

High throughput isotope ratio measurements of uranium particles for nuclear forensics using laser ablation and time of flight ICP-MS

Introduction

Being able to measure the abundance of uranium-235 (^{235}U) in a given sample is critical when trying to determine the origin of any material found in the environment or at a particular location of interest. Examining dust collected at a scene has traditionally involved dissolving the material and undertaking TIMS or MC-ICP-MS analysis. Such bulk analysis is slow and does not discriminate instances where enriched and natural uranium samples may be present in the same dust sample. Analysis of individual particles of uranium is possible using SIMS but this is a slower technique with a much higher cost compared to ICP-MS. This application note will show how statistically significant numbers of individual particles can be analysed for ^{235}U abundance in a matter of minutes using laser ablation and time of flight ICP-MS. Conventional ICP-MS using a magnetic sector or quadrupole mass analyser is not suited to multi-isotope measurements of transient signals less than 10ms long due to the time it takes to switch isotopes on the detector. The Vitesse can sample the ion beam every 5-28 μs and save accumulated spectra to disk every 50-100 μs making it an ideal instrument for this work.

Instrumentation

An ESL imageGEO configured with an imaging sample cup was used with helium gas flows of 140mL/min through the cup, 175mL/min through the chamber and a 0.8mm ID peek capillary used to transfer the sample to an ESL DCI torch fitted to the Nu Vitesse.

The Vitesse was configured with dry sample introduction cones and the analytical method edited to restrict the mass range of the TOF to between 200 and 260amu. This increased the sampling frequency of the ion beam and 12 collected spectra were baseline corrected and summed in real-time by the embedded PC's Graphics Processing Unit (GPU) before each summed spectra was stored to disk every 79 μs .

A segmented reaction cell using 20mL/min of helium and 4mL/min of hydrogen to remove argon from the ion beam before sampling by the TOF and to thermalise the analyte ions thus improving their transmission through the ion optics. Care was taken to setup the axial field across the reaction cell and not increase the gas flow so much that the fast transient signals from small particles were made unusable due to excessive tailing of signal for the single particle data processing method.

Automation between the imageGEO and the Vitesse was established using the hardware triggers so the Vitesse could be used in Batch analysis mode with single particle methods of fixed acquisition time. Bidirectional communication using TTL hardware triggering between the laser and the Vitesse allowed for multiple samples to be collected one after the other without the risk of incorrect sample timing.

Sample preparation

The samples consisted of microparticles of NBS uranium reference materials U500, U010 and U005 as well as particles from 4 unknown sample sites. The particles were immobilised on plastic disks with a thin layer of hard setting adhesive. The U500 and U005 standards and the samples were mounted on separate disks whilst the U010 sample was mixed with U500 in two different proportions before mounting on disks.

Methodology and discussion

Each sample was ablated with an area raster whilst data was collected for approximately 9 minutes for each analysis. The initial sample run used ablation conditions of a 10 μm spot with 100Hz and 1mm/second stage speed. The density of particles on each sample disk was such that for some samples only a few tens of particles were ablated in the 9 minute run whereas other samples produced a large number of particle signals leading to multiple overlaps of signals which impacted data processing. The particle numbers measured in subsequent runs were changed by altering the spot size and ablation rate to more closely match the particle sampling rates between the sample disks and improve the data processing technique.

Data was processed using the single particle mode with ^{238}U as the trigger isotope. Collected data was smoothed (3 points, 5 iterations) and for ^{238}U signals above 30 counts in each 79 μs summed spectra of the smoothed signal, the preceding and subsequent inflexion points were found and then all unsmoothed data for all isotopes was summed between the inflexion points. For each found peak the start point, end point and peak centroid positions were saved along with the width of the peak at the half-maximum and all of the integrated isotope data. The peak width and timing data were used to determine quality criteria for reporting of peak integrations, all data were reduced using in-built Python scripts which could be set to ignore data which was likely to be overlapping other particle data. All data that was not part of the signal from a particle contributed to the ionic background signal, knowing the standard deviation of the background and the time width of signal for each found particle, it was possible in the Python script to calculate the statistical limit of detection for each particle and then not use any ^{235}U abundance data where the ^{235}U signal was near the detection threshold.

The upper counting range of the TOF measurement system must also be considered to avoid inaccurate data. The Vitesse has a detector overrange protection system which operates once an isotope signal above the trip threshold has been measured continuously for approximately 8ms (i.e. the same high signal for an isotope over approximately 300 extractions of ions into the TOF). The transient signal from sub-micron particles can be only a few hundred micro-seconds long and even the signal from a laser shot on a larger particle is actually a cluster of particles rather than a single transient when analysed at 79 μs per spectrum as shown in figure 1. This means that it is possible to measure extremely high signals, over very short periods which do not damage the detector, do not trip the protection circuit but may exceed the range of the counting electronics for one of more of the spectra acquired for the particle signal.

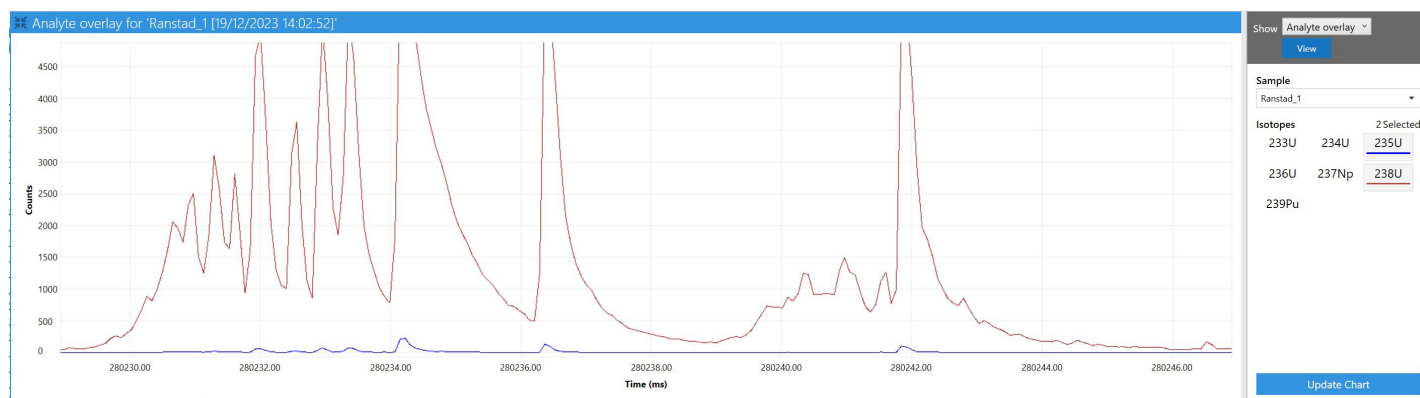


Figure 1 showing the pattern of nanoparticle signals from a single laser shot on a large uranium particle.

The Python scripts were used to filter out data where loss of linearity was anticipated and only report the isotope abundances for particles within the linear measurement range. It is worth noting that from a theoretical perspective, if the smallest particles have a signal width of 300 μ s then the lowest reasonable measured count of 5 ions for ^{235}U would equate to ~15,000 cps. For the lowest abundance standard U005, this would then equate to 3M cps for ^{238}U . From plots of the ^{235}U abundance vs. the total uranium signal such as shown in figure 2, it is possible to see that the linearity degrades above 12000 counts. This is the equivalent of almost 40M cps giving a dynamic range of just over 1 decade of signal for U005 where the method is able to accurately measure isotope abundance.

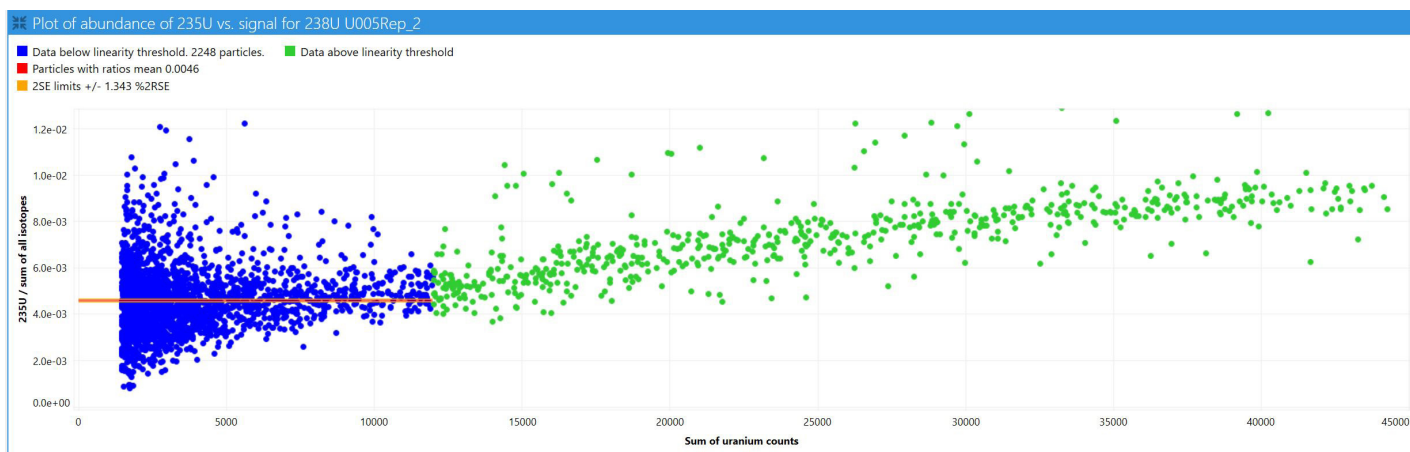


Figure 2: Showing the abundance of ^{235}U vs the total uranium signal for over 2000 individual particles seen during a raster ablation of immobilised particles on a sample disk.

It can be seen from this work that the optimum data is obtained when the particle density on the sample disk can be kept low enough to prevent multiple particles being sampled in the same laser shot but high enough to provide a minimum of a few particles per second to avoid longer acquisition times and requiring management of larger file sizes. An alternative methodology, when the particle sizes are so large such that many of the signals would be in the non-linear counting range, is to use the Vitesse's ion beam attenuator to reduce the total ion beam by approximately 40x before it is sampled by the TOF (figure 3). This does not change the dynamic range as the noise floor also increases by 40x but it does mean that more variability in the sample preparation can be accommodated. Using the Vitesse batch analysis technique, while each sample is being automatically ablated using a raster pattern, data can be acquired with two methods using unattenuated and attenuated signals. The Python script can then be used to select which data is valid from the quality criteria and even combine the data from both acquisition methods if desired.

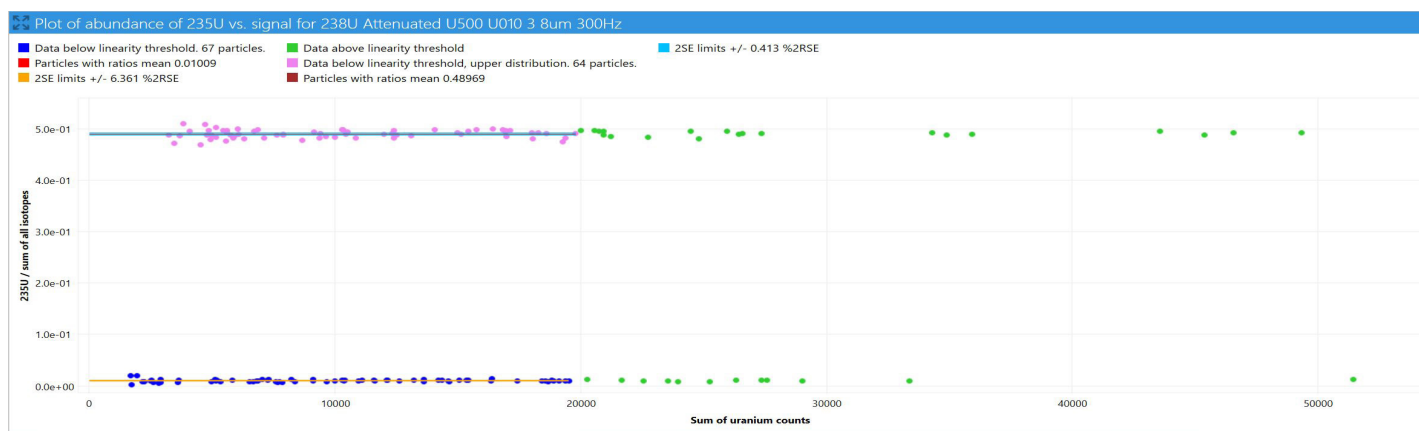


Figure 3: ^{235}U abundances reported for data acquired using ion beam attenuation for a mixed sample of U500 and U010.

Results

Data from the immobilised particles were acquired over 3 days of analysis, using various laser ablation conditions and with both full signal and ion beam attenuation. Table 1 shows the measured values for ^{235}U abundance for multiple particles in each sample. The relative standard errors are reported and reflect high numbers of particles in samples with a correspondingly lower %2RSE.

The average measure ^{235}U abundance for U500, U010 and U005 over multiple days, conditions and sampling methods shows good agreement to the NBS reference values within measured precision of the overall sample set (<https://www.energy.gov/nnsa/nbl-program-office>).

Conclusion

The combination of Vitesse with high speed, fast washout laser ablation has proven itself to be a simple and fast tool for nuclear forensics. It can provide abundance measurements for thousands of individual particles in a matter of minutes from a simple dust swab. As individual particles are measured, it is possible to differentiate mixtures of particles with different isotopic abundances within the same sample.

Acknowledgement

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	Rep rate, Hz	Spot size, mm	Signal attenuation	U005 abun- dance	%2RSE	Unknown abundance	%2RSE	U010 abun- dance	%2RSE	U500 abun- dance	%2RSE
U500	100	10								0.49972	0.121
U500	100	10								0.49983	0.075
U500	250	4								0.49746	0.666
U500	100	6								0.48986	0.769
U500	100	6	X							0.4882	0.477
U500	200	6	X							0.49156	0.46
U010 and U500	100	10						0.00943	6.061	0.49974	0.165
U010 and U500	100	10						0.00925	5.781	0.4992	0.233
U010 and U500	100	6						0.00982	10.212	0.49148	0.467
U010 and U500	100	6						0.01001	11.409	0.48943	0.513
U010 and U500	100	10	X					0.01044	28.113	0.48734	1.369
U010 and U500	100	10	X					0.01028	5.118	0.48999	0.889
U010 and U500	300	8	X					0.01018	5.49	0.48995	0.318
U005	100	10		0.00503	2.382						
U005	100	10		0.0046	1.343						
U005	250	4		0.00575	6.067						
U005	100	6		0.00504	5.097						
U005	100	10	X	0.00524	4.449						
U005	200	6	X	0.00547	2.324						
Bolet_1	100	10				0.00706	1.934				
Bolet_1	100	6				0.00781	3.41				
Bolet_1	100	10	X			0.00753	5.673				
Bolet_2	100	10				0.00748	0.957				
Bolet_2	100	6				0.0075	1.897				
Bolet_2	100	10	X			0.00733	1.668				
Olympic Dam	100	10				0.00751	5.185				
Olympic Dam	100	6				0.00746	2.166				
Olympic Dam	100	10	X			0.00729	2.622				
Ranstad	100	10				0.00697	0.347				
Ranstad	20	4				0.00698	0.878				
Ranstad	100	10	X			0.00728	7.741				
Ranstad	100	10	X			0.00751	0.699				
Averages (%1RSD)				0.00519	7.70%			0.00992	4.50%	0.49337	1.00%
NBS values (%bias)				0.00506	2.57%			0.01004	-1.20%	0.49696	-0.72%

Table 1: Results of ^{235}U abundance over multiple samples under multiple conditions.