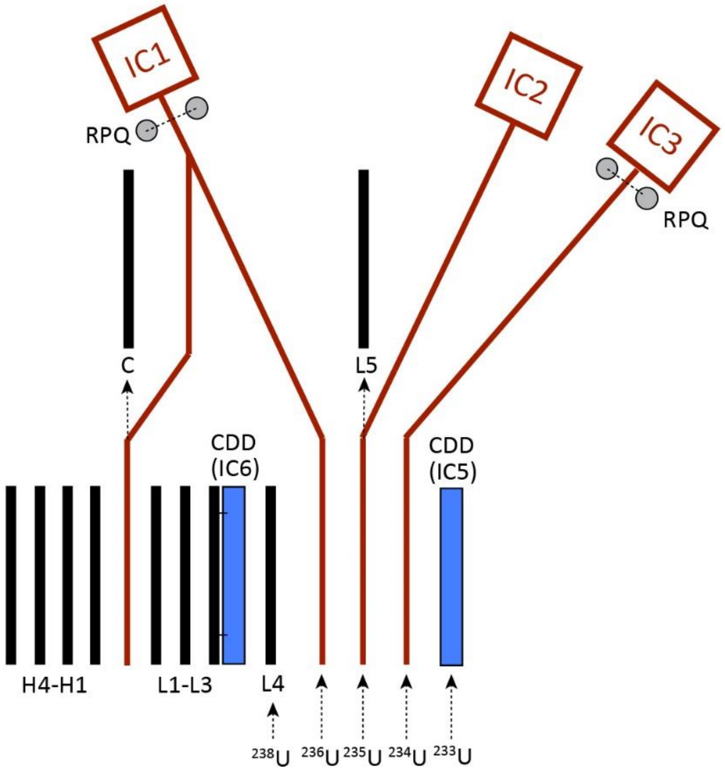

Figure 2 – The detector array on the Neptune-Plus MC-ICP-MS. Faraday detectors are in black, SEM's are in red, and CDD's are in blue. The IC1 and IC3 SEM's are fitted with energy filters (RPQ's). The U species and associated detectors are labeled.

b) Laser ablation system – Photon Machines Analyte 193nm excimer laser

The Photon Machines Analyte is a 193nm excimer laser system with a 4ns pulse length. It has advantages over solid state laser systems with longer wavelengths such as the Nd:YAG 213nm or 266nm systems because the 193nm laser energy couples better with IR transparent materials. Its relatively short pulse length reduces thermal effects of laser interaction with the sample surface (e.g. isotopic fractionation associated with kinetic processes), although not to the extent of newer, femtosecond laser systems. The system at LLNL is equipped with a two-volume laser cell, also termed the 'Helex' cell (Figure 3). The sample cell is a chamber in which the sample is housed and in which the ablation is performed. The cell is filled with helium carrier gas and ablated aerosol is transported out of the cell to the plasma-source on the ICP-MS. The dual volume cell has significant advantages over the older single volume model as its design eliminates the occurrence of spatial fractionation effects within the chamber and enhances response rate and washout time (i.e. the time between stopping ablation and the signal dropping to background values).

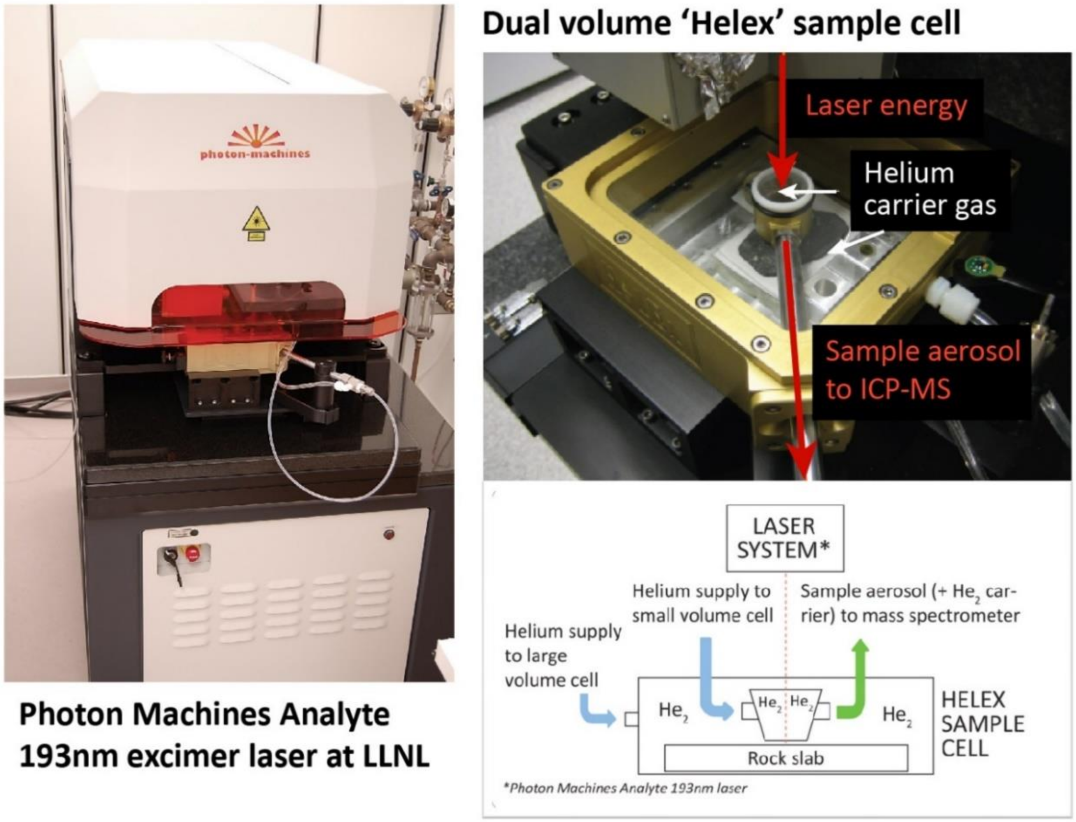

Figure 3 – The dual volume 'Helex' sample cell on the laser ablation system. Helium is supplied to both the main cell and inner cup as a carrier gas for the ablated sample aerosol, which is transported out of the cell to the ICP-MS.

Task 1 - Setup and Optimization of Laser Ablation MC-ICP-MS at LLNL

1. Basic Hardware Configuration

Testing of the hardware configuration aimed to ascertain the setup that produced the highest precision isotope ratio data. Higher sensitivities, lower oxide production and more stable ion beams typically produce higher quality data and thus were selected for during testing. The instrument and laser parameters used during testing are summarized in Table 2. To test signal stability and sensitivity several glass standards were ablated over the course of this work. The NIST glass standards 610 and 612 have U concentrations of ~460 and 37 ppm respectively, with highly depleted ^{235}U/^{238}U ratios of 0.00238 (Duffin et al., 2015). The USGS glass standard GSD-1G has a U concentration of ~40 ppm and a depleted ^{235}U/^{238}U ratio of 0.00369 (Jochum et al., 2011). Because these samples contain depleted uranium most of the analyses were performed with ^{235}U on IC2, although some limited testing was also performed with ^{235}U on L5. We anticipate that switching between IC2 and L5 will be important in future studies where samples with variable ^{235}U enrichment levels are analyzed.

The laser system is supplied with helium carrier gas to the Helex cell. Flow rates of 0.6 l/min to the main cell and 0.5 l/min to the smaller sample cup were found to give relatively rapid response time from the start of ablation to the detection of ions on the mass spectrometer. The sample aerosol is carried in high purity helium to the mass spectrometer, where it is mixed with a flow of argon (termed the 'sample gas' flow) before hitting the plasma source (Figure 4). The sample gas flow rate was tuned for maximum sensitivity at between 0.9-1.05 l/min. Higher sample gas flow rate often increased the sensitivity but also generated higher percentages (from 3-20%) of U-oxide. Changes in the oxide abundance did not change the measured $^{235}U/^{238}U$ ratio, but further testing will be required to ascertain whether higher oxide generation (and potentially other polyatomic species) could affect the measurement of minor U isotopes.

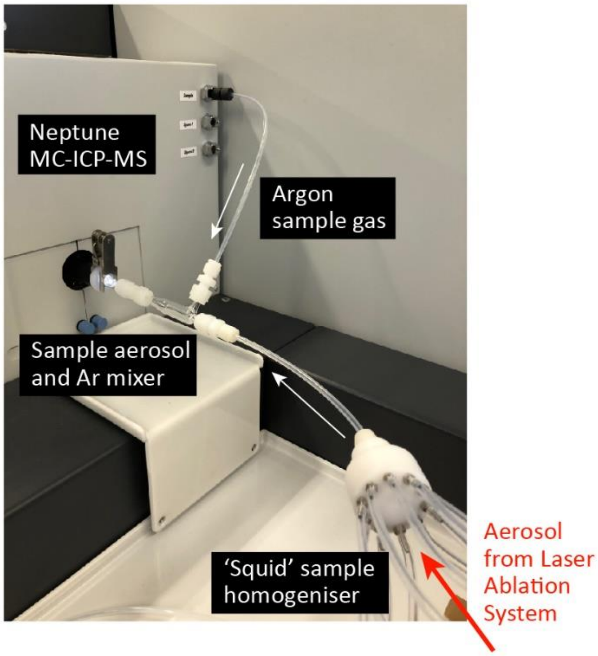

Figure 4 – The sample introduction setup. Aerosol is transported from the laser system through a sample smoothing device ('squid') before mixing with Ar 'sample gas' before the aerosol hits the plasma.

The Neptune hardware required minimal testing; the torch and injector types and auxiliary argon gas flows are typically constant and do not affect the instrument response. Uranium isotope analyses have been performed on a regular basis using the Neptune and so the cup configuration and instrument tune parameters were already optimized. We also have a long-term record of the instrumental mass bias factor and ion counter-Faraday gain factors for isotopic analyses of uranium reference standards in solution. The applicability of these factors to the accurate isotopic analyses of uranium by laser ablation will be tested during Task 2. The most important hardware changes are the sample and skimmer cones used on the Neptune's front end. The Neptune can be fitted with high sensitivity cones ('Jet' sampler and 'X' skimmer) which increase sensitivity over the standard ('H') cones, the downside being that they can also increase oxide production and degrade the low-resolution peak shape. However, in testing the ablation of NIST 610 we were able to obtain an increase in sensitivity by a factor of ~10 using the high sensitivity setup, while keeping oxide levels below <5% and a flat-topped U-peak. Thus, all tests in this report were performed using the high-sensitivity cones. Ultimate sensitivity depends on a combination of ICP-MS and laser parameters. Using a 50 µm spot size, frequency of 7Hz and fluence of 2.1 J/cm^2 we typically obtain a signal of 0.6-0.7 V ^{238}U from NIST 610.

Table 2 – Basic instrumental parameters used during the hardware setup.

	Neptune MC-ICP-MS		*Photon Machines Analyte*
Sample cone	H/Jet	Helium 1 (main cell)	0.6 l/min
Skimmer cone	H/X	Helium 2 (inner cup)	0.5 l/min
Sample gas (Ar)	0.9-1.05 l/min	Spot size (microns)	40-85
Aux gas	0.8 l/min	Ablation Frequency	5-7 Hz
Cool gas	16 l/min	Fluence (J/cm^2)	2.1-3.8
Center mass	254.15		
Integration time	0.13-0.26s		
No. of integrations	200-400		
Resolution (m/Δm)	Low (400)		

2. Laser Ablation Analytical Protocol

Laser ablation analyses can be performed on a range of sample matrices (e.g. glass, particle) and range of ablation configurations (e.g. line, raster, spot). The laser energy and optics are co-focused, so focusing the optics on the sample surface also focuses the laser energy. During a spot analysis the laser bores down through the sample, and in doing so the amount of ablated material that reaches the plasma decreases with time. This is because the laser becomes progressively out of focus as the pit is excavated, and the ablated material is more difficult to mobilize out of the excavated laser pit. A characteristic decaying profile is produced during spot analyses, as illustrated in Figure 5a. Ablating lines and performing rastering scans avoid these problems and can, in theory, produce a stable ablation signal that mirrors the signal generated by aspirating a solution. However, these types of scan require a sample that has a large and compositionally homogenous area to produce meaningful data, which is not common in most natural samples. Because the ablation of micron scale particles will produce a short-lived transient signal it is most appropriate to test the laser ablation hardware by performing spot analyses.

A trace from a typical analysis of NIST 610 is shown in Figure 5. The method acquires data for ^{233}U, ^{234}U, ^{235}U, ^{236}U and ^{238}U but only data for ^{235}U and ^{238}U is presented here. A total of 200×0.26s integrations are made during each sample analysis, equating to a sampling time of ~50s. The first 20s of that data collection period is left with the laser off in order to characterize the instrumental background, which is subtracted from the final ablation signal. After 20s the laser fires, which is marked by a rapid increase in signal and followed by a steadily decaying signal for all isotopes. The isotope ratio measurements are taken from the most stable part of the curve, typically 2-5s after the start of ablation. To assess the various hardware options used here we have focused on the uncertainties associated with the measured ^{235}U/^{238}U ratio, although other isotope ratios were also calculated (see Appendix A and B for representative isotopic data for all three standards). All uncertainties are presented as 2× the standard error of the mean. For consistency, the average isotopic compositions for all samples were calculated using the final 100 measurements of each analysis (Figure 5b). Depending on the analytical parameters, the uncertainties generated for the $^{235}U/^{238}U$ ratio of NIST 610 ranged from 0.2-1.5% (2σ). For reference, internal uncertainties for $^{235}U/^{238}U$ ratios in reference standards measured in solution by the Neptune-Plus MC-ICP-MS at LLNL are <0.05%.

The IAEA recommended International Target Values (ITVs) for relative uncertainties associated with traditional MC-ICP-MS methods but have not recommended separate values for isotopic analyses by laser ablation (Zhao et al., 2010). The ITV for a ^{235}U abundance measurement by solution MC-ICP-MS is 0.7% for depleted uranium and 0.07% for HEU. Our testing indicates that raw $^{235}U/^{238}U$ ratios can be constrained to within 0.2% in a glass CRM by laser ablation MC-ICP-MS. However, this relative uncertainty does not incorporate corrections for mass bias and ion counter gains and is likely to be much larger for ablation of micron-sized particles. Recently reported relative uncertainties (1σ) for $^{235}U/^{238}U$ ratios in U particles measured by laser ablation MC-ICP-MS are between 1 and 4% (Donard et al., 2017; Ronzini et al., 2019; Craig et al., 2020), which may be a more realistic range to target during future development work.

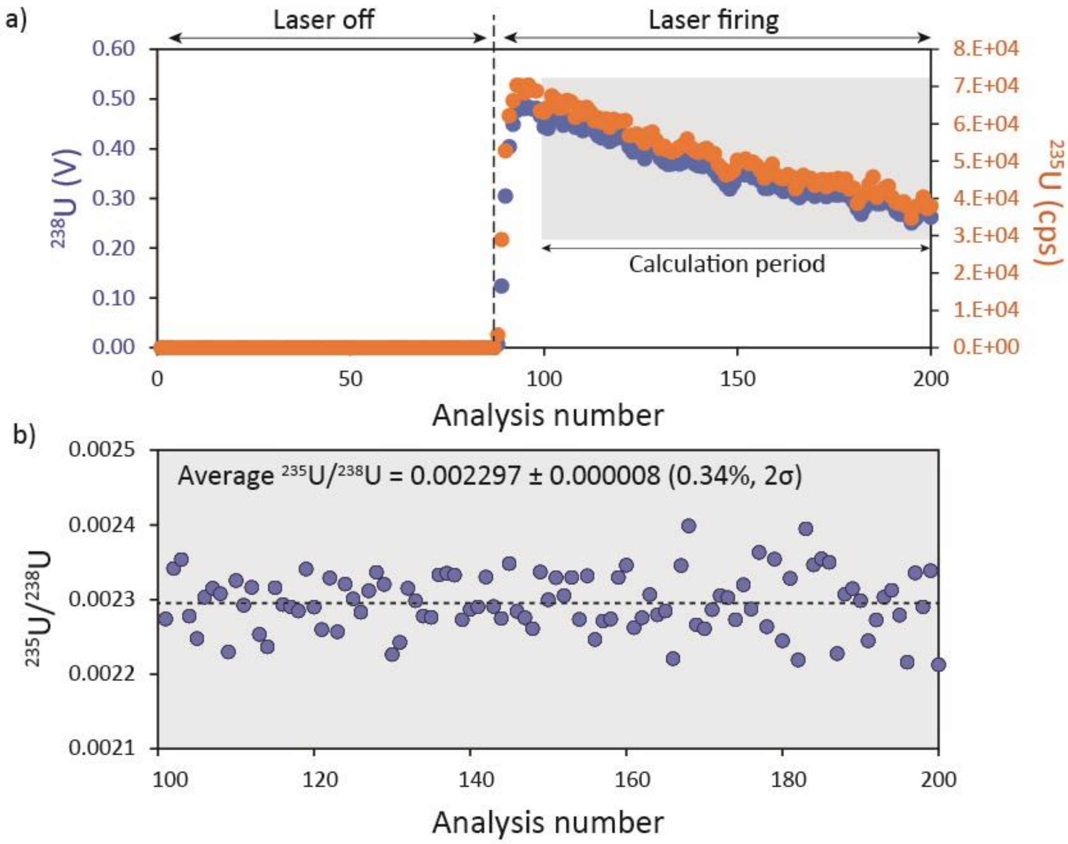

Figure 5 – A trace from an isotopic analysis of NIST 610 glass. The top trace (a) shows the intensities of ^{238}U (blue) and ^{235}U (orange) before and during ablation of the sample. Data was also collected for ^{233}U, ^{234}U and ^{236}U but is too low to show here. The shaded region in (a) shows the data used to calculate the $^{235}U/^{238}U$ isotope ratio shown in (b).

The precision of an isotope ratio measurement will decrease with signal intensity; thus although analyses of NIST612 and GSD-1G were performed during testing the ~10× lower U concentration in these materials doubled the uncertainties (Figure 6). This also means that changes in laser parameters that act to ablate more sample material (i.e. spot size, frequency, laser fluence) also increase the signal intensities and decrease uncertainties. These are less relevant when considering the ablation of micron scale particles, which are likely to be ablated by a single shot.

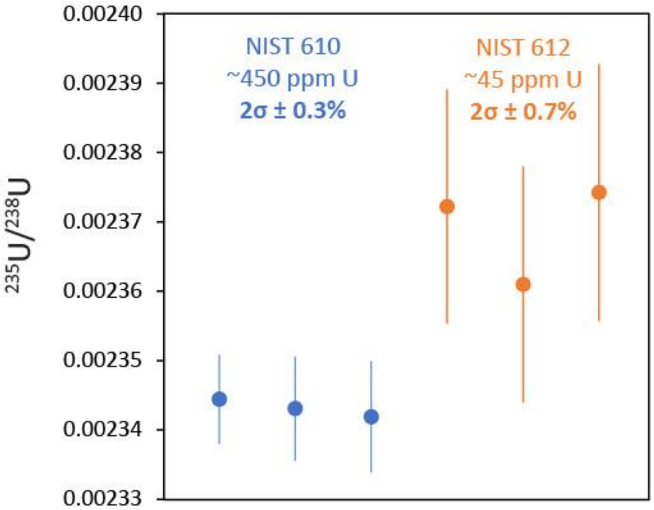

Figure 6 – A plot showing the difference in precision when analysing the $^{235}U/^{238}U$ isotope ratio in NIST 610 and NIST 612, which have different U concentrations.

3. Optimizing the Laser Ablation Technique

a) Sample introduction from laser to ICP-MS

Because the sample aerosol is generated by discrete laser pulses the signal that reaches the plasma can exhibit instability that reflects the laser frequency (Figure 7). In addition to potentially affecting the precision of the isotopic analyses, studies have shown that at lower frequencies (<3-5Hz) this pulsing can produce a spectral skew affect (Muller et al., 2009) that can produce offsets in trace element data produced by laser ablation depth profiling. Thus, attempts have been made to smooth out the signal generated by laser ablation analyses to avoid this type of analytical artifact and produce a higher precision dataset. To this end, we tested the use of a signal smoothing device called a ‘squid’, as illustrated in Figure 7. The squid splits the sample aerosol into ten separate lines of varying lengths that then recombine prior to mixing with the Ar sample gas (Figure 4), producing a much smoother signal. However, although the laser trace was less noisy using this smoothing device, the isotope ratio measurements were, on average, not significantly improved over a standard inlet tube. This probably reflects the fact that multi-collection tends to overcome instabilities in signal generated by the plasma or the laser pulsing.

Ultimately, although any increase in precision appears to be tenuous, there is no reason not to use the squid in further testing; it clearly reduces noise generated by the laser pulsing and there is no reduction in signal intensity from ablation. We saw no change in background levels over the course of the analytical sessions, indicating that neither the squid nor the standard inlet tube impart measurable memory effects. One question mark will be whether the squid remains beneficial during particle analyses. As individual particles may be ablated by a single laser pulse the associated signal will be extremely short lived. We predict that the squid will produce a slightly longer, but lower intensity signal than the standard inlet tube. Testing will be performed during Task-3 to confirm this, and to assess any impact on precision.

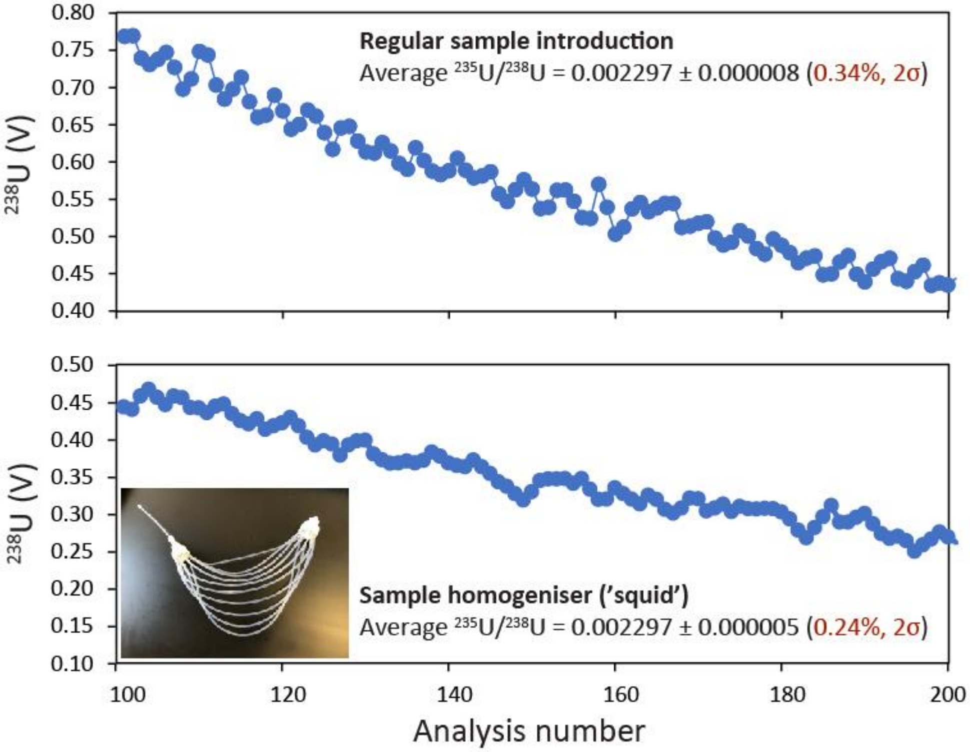

Figure 7 – Plot showing the effect of using a sample smoothing device ('squid') to eradicate instability from laser pulsing. In general, there was not a significant improvement in the precision of the ^{235}U/^{238}U ratio when using the squid.

b) Detecting ^{235}U using a Faraday (L5) or Ion Counter (IC2)

In samples with varying ^{235}U/^{238}U ratios it will be important to be able to switch between Faraday detector and ion counter. In general, a 1 mV signal on a Faraday cup is equivalent to 62500 cps on an ion counter, and signals of 10 mV or greater are more precisely measured by a Faraday detector. To test this, NIST 610 was analyzed with ^{235}U on the L5 Faraday and IC2 SEM (Figure 8). Spot sizes of 50 and 85µm were tested to generate ^{235}U signals of ~1 mV and 4 mV on L5. As shown in Figure 8a, signals of ~1 mV on L5 generate ^{235}U/^{238}U ratios with uncertainties of 1.1-1.5%, far less precise than comparable signals on IC2. Increasing the ^{235}U signal to 4 mV on L5 also increased the precision of the ^{235}U/^{238}U ratios to ~0.4%, approaching the measurement uncertainty using IC2 (Figure 8b). Based on these data, any ^{235}U signal of >5 mV should be placed on the L5 Faraday. The advantage of the Faraday detector is that the final ^{235}U/^{238}U ratio need only be corrected for mass bias effects whereas the ^{235}U/^{238}U ratio generated with ^{235}U on IC2 must also be corrected for the IC-Faraday gain, which imparts additional uncertainty. Testing in Task-2 found a clear advantage in precision by measuring ^{235}U by Faraday detector in reference glasses. That being said, measuring ^{235}U on an ion counter will produce accurate data if the ion counter gain factor used for IC2 is also accurate.

The ion beam detected by the Faraday's produces a current that is converted into a voltage using high resistivity amplifiers. The Neptune has a virtual amplifier configuration in which there is the option of assigning a 10^{10}, 10^{11} or 10^{12} Ω resistor to any Faraday cup. As standard, the Faraday detectors are assigned with 10^{11} Ω resistors, but in theory the use of 10^{12} Ω resistors should be beneficial for the measurement of mV-level signals. However, as shown in Figure 8 the data obtained when assigning a 10^{12} Ω resistor to L5 (orange) does not produce higher precision data. Because the 10^{11} Ω resistor can be used at higher intensities, and potentially for samples with a wider range of ^{235}U enrichment levels, we will use this resistor during testing in Task-2.

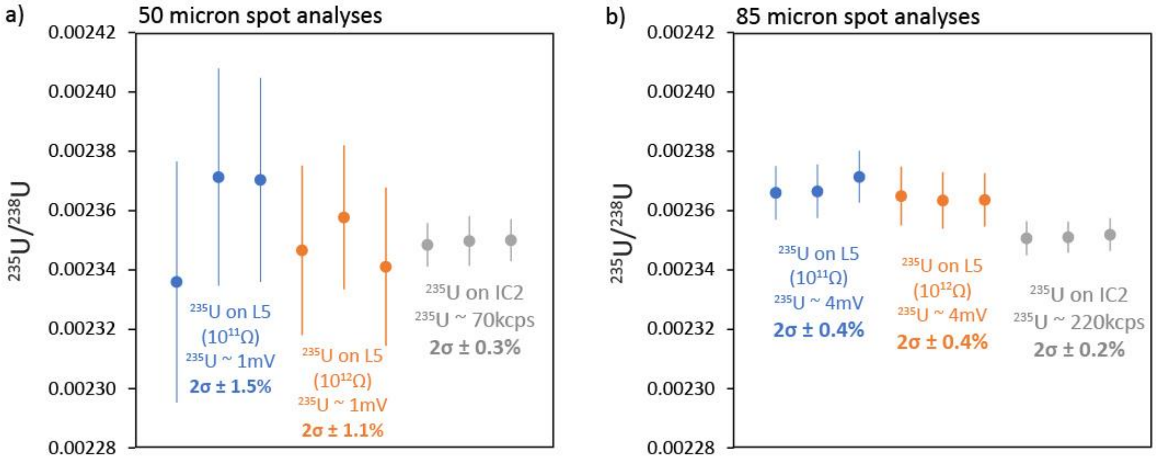

Figure 8 – Plot showing a comparison between measuring the ^{235}U signal on a Faraday detector (L5) and SEM (IC2). With a 1 mV signal the difference in precision between IC and Faraday was a factor of 4-5 (a). With a larger ^{235}U signal of ~4 mV the difference in precision decreased to a factor of ~2 (b). A correction factor of 1.019 for the IC2-Faraday gain was applied to the IC data.

c) Laser fluence

The laser fluence is a measurement of the energy delivered per unit area (in J/cm^2). At higher fluence more energy will be delivered to the sample surface and more material is ablated per pulse, resulting in higher signals delivered to the mass spectrometer. However, the laser will also bore down through the sample faster, resulting in a less stable signal with a steeper decay profile. To test whether changes in fluence inherently change the uncertainty associated with an isotopic analysis we performed a limited test on NIST 610 using fluences of 2.1 and 3.85 J/cm^2. These were combined with spot sizes of 50 µm and 40 µm respectively, to ensure that the intensities generated by the ablation matched. Using these ablation parameters, the uncertainties on the ^{235}U/^{238}U ratio were identical at ~0.24% (2σ), indicating that small differences in fluence do not change the uncertainty of the isotope ratio measurement. This is especially true in the case of laser ablation of micron-scale particles where more than likely a single laser pulse will be involved such that the interaction between the laser energy and sample substrate is less substantial.

d) Guard Electrode

The platinum guard electrode (GE) sits between the quartz torch and load coil on the ICP-MS. Its purpose is to narrow the ion energy spread and produce higher ion transmission efficiencies (e.g.

Xu et al., 2014) and thus it is typically turned on during ICP-MS analyses. However, it also increases the production of polyatomic species, meaning it can be problematic for some laser ablation studies. To test the importance of the GE a simple test was performed with the guard electrode turned on and off while all other laser ablation parameters were kept constant (50 µm spot, 7 Hz, 2.1 J/cm^2). When the GE was turned off the Ar sample gas flow had to be reduced from ~1.035 l/min to a new optimal level of 0.89 l/min. Oxide levels decreased with the GE off from 3-5% to negligible levels. Signal intensities also decreased by ~50% from previous levels (i.e. ~0.7V ^{238}U in NIST 610 to ~0.3V ^{238}U).

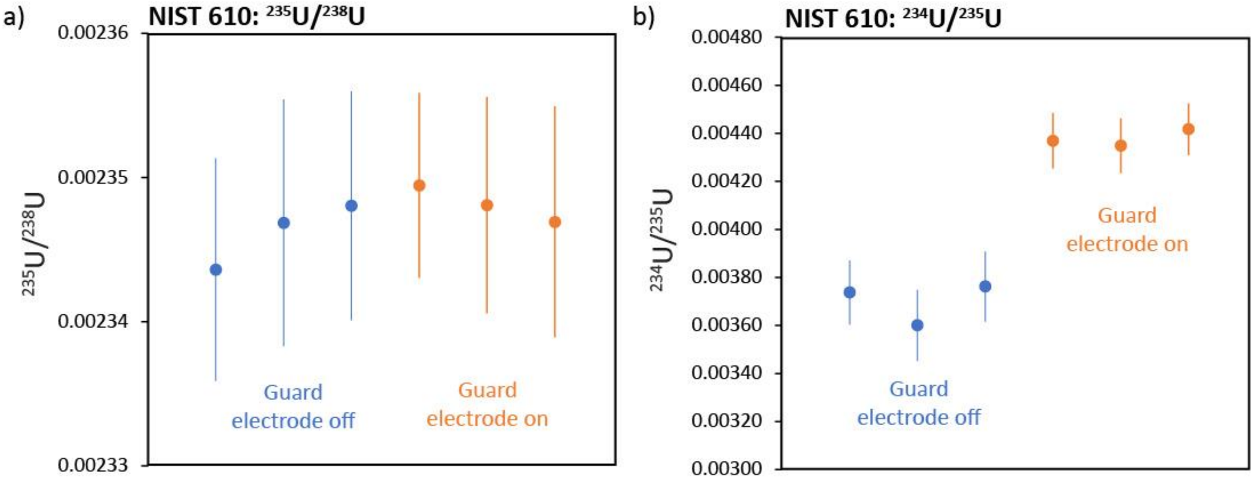

Figure 9 – Plot showing the comparison between performing analyses with the guard electrode on (orange) and off (blue). Although this makes no difference to the ^{235}U/^{238}U ratio (a) there is a significant shift in the ^{234}U/^{235}U ratio (b).

Isotopic analyses produced identical ^{235}U/^{238}U data with the GE on or off, and the isotope ratio data had similar precision (Figure 9a). However, for the ^{234}U/^{235}U ratio there were significant differences between data generated with the GE on or off (Figure 9b). Analyses performed with the GE off had lower ^{234}U/^{235}U ratios outside of analytical precision. Similar effects were also observed for NIST 612 and GSD-1G (see Appendix B). More testing would be needed to fully understand the cause of this shift. It is likely that polyatomic species such as ^{194}Pt^{40}Ar are less readily formed with the GE off, and these have a disproportionate effect on the minor isotopes of U such as ^{234}U. However, during testing in Task-2 we found that the raw ^{234}U/^{238}U and ^{236}U/^{238}U ratios were systematically closer to reference values with the GE on. Higher signal intensities also give better raw measurement uncertainties. For this reason, we defaulted to having the GE on during continued isotopic analyses in Task-2.

Task 2 – Testing the accuracy and precision of U isotopic analyses by laser ablation MC-ICP-MS

1. Reference Materials

To test the accuracy of U isotopic analyses by laser ablation requires access to solid-form standard reference materials with known isotopic compositions. Glass standards are ideal for this purpose as they couple well with the laser energy and have a high degree of isotopic homogeneity. Most widely available reference materials, such as NIST and USGS glasses, have natural or depleted $^{235}U/^{238}U$ ratios and low abundances of minor U isotopes, which means they are inappropriate for testing the ability measure samples with enriched isotopic compositions. For this reason, the testing performed in Task-2 also utilized a series of U-doped glasses that were prepared in house at LLNL from calcium-aluminum silicate base glasses (Knight et al., 2018). These have a variance in ^{235}U content from ~0.725% (natural uranium), ~50%, and ~93%, across three U concentrations from ~5, ~50, and ~500 ppm. The isotopic compositions of these glasses were previously characterized by dissolving small fragments (~10 mg) and analysing in solution-mode by MC-ICP-MS at LLNL (Table 3). The wide range of isotopic compositions of these materials enables robust evaluation of our ability to characterize samples with variable ^{235}U enrichment factors.

Table 3 – Isotopic compositions of the 6 reference glasses analyzed in this study. Isotopic compositions taken from in house analyses by solution MC-ICP-MS unless otherwise stated.

	$^{234}U/^{238}U$	Std Uncert (2σ)	$^{235}U/^{238}U$	Std Uncert (2σ)	$^{236}U/^{238}U$	Std Uncert (2σ)
CAS3-53-500	0.007995	0.000035	1.1240	0.0029	0.005639	0.000024
CAS3-94-500	0.1682	0.0018	15.91	0.16	0.05031	0.00054
CAS3-NAT-500	0.0000580	0.0000021	0.007936	0.000031	0.0000015	0.0000015
SAC-53-50	0.007806	0.000020	1.0985	0.0022	0.005498	0.000013
SAC-53-500	0.008017	0.000013	1.1283	0.0013	0.0056467	0.0000082
GSD-1G[a]	0.00001798	0.00000003	0.0036846	0.0000018	N/A	N/A
NIST 610[b]	0.00000945	0.00000005	0.00239555	0.00000047	0.00004314	0.00000004

[a]Jochum et al., (2011); [b]Zimmer et al., (2014)

2. Correcting for instrumental mass bias

There is an inherent bias present in the raw isotope ratios measured by mass spectrometers. In ICP-MS instruments, this is typically associated with the transfer of ions through the ion optics region of the mass spectrometer. Here, the lighter isotopes are preferentially deflected, leaving a population that is relatively enriched in heavy isotopes. This artifact, known as a mass bias effect, must be corrected to obtain accurate isotope ratio data. For isotope systems where internal normalization is not appropriate, this correction is usually performed by analyzing the isotopic composition of a standard reference material with known isotopic composition and using the difference between measured and true isotope ratios to calculate a mass bias correction factor that is applied to the unknowns. Because the extent of mass bias is not constant and will change between and within analytical sessions the mass bias correction factor must be calculated regularly within an analytical session. To obtain accurate U isotope ratio data by laser ablation MC-ICP-MS requires the selection of an appropriate reference standard that contains sufficient U and high enough ^{235}U enrichment for both ^{235}U and ^{238}U to be measured on Faraday detectors. This prevents the additional uncertainty arising from cross calibration of ion counters. Furthermore, the reference material must be isotopically homogenous at the level of analytical precision (i.e. <0.2-0.4%). The in-house U glass standards have enriched ^{235}U compositions and high enough U concentrations (50-500 ppm) to be used as mass bias correction standards. However, their spatial heterogeneity could not be assessed by solution MC-ICP-MS. Instead, the U-glasses were analyzed using Secondary Ion Mass Spectrometry (NanoSIMS) at LLNL, and SIMS-Single-Stage Accelerator Mass Spectrometry (SIMS-SSAMS) at the U.S. Naval Research Laboratory. The average composition of multiple in-situ analyses are presented in Table 4 and the degree of isotopic heterogeneity is represented by the reproducibility of the analyses (in %).

Table 4 – Isotopic composition of 5 reference glasses measured in situ by NanoSIMS and SIM-SAMS. Here, the RSDs are used as a first order indictor of the isotopic heterogeneity within in each glass.

Sample	Technique	^{234}U/^{238}U	2σ	RSD	^{235}U/^{238}U	2σ	RSD	^{236}U/^{238}U	2σ	RSD
CAS-94-500	NanoSIMS	0.166603	0.022711	13.6%	16.19534	1.676335	10.4%	0.049957	0.005356	10.7%
	SIM-SAMS	0.1686	0.006083	3.6%	16.06051	0.268602	1.7%	0.050714	0.002338	4.6%
CAS-53-500	NanoSIMS	0.008026	0.000504	6.3%	1.139124	0.025083	2.2%	0.005541	0.000655	11.8%
	SIM-SAMS	0.007974	0.000123	1.5%	1.120241	0.004958	0.4%	0.005677	6.37E-05	1.1%
CAS-Nat-500	NanoSIMS	8.7E-05	5.7E-05	65.5%	0.008279	0.001014	12.2%	not measured		
	SIM-SAMS	5.95E-05	1.79E-05	30.1%	0.007915	0.000304	3.8%	3.47E-06	2.68E-06	77.3%
SAC-53-50	NanoSIMS	0.007734	0.002855	36.9%	1.078263	0.076112	7.1%	0.005974	0.002397	40.1%
	SIM-SAMS	0.007894	0.001556	19.7%	1.089784	0.03103	2.8%	0.005504	0.000748	13.6%
SAC-53-500	NanoSIMS	not measured								
	SIM-SAMS	0.00792	0.000257	3.2%	1.122397	0.021632	1.9%	0.005616	0.000419	7.5%

Based on these data, the U-glasses CAS-53-500 and SAC-53-500 are the most suitable materials to use as mass bias correction standards, with relative uncertainties associated with duplicate ^{235}U/^{238}U ratios ranging from 0.4-2.2%. To further assess the suitability of these reference glasses as mass bias standards, we made 20 isotopic analyses of U in CAS-53-500 and SAC-53-500 by laser ablation MC-ICP-MS. The analyses were performed systematically in a grid across ~2mm chips of each standard, with ^{238}U and ^{235}U intensities of >100mV. The raw ^{235}U/^{238}U ratios are plotted in Figure 10. Systematic drift in the ^{235}U/^{238}U ratio of CAS-53-500 is likely caused by drift in the instrumental mass bias rather than sample heterogeneity. Regardless, this simple test indicates that both standards have spatially homogeneous U isotope ratios with relative uncertainties on the ^{235}U/^{238}U ratio of <0.1%. Because CAS-53-500 has been more thoroughly characterized by solution MC-ICP-MS this was ultimately chosen as the best standard to use for mass bias corrections during Task-2 and in future work.

During each analytical session, the CAS-53-500 glass was analyzed multiple times as a verification standard. Each session was set up with the same structure, in which 6 'unknowns' were bracketed by CAS-53-500 and mass bias factors were calculated for the unknowns from the measured ^{235}U/^{238}U ratio of the standards. The uncertainty associated with the ^{235}U/^{238}U ratios of the bracketing standards were propagated into the final isotopic compositions of the unknowns. The significance of this uncertainty is dependent on how well each isotope ratio can be measured. This is discussed further in Section 5.

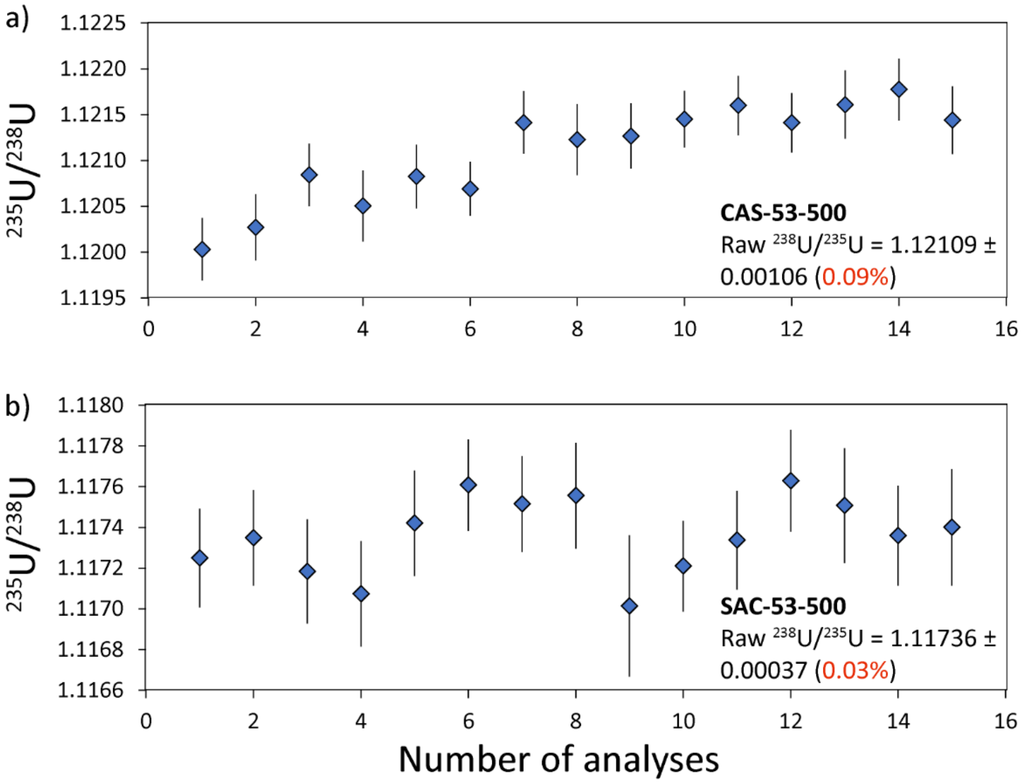

Figure 10 – The raw $^{235}U/^{238}U$ ratios of replicate analyses of CAS-53-500 (a) and SAC-53-500 (b) by laser ablation MC-ICP-MS. The 2σ relative uncertainty associated with these analyses is <0.1%, indicating isotopic homogeneity at the spatial scale of these analyses.

3. Ion Counter Gain Corrections

The minor isotopes of U (^{233}U, ^{234}U and ^{236}U) are present at relatively low abundances in most samples, meaning they must be detected using ion counters. Because the response of ion counters to an ion beam varies and is not necessarily equivalent to the signal produced on a Faraday detector, the ion counters must be calibrated to obtain accurate isotope ratio data. The offset between the response of the ion counter and the signal generated on a Faraday detector (assuming 1mV = 64150 cps) is called the ion counter gain. We tested two methods to calculate the ion counter gain factors during this study. The first used ion counter gain factors calculated during solution MC-ICP-MS analyses over the past 3 months. These are termed the 'assumed' gain factors. Whereas the instrumental mass bias must be calibrated daily and is highly sensitive to changes in the running parameters (e.g. sample gas flow), the ion counter gains are generally more stable within and between analytical sessions. The advantage of calculating the gain factors by solution MC-ICP-MS is that the measurement is more stable and relative uncertainties are smaller. Also, we can apply half-mass baseline correction to account for peak tailing of major isotopes onto ion counters, which cannot be performed by laser ablation. The disadvantage is that although the gain factors are relatively stable over the long term, in-run drift does still occur, as do small variations in gain factor between each analytical session. The alternative method is to perform the gain correction online, i.e. using laser ablation analyses of CAS-53-500 to calculate ion counter gain factors during sample-standard bracketing. These are termed ‘interpolated’ gain factors. This overcomes any drift in gain factors within and between runs, but the half mass baseline measurements that are used to correct for tailing effects cannot be performed. In addition, because ^{235}U is measured by Faraday collector this method cannot be used to calculate the ion counter gain factor for ^{235}U on IC2.

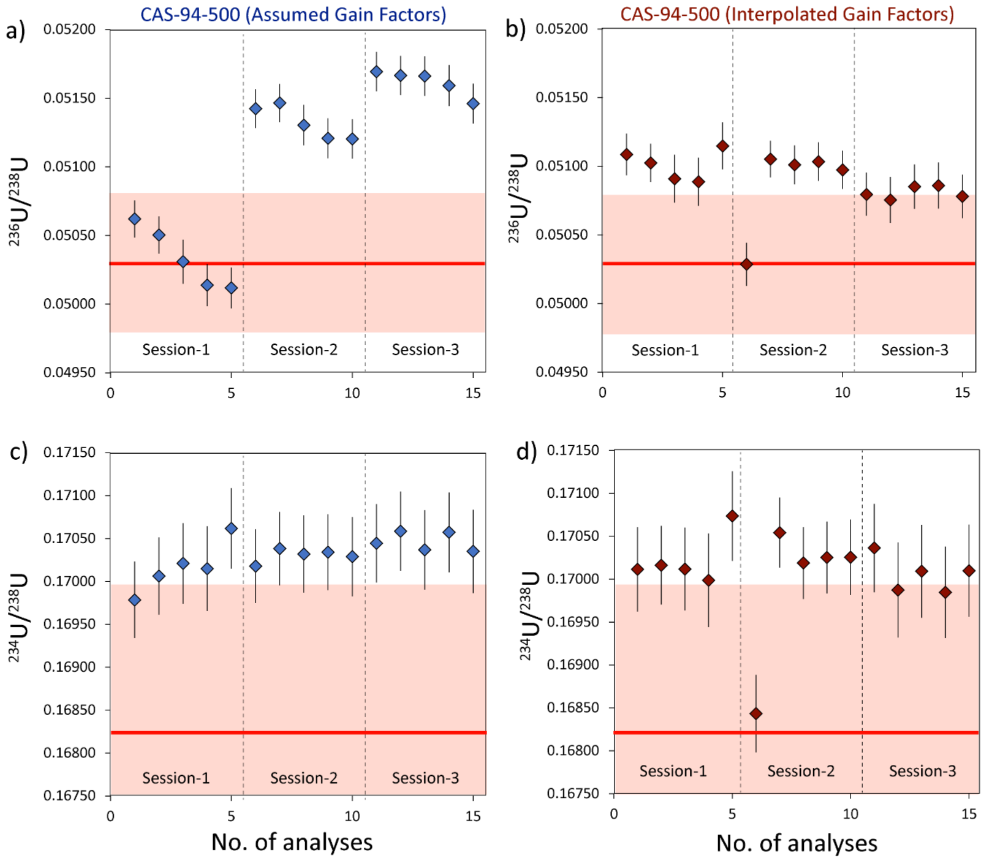

Figure 11 – The ^{236}U/^{238}U (a, b) and ^{236}U/^{238}U (c,d) ratios of the reference glass CAS-94-500. The ratios in a) and c) were calculated using assumed gain factors. The ratios in b) and d) were calculated using interpolated gain factors.

To establish the optimal method of gain factor correction we directly compared data calculated by both techniques for CAS-94-500 (Figure 11). As shown, when calculating the ^{236}U/^{238}U ratio using an assumed gain factor there is significant drift in the isotope ratio between analytical session outside of the 1σ analytical precision (Figure 11a). In contrast, using the interpolated gain factor results in more reproducible ^{236}U/^{238}U ratios within and between analytical session (Figure 11b). This indicates that the gain factor on IC1 is not stable at the degree of precision of our isotopic analyses. Interestingly, the ^{234}U/^{238}U ratio is far less sensitive to whether assumed or interpolated gains are used during the data reduction process (Figure 11c, d). This likely indicates a discrepancy in performance between IC3 and IC1 over the long term. Ultimately, because interpolated gain factors gave a significant improvement in the ^{236}U/^{238}U data we used this correction method for all

^{236}U and ^{234}U data. Because CAS-53-500 has subequal ^{235}U and ^{238}U levels we could not use it to calculate an interpolated IC gain factor for measurement of ^{235}U on IC2. For samples with low-levels of ^{235}U (i.e. samples with natural or depleted ^{235}U/^{238}U ratios) the ^{235}U gain correction was calculated from an assumed value measured by solution MC-ICP-MS.

4. Isotopic Analyses of U in Reference Glasses

Six of the seven U reference glasses (excluding CAS-53-500) were each analyzed 15 times by laser ablation MC-ICP-MS over 3 analytical sessions. In each case, the mass bias and gain factors for IC1, IC3 and IC5 were calculated using the measured composition of CAS-53-500. The experimental setup used the basic parameters presented in Table 2 and described in Task-1 (i.e. 50µm spot size, 7Hz repetition rate, fluence ~2 mJ/cm^2). The instrument was tuned so that the ablation of NIST-610 produced a ^{238}U signal of 0.5-0.7V. The average results of these analyses and the % difference between our measured values and reference values are presented in Fig. 12-14 and Tables 5 and 6. In the following, we summarize the most important observations from these isotopic analyses.

c) Glass standards with natural or depleted ^{235}U contents

Three of the reference glasses have natural or depleted ^{235}U contents: NIST 610, GSD-1G and CAS-Nat-500. The ^{235}U/^{238}U ratios were reproducible between and within analytical sessions with RSDs <0.5% for all samples. However, the ^{235}U/^{238}U ratios were all systematically lower than the reference values by between 0.4 and 1.7% (Fig. 12, 13a, Table 5).

Table 5 – Average U isotope ratios measured in the three reference glasses with natural or depleted ^{235}U contents.

	^{234}U/^{238}U	2σ	RSD (%)	Offset (%)	^{235}U/^{238}U	2σ	RSD (%)	Offset (%)	^{236}U/^{238}U	2σ	RSD (%)	Offset (%)
CAS3-NAT-500	0.0000631	0.0000025	3.88	8.9	0.007882	0.000021	0.27	-0.7	0.0000051	0.0000020	39.6	231.7
GSD	0.0000447	0.0000088	19.68	148.7	0.003670	0.000017	0.45	-0.4	0.0000496	0.0000075	15.2	N/A
NIST 610	0.0000107	0.0000004	3.51	13.4	0.0023544	0.0000032	0.14	-1.7	0.0000445	0.0000005	1.20	3.3

Because ^{235}U was measured using an ion counter (IC2) we hypothesize that the relatively low ^{235}U/^{238}U values reflect a small discrepancy between the assumed and true gain factors. A relatively small shift in this gain factor by ~1% would shift the ^{235}U/^{238}U of these glasses to within uncertainty of their reference values. This highlights the drawback in using an assumed gain factor for calculating isotope ratios, particularly when the offset between assumed and true factors is greater than precision of the isotopic analyses. Robust characterization of the ion-counter gain factor, for example by using a secondary standard with ^{235}U measured on IC2, would be required to correct for small offsets in the ^{235}U/^{238}U ratio. Of course, the ultimate goal of this project is to characterize the isotopic composition of U in micron scale particles; if their ^{235}U/^{238}U ratios can only be constrained to 5-10% (e.g. Pointurier et al., 2011; Craig et al., 2020) then such small offsets in the ion counter gain factor become largely irrelevant.

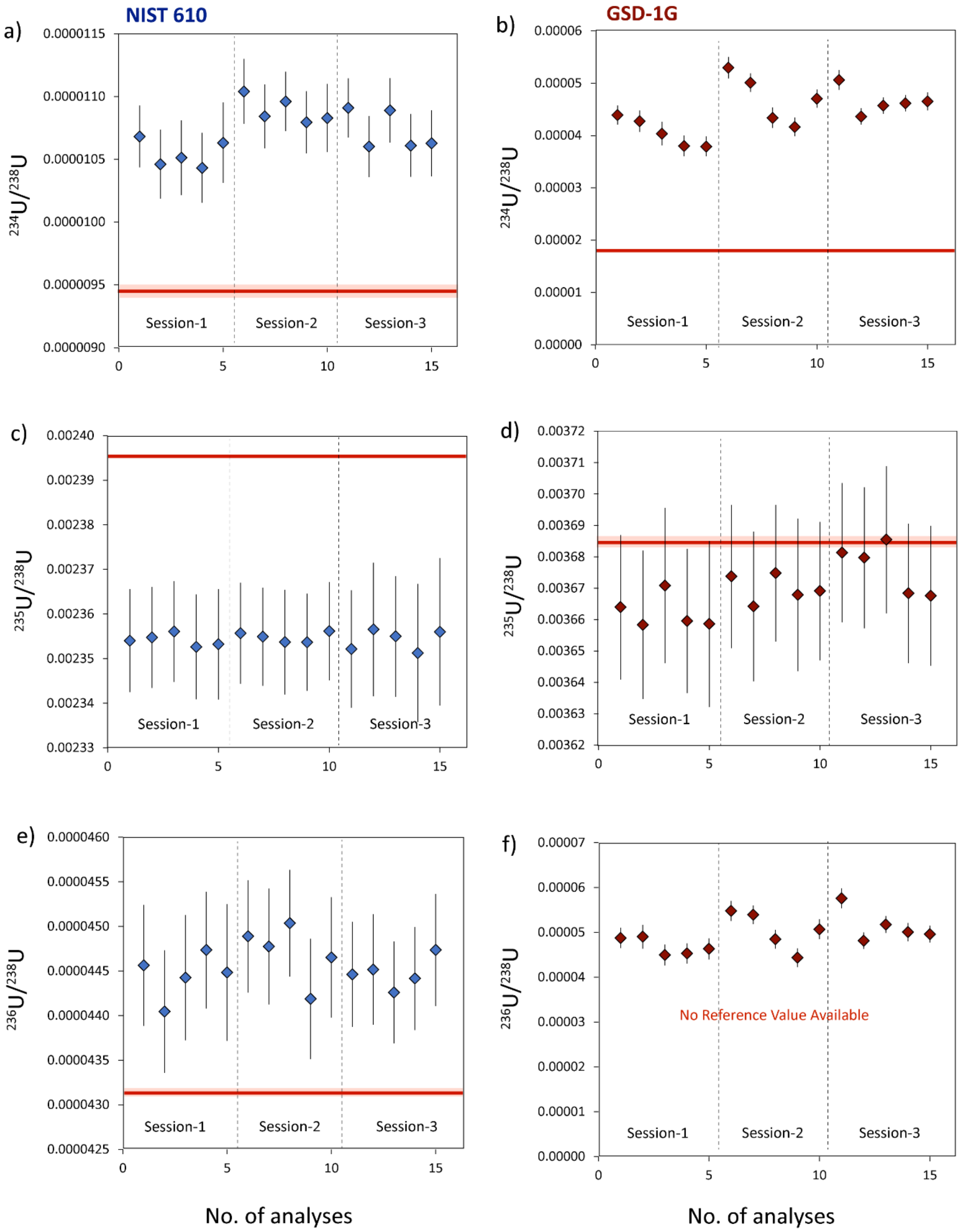

Figure 12 – Uranium isotope systematics in NIST 610 and GSD-1G. Reference values and 2σ uncertainties are shown in red. Error bars on individual data points are 2σ and incorporate mass bias, ion counter gain and measurement uncertainties.

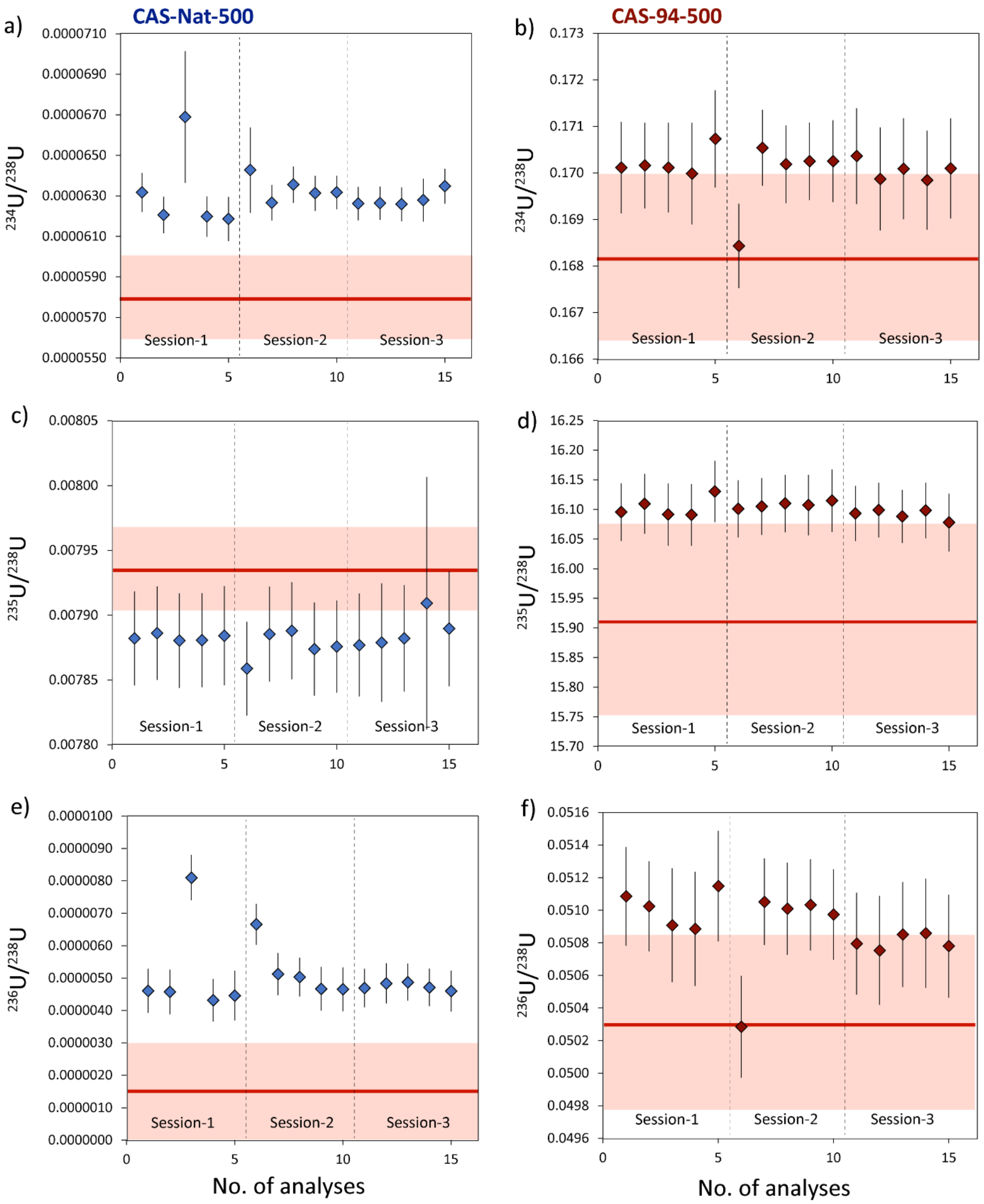

Figure 13 – Uranium isotope systematics in CAS-Nat-500 and CAS-94-500. Reference values and 2σ uncertainties are shown in red. Error bars on individual data points are 2σ and incorporate mass bias, ion counter gain and measurement uncertainties.

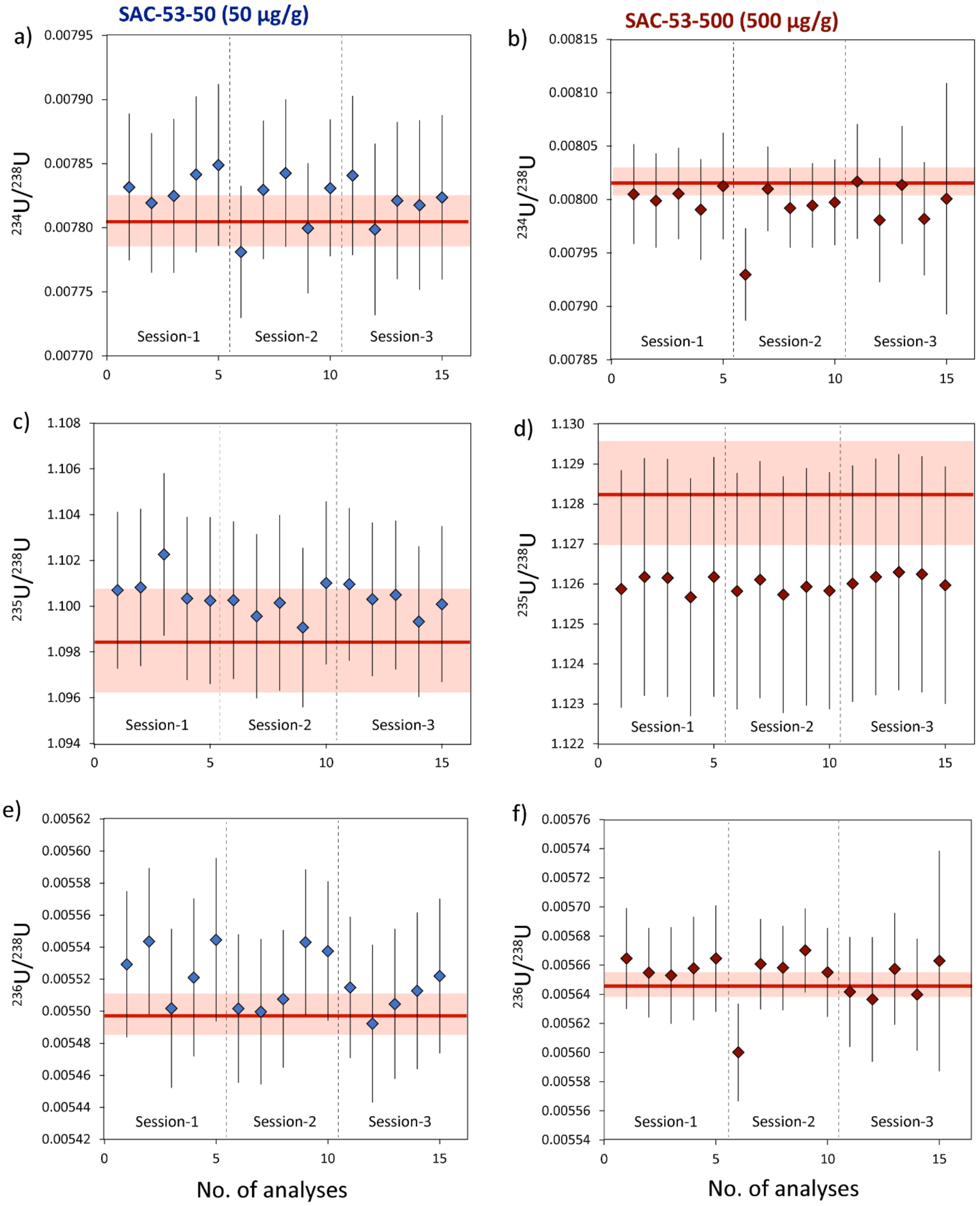

Figure 14 – Uranium isotope systematics in CAS-53-50 and CAS-53-500. Reference values and 2σ uncertainties are shown in red. Error bars on individual data points are 2σ and incorporate mass bias, ion counter gain and measurement uncertainties.

The ^{234}U/^{238}U and ^{236}U/^{238}U ratios were less reproducible than the ^{235}U/^{238}U ratio within and between analytical session, with RSDs between 1.2 and 39.6%. This relative instability is due to the fact that ^{234}U and ^{236}U are present at ~2 orders of magnitude lower than ^{235}U. The relatively low abundances of ^{234}U and ^{236}U also means that their isotope ratios are highly sensitive to the presence of polyatomic interferences and/or peak tailing effects from the major isotope (^{238}U) into ^{236}U. This can explain why the ^{234}U/^{238}U and ^{236}U/^{238}U ratios are systematically elevated above reference values (Table 5). NIST 610 is a synthetic glass with >50 trace elements doped into the matrix at ~450ppm. The USGS glass standard GSD-1G is similarly doped with trace elements to ~50ppm but has a basaltic matrix to more closely mimic natural rock samples (Jochum et al., 2011). The trace element composition of CAS-Nat-500 has not been characterized but it was synthesized from a calcium-silicate precursor under conditions that could have introduced trace element contaminants. For all three glasses, elements such as lead and platinum in the matrix can form polyatomic interferences in the MC-ICP-MS that directly interfere at the uranium masses. For example, NIST-610 is well known to have an elevated platinum content due to its preparation in a platinum-rhodium lined furnace (Duffin et al., 2013) and the polyatomic species ^{194}Pt^{40}Ar^{+} and ^{196}Pt^{40}Ar^{+} are potential interferences on ^{234}U and ^{236}U respectively. Our results illustrate the challenge with obtaining highly accurate and precise ^{234}U and ^{236}U data by in situ techniques in samples with variable trace element impurities and depleted ^{235}U contents. From a Safeguards perspective, it is unknown whether U-particles would contain such high concentrations of trace elements so it is possible that the minor U isotopes would be less affected by polyatomic interferences.

d) U-glass standards with enriched ^{235}U contents

The three U-glasses CAS-94-500, SAC-53-50 and SAC-53-500 have elevated ^{235}U/^{238}U ratios, with higher ^{235}U contents corresponding to higher abundances of ^{234}U and ^{236}U (See Table 6 for compositions). The higher count rates generated during ablation improves the counting statistics and renders polyatomic interferences less important, meaning we obtain more accurate and precise U isotope ratios.

Table 6 – Average U isotope ratios measured in three reference glasses with enriched ^{235}U contents.

	^{234}U/^{238}U	2σ	RSD (%)	Offset (%)	^{235}U/^{238}U	2σ	RSD (%)	Offset (%)	^{236}U/^{238}U	2σ	RSD (%)	Offset (%)
CAS3-94-500	0.1701	0.0010	0.60	1.1	16.101	0.025	0.16	1.2	0.05090	0.00041	0.81	1.2
SAC-53-50	0.007823	0.000037	0.48	0.2	1.1004	0.0015	0.14	0.2	0.005518	0.000035	0.64	0.4
SAC-53-500	0.007995	0.000042	0.53	-0.3	1.12601	0.00039	0.03	-0.2	0.005652	0.000034	0.61	0.1

As presented in Table 6, the isotope ratios generated by laser ablation match the reference values to within ~1%, and RSDs of the 15 replicate analyses are typically better than 1%. The highest precision and most accurate data were produced from the SAC-53-50 and -500 glasses, which generated data that matched the reference values to within 0.5%. There was no clear difference in data quality between the 50 ppm and 500 ppm glass. The glass with the highest ^{235}U enrichment, CAS-94-500, yielded U isotope ratios that are systematically ~1.2% higher than the reference values. We hypothesize that this offset reflects variable contamination of the CAS-94-500 sample aliquots during the chemical purification procedure prior to solution mode analyses. Even a small amount of natural U or LEU would have had a significant effect on the composition of such an isotopically enriched sample. This is illustrated in Figure 15 where the $^{235}U/^{238}U$ values are plotted vs $^{234}U/^{238}U$ for both laser ablation and solution data. The isotopic data from solution analyses form a well constrained mixing line between a highly ^{235}U enriched endmember and low ^{235}U enriched contaminant, with the laser ablation data lying in a cluster at the highly enriched end. This illustrates one of the major benefits of U isotopic analyses by laser ablation; the zero sample preparation requirements means there is no addition of U blank that could alter the final U isotope ratio.

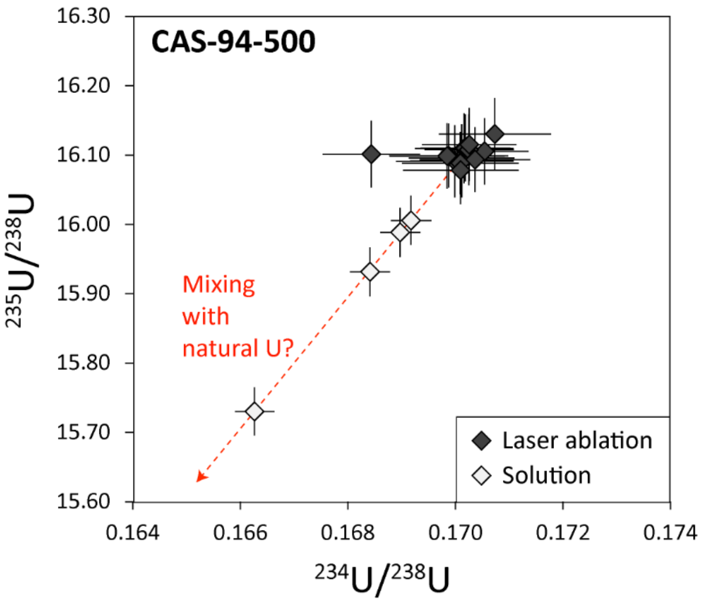

Figure 15 – The U isotope systematics in samples of CAS-94-500 measured by solution and laser ablation MC-ICP-MS. A clear mixing line extends from the laser ablation measurements to the solution analyses, indicating a mixing between HEU and less enriched contaminant. Uncertainties are 2σ.

Ultimately, the data described in Section 4 show that we have successfully setup a laser ablation MC-ICP-MS system that can obtain accurate and precise U isotope data in glass substrates for a wide range of U isotope ratios. The $^{235}U/^{238}U$ ratio is relatively easy to measure, even in samples with depleted ^{235}U contents and relative uncertainties equating to 0.1-0.5% are achievable. Presumably, the ablation of micron-scale particles will generate relatively low count rates, together with a highly transient signal, which may be detrimental to the data quality and uncertainties associated with final isotope ratios. However, the relatively robust $^{235}U/^{238}U$ data obtained during Task-2 indicate that we should also expect to obtain accurate $^{235}U/^{238}U$ ratios from U-particles, albeit with much lower precision. As one would expect, the measurement of minor U isotopes (^{234}U and ^{236}U) by laser ablation is challenging, even in U-rich glasses. Testing will be undertaken during Task-3 to assess whether it is possible to obtain robust isotopic data for the minor U isotopes from micron scale U-particles.

5. Isotope ratio uncertainties

The final uncertainties associated with the isotopic data are a product of several factors: the measurement itself, the reproducibility of the mass bias and ion-counter gain standard and how precisely the reference value of that standard is known. This last factor is a critical component of the final combined standard uncertainty (CSU); it constrains the lowest possible uncertainty that can be achieved in the theoretical scenario where no uncertainty is associated with the sample analysis and correcting standards.

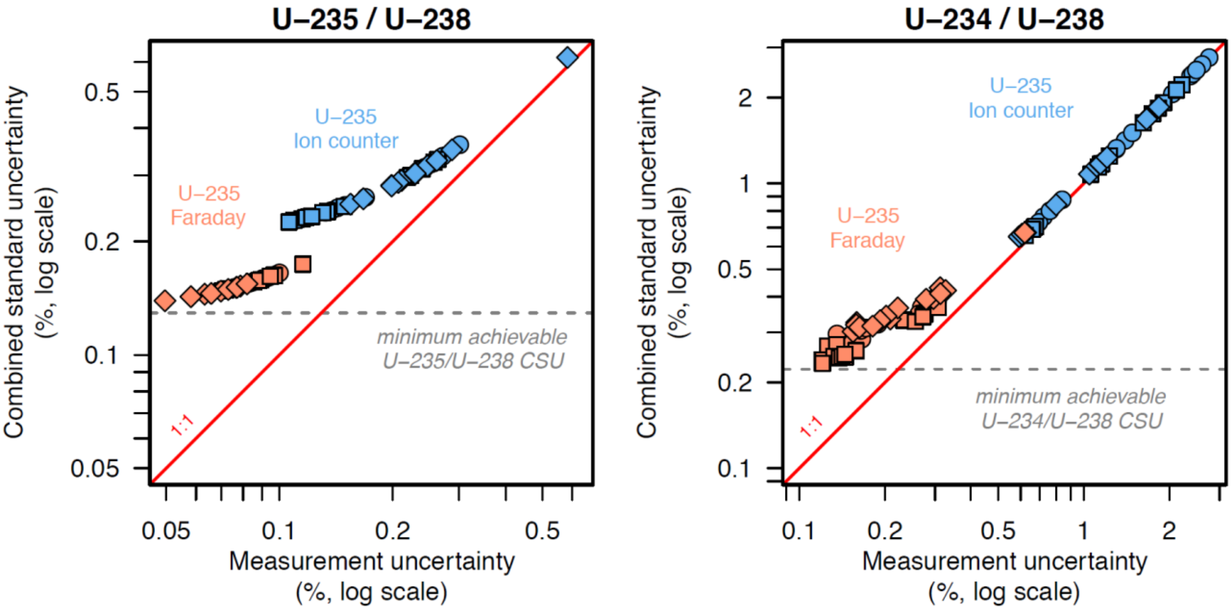

Figure 16 – Relationship between the measurement uncertainty and final combined standard uncertainty. The minimum achievable CSU is based on the uncertainty of the reference standard. Data points in blue represent those where ^{235}U was measured by ion-counter.

In Figure 16 we show the relationship between the measurement uncertainty and final CSU for ^{235}U/^{238}U and ^{234}U/^{235}U analyses of the reference glasses. The 1:1 line represents the case where the final CSU is equal to the measurement uncertainty, i.e. any uncertainties associated with the normalizing standard are negligible. The data in red were collected with ^{235}U on a Faraday detector (enriched ^{235}U) and the data in blue were collected with ^{235}U on an ion counter (depleted ^{235}U). The data in red tend towards the theoretical lowest possible CSU. In other words, the final uncertainties are largely controlled by the uncertainty on the mass bias/gain factor standard rather than the measurement uncertainty. This indicates that when ^{235}U could be analyzed on a Faraday collector our analyses are close to optimal; changes in data collection or experimental parameters would not greatly improve the final precision of these analyses. Better constraints over the isotopic composition of U in CAS-53-500 would be required to improve these data. The data in blue are closer to the 1:1 line, indicating that the measurement uncertainty is dominant, probably due to low count rates in glass samples with depleted U isotopic compositions. Irrespective of the isotopic composition, we expect the particle analyses to generate even lower count rates meaning the quality of the isotopic data will almost certainly be constrained by the particle measurement itself.

Thus, to optimize the particle analyses in Task-3 will require focus on how to reduce the measurement uncertainty, e.g. by prolonging the expected transient signal. It follows that factors controlling the data quality of the reference glasses, such as the mass bias and ion counter gain factors, will be a negligible source of uncertainty during the isotopic analyses of U particles.

6. Data reduction

Laser ablation MC-ICP-MS data reduction, results tabulation, and visualization was performed using the open-source R statistical programming environment (R Core Team, 2017). An automated data reduction algorithm was developed that accesses the raw, time-resolved isotope signal intensities output by the Neptune MC-ICP-MS software (.exp-formatted data files), with all subsequent calculations and corrections executed in R. The algorithm permits data reduction of either single or multiple analytical sessions concurrently.

In the data reduction algorithm, multi-pulse analyses of glass standards were automatically extracted. A simple logical screening routine was added to identify the pulse cycle index of maximum ^{238}U intensity, which unequivocally corresponded to the beginning of “on-peak” U measurement shortly after initiating the ablation process. All data from this cycle to the completion of the analysis routine was used to calculate ^{238}U-normalized uranium isotope ratios and corresponding uncertainties (standard deviation and standard error). In addition to data extraction, valuable analytical metadata was extracted from the raw .exp-formatted data files, including sample name, measurement timestamps, and the analysis routine employed (e.g., ^{235}U measured by Faraday vs. ion counter), all of which were tracked and used for automated corrections, figures and results table generation.

Instrument calibration was performed through a combination of “online” corrections and corrections using data collected during previous, non-LA analytical sessions. Glass standard CAS-53-500 was used as the primary instrument calibrant, with ^{235}U/^{238}U measured by Faraday multicollection for mass bias, and ^{234}U/^{238}U and ^{236}U/^{238}U by mixed Faraday-ion counter (IC) multicollection for relative Faraday/IC1 and Faraday/IC3 gain factor determination, respectively. For applying these corrections, measured isotope ratios were compared to those determined previously by solution-based MC-ICP-MS (see Table 3 for reference values). For Faraday/IC2 (^{235}U when measured by IC) and Faraday/IC5 (^{233}U) gain corrections, assumed gain factors based on solution MC-ICP-MS measurement were used, with values of 1.019 ± 0.0015 and 1.0371 ± 0.0042, respectively. The six reference glasses were measured as unknowns via standard–sample bracketing relative to the CAS-53-500 primary standard glass. Mass bias and Faraday/IC gain corrections were applied by linear interpolation using bracketing CAS-53-500 analyses, with a conservative expansion of uncertainty for these terms applied to unknowns to account for potential drift over the course of the analytical session. All relevant sources of measurement and instrument calibration uncertainty were propagated into the reported and plotted U isotope ratios via the Monte Carlo method. These corrected, fully traceable uranium isotopic compositions were then tabulated and plotted to assess measurement repeatability and to compare measured values with the known isotopic compositions of these materials.

Summary

In this mid-year report, we detail the setup and optimization of hardware to perform isotopic analyses of uranium by laser ablation MC-ICP-MS, followed by an assessment of the accuracy of U isotope ratio measurements in reference glasses with compositions ranging from highly depleted ($^{235}U/^{238}U = 0.00235$) to highly enriched ($^{235}U/^{238}U = 16.101$). The typical precision of $^{235}U/^{238}U$ measurements is better than 0.5%, irrespective of glass composition. The average $^{235}U/^{238}U$ values of the glasses are also consistent with the reference values (within 1.7%). The $^{234}U/^{238}U$ and $^{236}U/^{238}U$ data is of variable quality. Reference glasses with natural or depleted isotopic compositions have very low ^{234}U and ^{236}U contents, making the measurement difficult and prone to disturbance by interferences. In contrast, glasses with enriched U compositions have higher ^{234}U and ^{236}U contents and we were able to obtain accurate and precise isotopic compositions to within ~1% of reference values. At this stage, we are confident that the technique can produce high quality U isotope ratio data in U-glass samples. However, the ablation of micron scale U-particles will be very different from that of the reference glasses. We would expect to obtain a very short-lived signal for each particle, which would reduce the total U that could be analyzed and worsen the counting statistics. Based on previous isotopic analyses of U-particles (e.g. Craig et al., 2020) it is likely that the uncertainty on a $^{235}U/^{238}U$ ratio would be between 5-10%, i.e. an order of magnitude larger than what we have obtained with glasses. The effort in Task-3 will be to develop methodology to optimize collection of the transient signal from laser ablation and to effectively reduce the data, building on current data reduction protocols that have been developed in R.

Disclaimer

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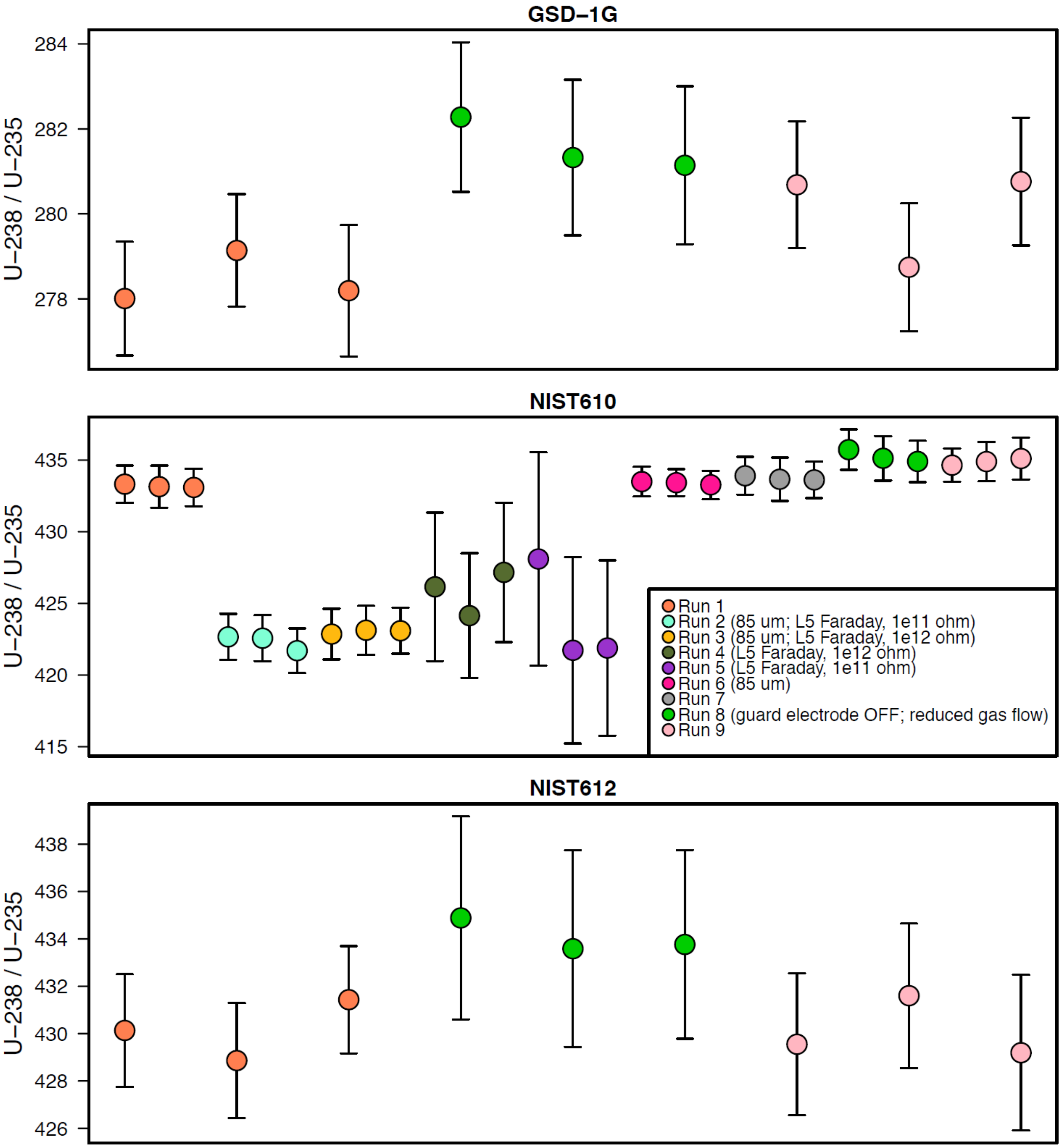
Appendix

Appendix A – $^{238}U/^{235}U$ data produced for the reference standards GSD-1G, NIST 610 and NIST 612 in a single analytical session. Uncertainties are 2σ (standard error). No correction for IC2-Faraday gain is applied to these data.



Appendix B - ^{234}U/^{235}U data produced for the reference standards GSD-1G, NIST 610 and NIST 612 in a single analytical session. Uncertainties are 2σ (standard error).