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Lawrence Livermore National Laboratory

Method Development for Measuring U Isotope Ratios by Laser Ablation MC-ICP-MS. Task 1: Hardware Setup

[Subject]

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Executive Summary

The aim of this project is to develop methodology to identify and analyze U and Pu containing particles using laser ablation MC-ICP-MS. The final methodology will ultimately be described in a detailed procedural document that will be shared with IAEA-NWAL laboratories. In this report, we describe the Task-1 deliverable; the setup and optimization of hardware required to perform U isotopic analyses by laser ablation MC-ICP-MS.

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 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). The sample aerosol is 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 ratio of mass to charge. 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 best method is to use an instrument with multiple detectors (multi-collector ICP-MS or MC-ICP-MS), meaning the different isotopes of an element can be detected simultaneously. This overcomes the inherent instability of the plasma source while also helping to negate 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.

A key application that directly addresses IAEA mission needs is using laser ablation MC-ICP-MS to identify U and/or Pu particles in environmental samples. For this purpose, a new capability will be 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). Initial setup and optimization of the hardware is described in this report. Future work 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 Lawrence Livermore National Laboratory (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

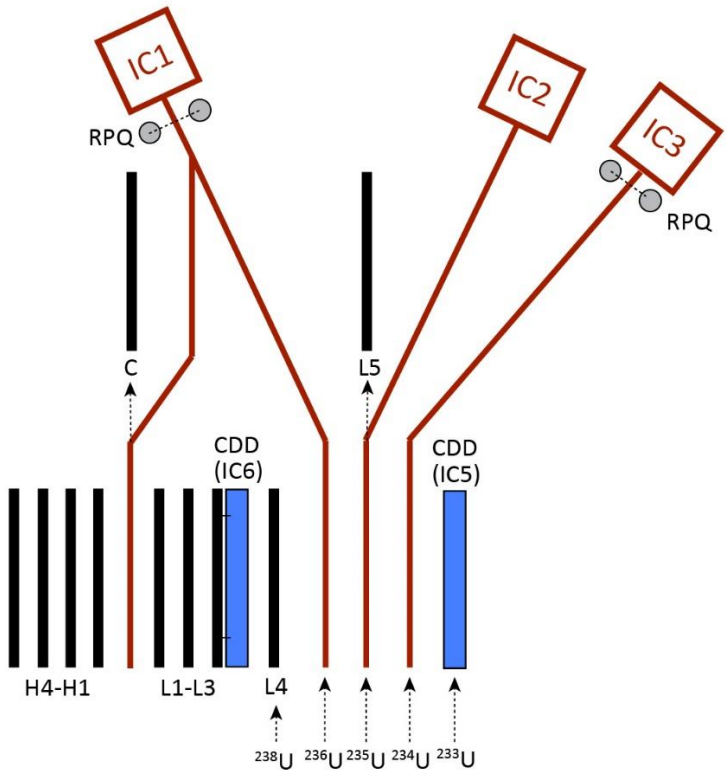

Figure 2 – The detector array on the Neptune-Plus MC-ICP-MS. Faraday detectors are in black, SEM's are in red, and CDD's are in blue. The IC1 and IC3 SEM's are fitted with energy filters (RPQ's). The U species and associated detectors are labeled.

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).

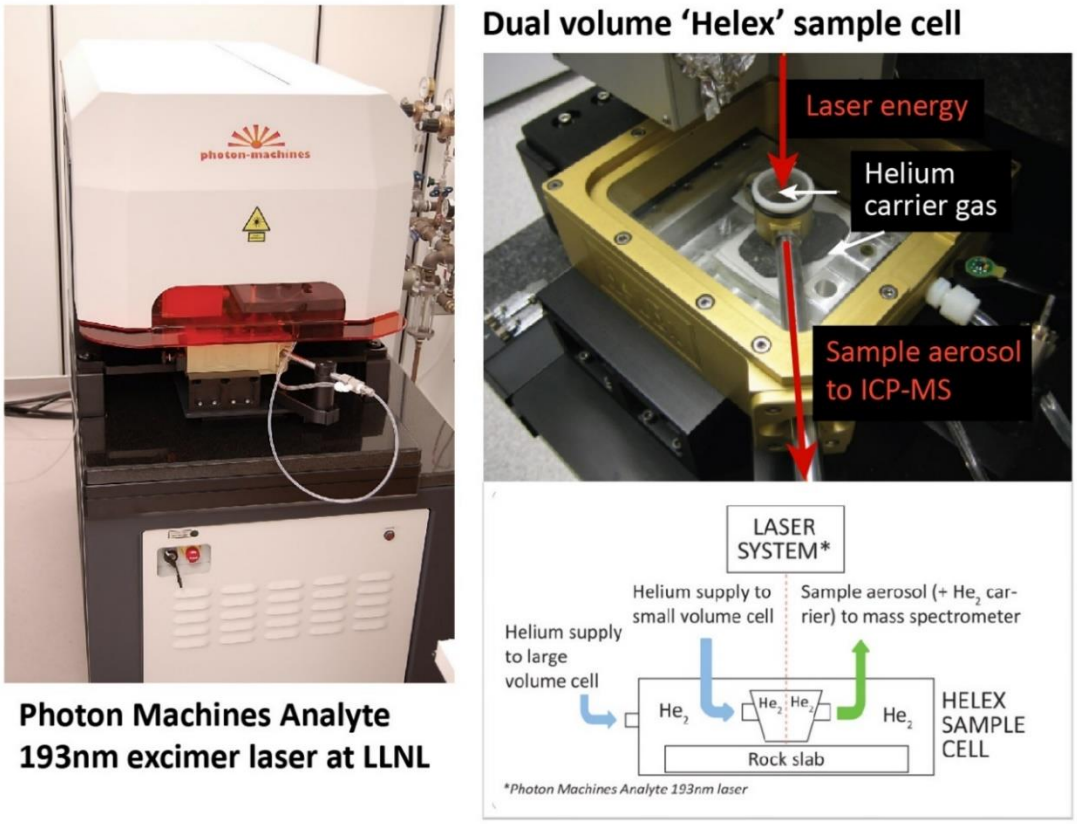

Figure 3 – The dual volume 'Helex' sample cell on the laser ablation system. Helium is supplied to both the main cell and inner cup as a carrier gas for the ablated sample aerosol, which is transported out of the cell to the ICP-MS.

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.

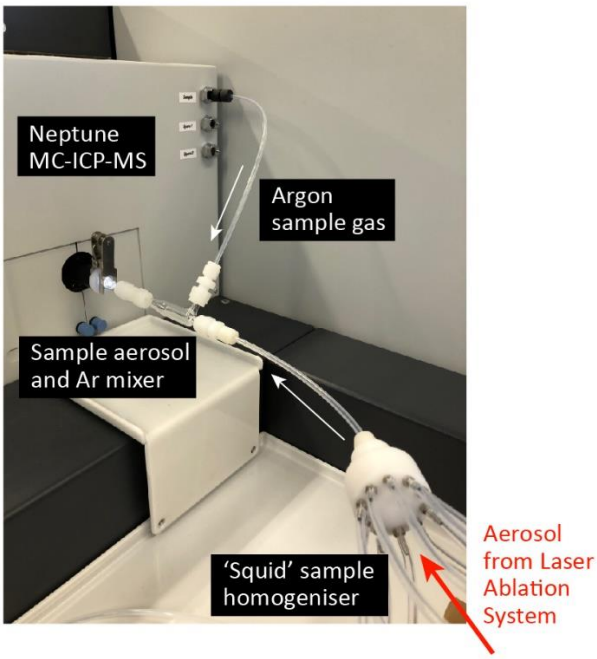

Figure 4 – The sample introduction setup. Aerosol is transported from the laser system through a sample smoothing device ('squid') before mixing with Ar 'sample gas' before the aerosol hits the plasma.

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.

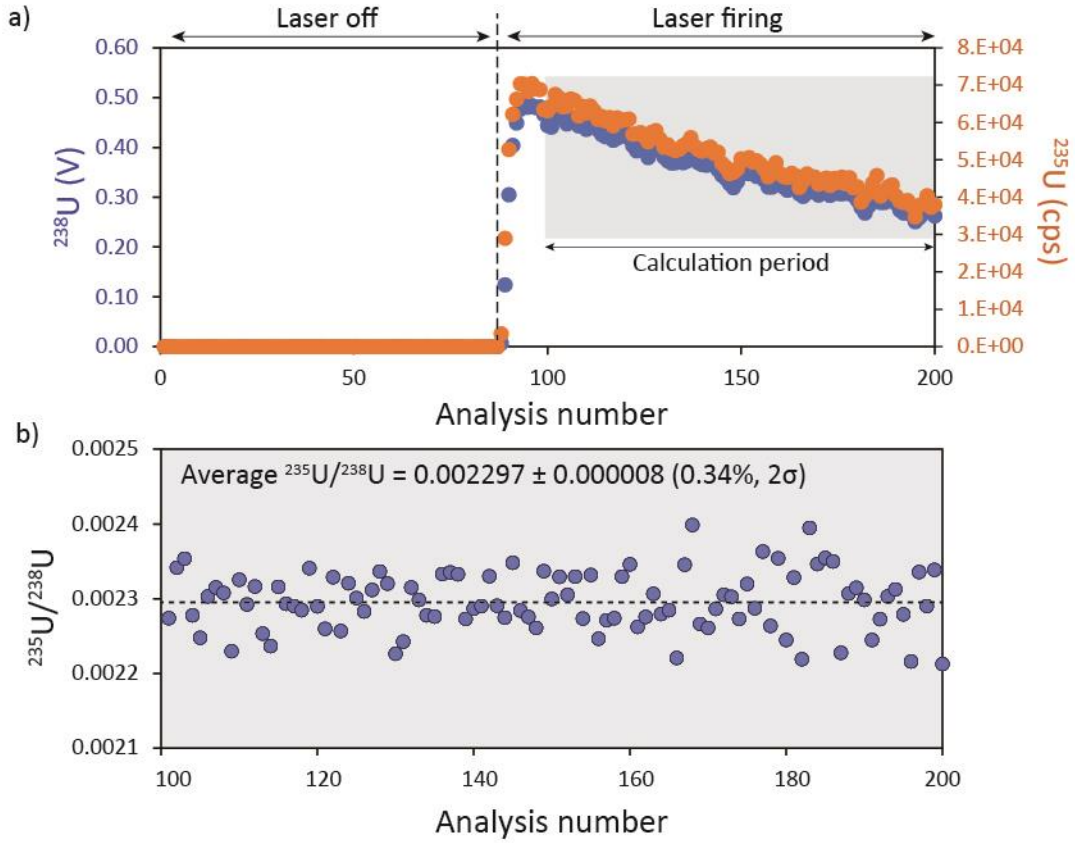

Figure 5 – A trace from an isotopic analysis of NIST 610 glass. The top trace (a) shows the intensities of ^{238}U (blue) and ^{235}U (orange) before and during ablation of the sample. Data was also collected for ^{233}U, ^{234}U and ^{236}U but is too low to show here. The shaded region in (a) shows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

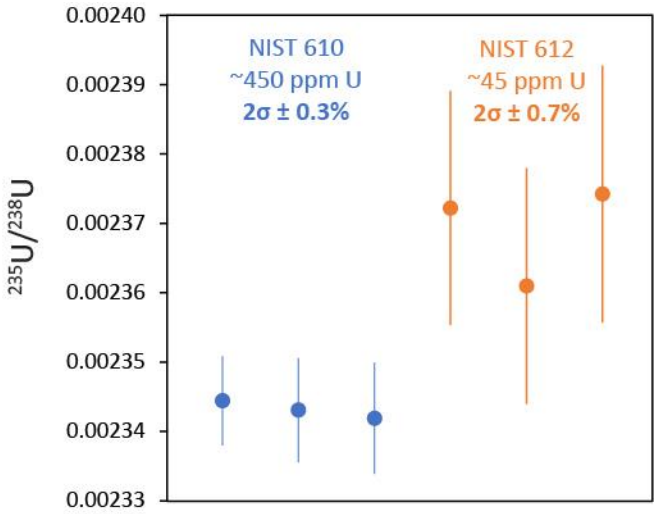

Figure 6 – A plot showing the difference in precision when analysing the $^{235}U/^{238}U$ isotope ratio in NIST 610 and NIST 612, which have different U concentrations.

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.

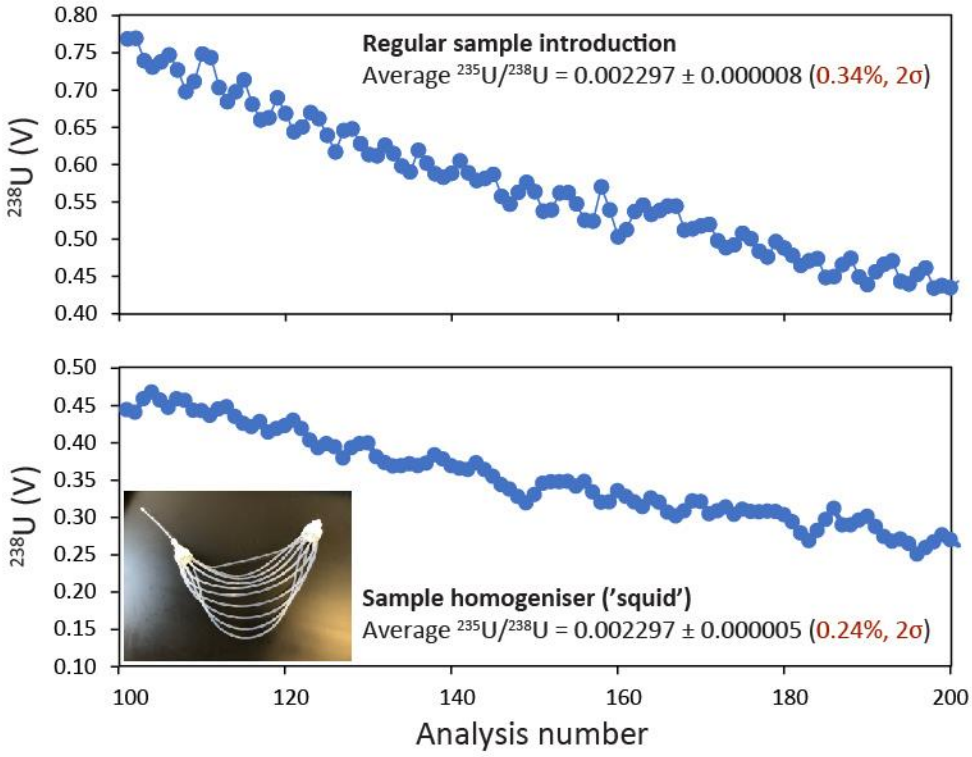

Figure 7 – Plot showing the effect of using a sample smoothing device ('squid') to eradicate instability from laser pulsing. In general, there was not a significant improvement in the precision of the $^{235}U/^{238}U$ ratio when using the squid.

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. The relative advantages of measuring ^{235}U by ion counter or Faraday detector will be investigated further in Task-2.

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.

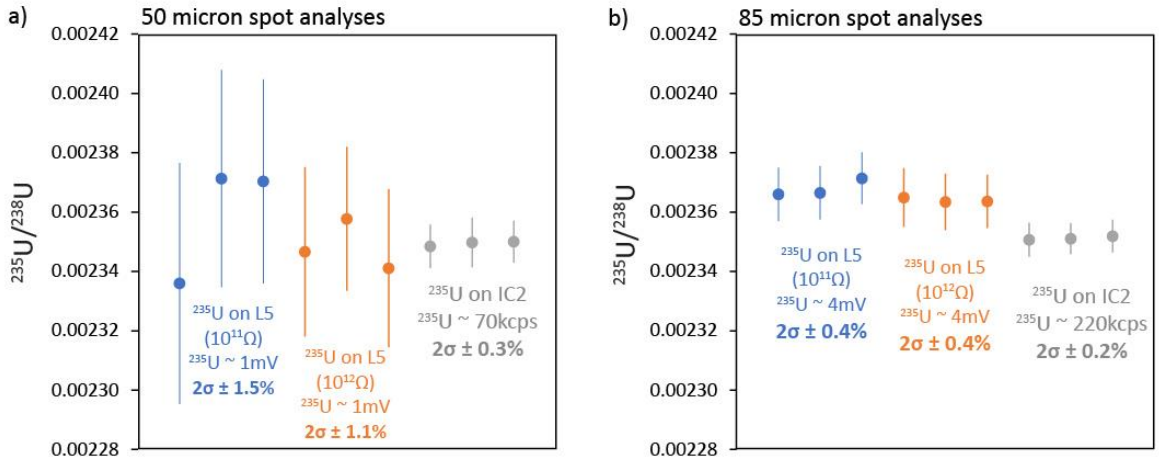

Figure 8 – Plot showing a comparison between measuring the ^{235}U signal on a Faraday detector (L5) and SEM (IC2). With a 1 mV signal the difference in precision between IC and Faraday was a factor of 4-5 (a). With a larger ^{235}U signal of ~4 mV the difference in precision decreased to a factor of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

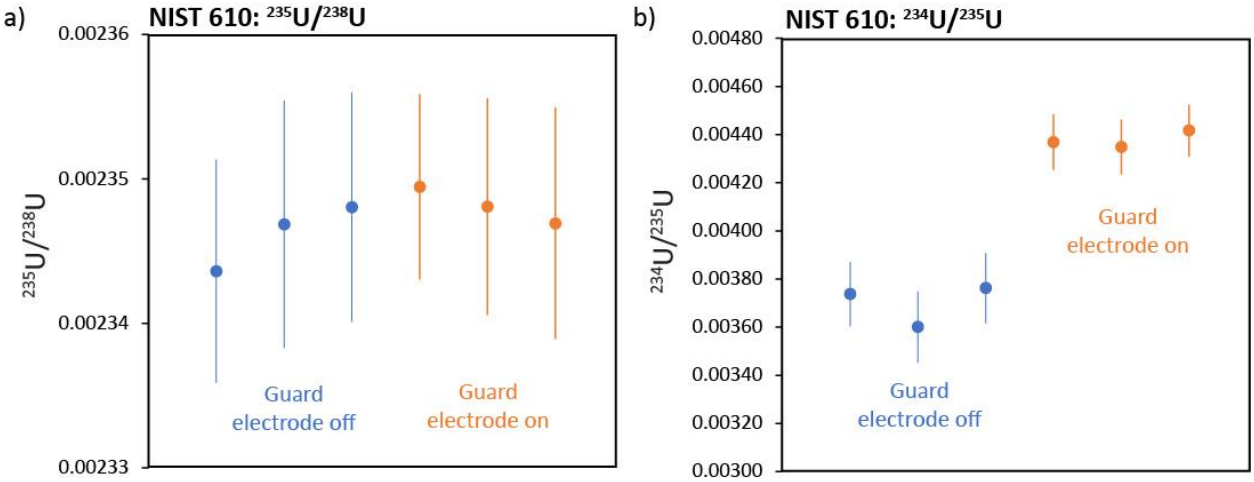

Figure 9 – Plot showing the comparison between performing analyses with the guard electrode on (orange) and off (blue). Although this makes no difference to the ^{235}U/^{238}U ratio (a) there is a significant shift in the ^{234}U/^{235}U ratio (b).

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, however, we hypothesize 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. If so, it may be necessary to run the isotopic analyses with the GE off in order to obtain robust minor isotope data for uranium, despite the significant decrease in sensitivity. This will be tested fully in Task 2, where the focus of the work will be to test the accuracy of isotope ratio measurements.

4. Accuracy of the isotope ratio data

At this stage of hardware testing the focus was on the parameters that influence the precision of isotopic analyses rather than accuracy. To obtain robust isotope ratios requires corrections be performed for instrumental mass bias, and that gain factors between ion counters and Faraday detectors are well characterized. We note that it was possible to produce comparable ^{235}U/^{238}U data for NIST 610 with ^{235}U on L5 or IC2 (Figure 8) by applying the previously calculated gain factor for IC2 of 1.019. This suggests that the current gain factors for ion counters will be

appropriate for correcting laser ablation data. It will also be imperative to produce a robust data reduction protocol with full error propagation in order efficiently assess the accuracy of these analyses. A software package is currently being developed in R for this purpose. Task 2 will involve new isotopic analyses of a range of glass standards with variable U concentrations and U isotope ratios to assess the accuracy of the analyses and establish the best methods to correct for analytical artifacts such as mass bias effects and polyatomic interferences. This step will be an important prerequisite to developing analytical protocols for isotope ratio measurements of single particles during Task-3.

Summary

In this report we detail the setup and optimization of hardware to perform isotopic analyses of uranium by laser ablation MC-ICP-MS. This is the Task-1 deliverable and is an important prerequisite to establishing techniques to analyse U and/or Pu particles for nuclear safeguards. Typical precision of the raw $^{235}U/^{238}U$ ratio in NIST 610 is between 0.2 and 0.4% (2σ) from ^{238}U intensities of 0.6-0.7 V. The precision is controlled, to a large extent, by the intensity of signal derived from ablation. At this stage we cannot constrain the final uncertainty of an isotope ratio measurement by laser ablation MC-ICP-MS, as this would require incorporation of errors associated with mass bias and ion counter gain corrections. More robust quantification of uncertainty and accuracy will take place in Task-2. Assessment of the applicability of these techniques to particle analyses will take place in Task-3.

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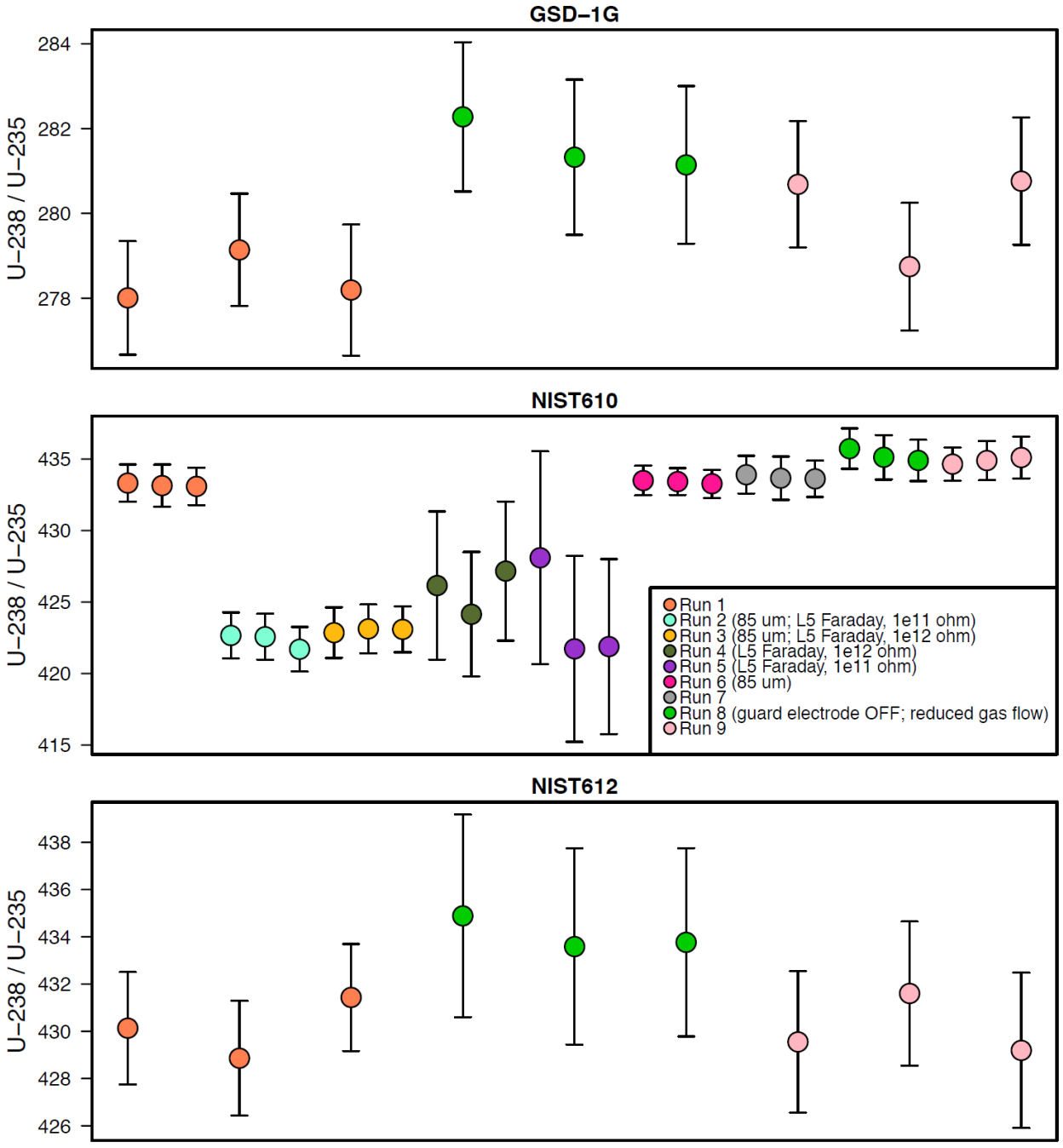
Appendix

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).