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Minimizing Sample Consumption Using Single Shot Laser Ablations for Isotope Ratios

- **Accurate isotope ratios on single laser shots**
- **Negligible signal skew using sub-millisecond dwells**
- **Increased duty cycles using 70 µs settle times**
- **Data processing automation through Nu Quant NICE**

Introduction

High spatial resolution measurement by laser ablation ICP-MS has continuously improved in recent years addressing challenges in depth and lateral resolution, especially for samples that require precise isotope ratio measurements. Such applications would include spatial discrimination of uranium/lead isotope ratios of zircons and single particle analysis for uranium ratios where the isotope ratios of a single laser shot need to be measured to the best possible precision. All aspects of instrumentation and methodology need to be optimised to improve performance and ease of use for this technique. This application note will discuss recent areas of improvement and show some characteristic performances for the Attom ES.

Instrumental Method

An ESI NWR213 laser ablation system with a TwoVol^2 cell was coupled to the Attom ES or Nu Plasma II with the argon make-up provided from a Cetac Aridus II so tuning was possible with solutions. The helium output from the laser used 1.6 mm ID tubing to connect with the argon from the Aridus II as close to the torch as possible using a t-piece. This provided the sharpest peaks for a single shot and the fastest washout of signal.

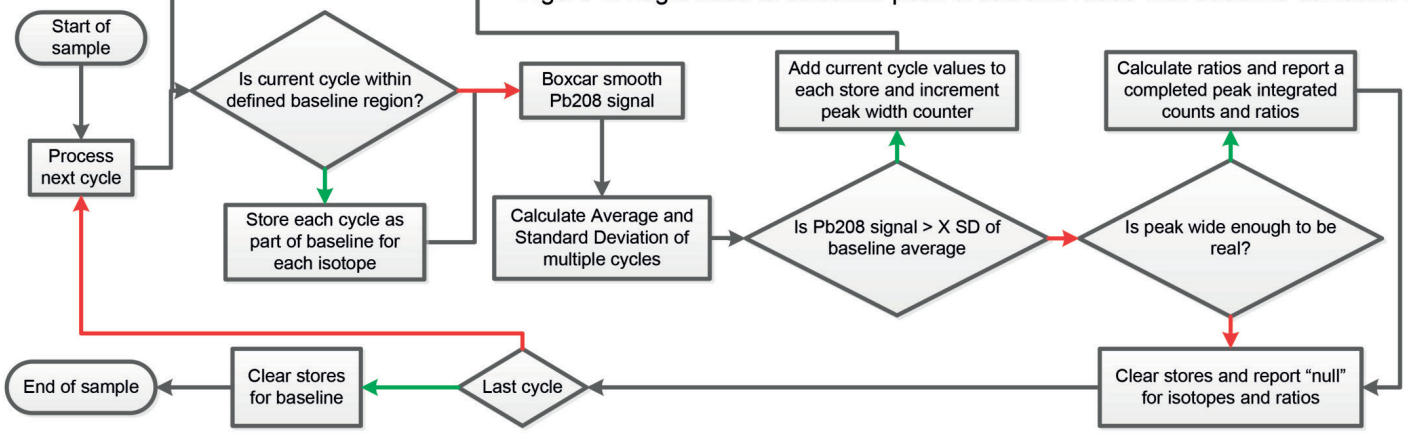
600-800 ml/min of He was used and the argon flow then optimised to obtain the minimum UO/U ratio. This ensured a robust plasma for particle processing and improved the accuracy of the Pb/U ratio as the minimum amount of U signal was lost as the oxide.

Attom ES data was acquired with a parked magnet, using the deflectors to jump between Pb and U peak tops with 70 µs delay between jumps. For the zircon work all isotopes were acquired at 300 µs and 20 sweeps per cycle (~18 ms total) and for U series work ^{235}U was acquired with 3 ms dwell and ^{238}U with 300 µs and 20 sweeps per cycle (~70 ms total). The very fast settle time ensured that as much time as possible was spent analysing signal and the sub-millisecond dwells ensured that the effects of signal instability were minimised.

The Nu Plasma II was configured so all Pb isotopes were measured on full sized ETP discrete dynode multipliers and the ^{238}U was measured on a fast 100 GΩ amplifier, data was acquired in 100 ms cycle increments.

As some data skew was anticipated for both Attom ES (due to the sequential measurement of isotopes) and Nu Plasma II (due to the response time difference between the multipliers and the faraday detectors), a peak integration method was adopted as described previously by Cottle et al. [1]. In the case of Attom ES this methodology could be automated via the Nu Instruments Calculations Editor (NICE) scripts available in Nu Quant. Figure 1 shows the general logic used for the NICE script.

Figure 1: Logic used to calculate peak areas and ratios with baseline correction



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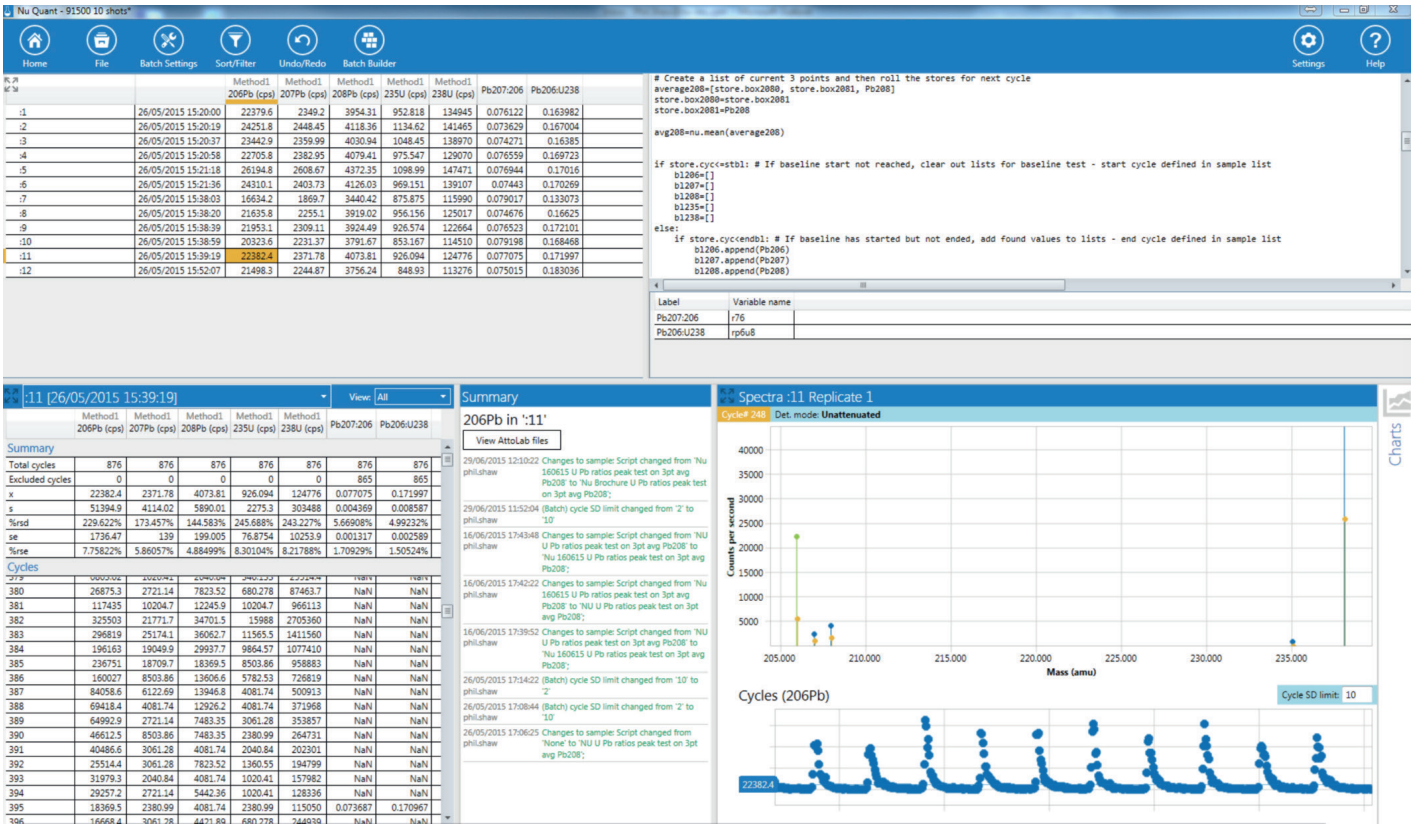

Figure 1a: Nu Quant screen showing the single shot laser data and NICE processing script

Figure 1a shows a screen shot of the Nu Quant software used to process the batches of samples. As changes could easily be applied globally to multiple samples at once and the algorithm was written to automatically detect and integrate peaks, the NICE scripts reduced the processing time to minutes compared to the hours required when using spreadsheets.

Methodology for Pb/U isotope ratios.

Zircon 91500 was analysed using both Attom ES and Nu Plasma II instrumentation. When the Attom ES was tuned, the signal difference for all isotopes measured from the central park mass was only a few percent so no mass bias correction was applied. For the Nu Plasma II the multipliers and faraday detector were normalised using the average of 20 individual shots. This normalisation was then applied to all subsequent data for that analysis session. Test ablations showed that the transient signal returned to baseline quickly enough that the minimum 1 Hz ablation rate could be used making automation of spot measurement much simpler as 20 shots could be fired at each spot position on the zircon and an automated run of multiple spots could easily be setup. Figure 2 shows the trace profiles for the single shots on the Attom ES and Figures 3 and 4 show the $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ regression plots.

Figure 5 shows the trace profiles for the single shots on The Nu Plasma II and Figures 6 and 7 show the comparison of precision for 11 spots of 20 shots each for both Attom ES and Nu Plasma II for the $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ respectively.

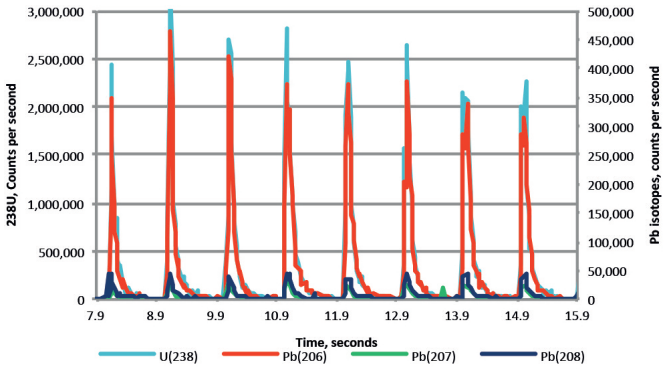

Figure 2: 6 J/cm², 25 um single shots of 91500 zircon using Attom ES and NWR213 with TwoVol² cell.

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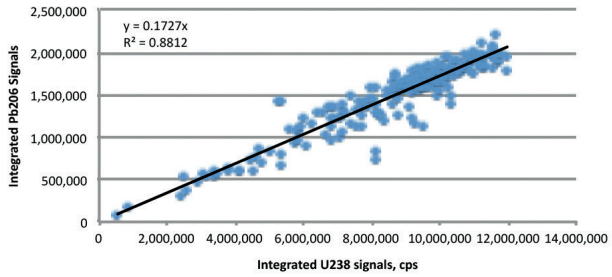

Figure 3: 91500 $^{206}Pb/^{238}U$ - Individual shot ratios on Attom ES 2 Σ exclusion 0.1715 (8.4% RSD); (Wiedenbeck et al. 0.17917)

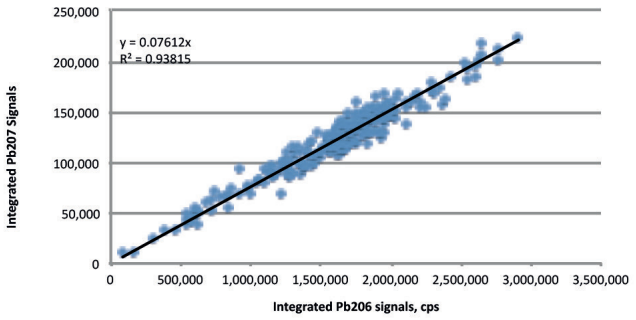

Figure 4: 91500 $^{207/206}Pb$ - Individual shot ratios on Attom ES 2 Σ exclusion 0.07659 (7.23% RSD); (Wiedenbeck et al. 0.07488)

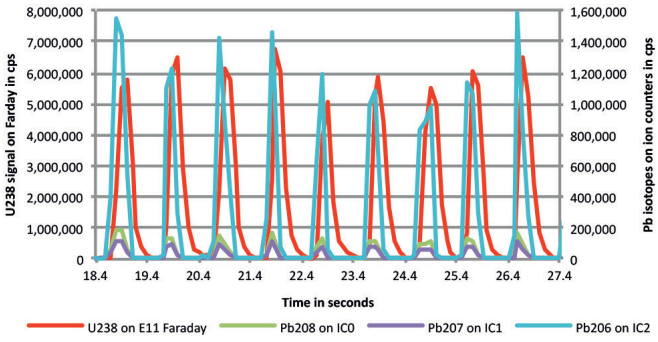

Figure 5: Single shot signal traces for 91500 zircon on Nu Plasma II 40 µm, 1 Hz 6 J/cm².

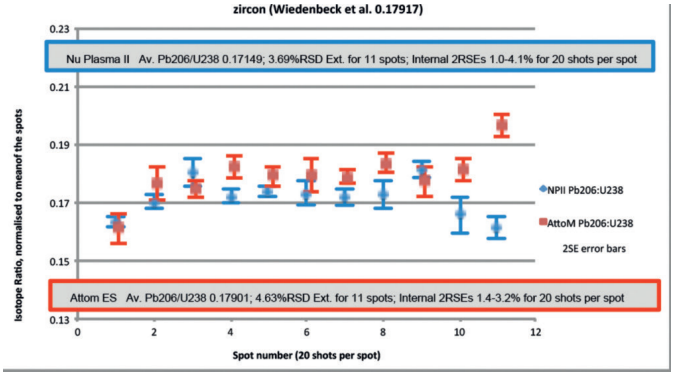

Figure 6: Comparison of Nu Plasma II with Attom ES for single shot isotope ratios using 91500 zircon (Wiedenbeck et al. 0.17917)

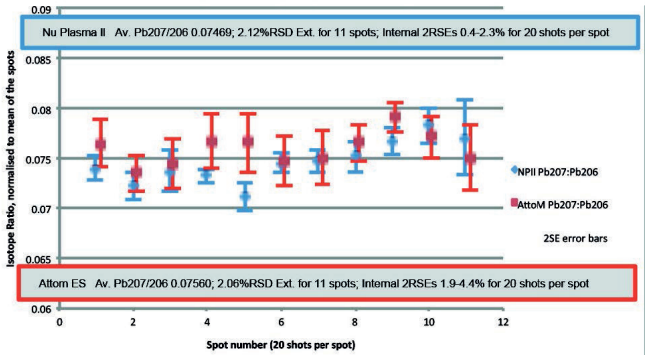

Figure 7: Comparison of Nu Plasma II with Attom ES for single shot isotope ratios using 91500 zircon (Wiedenbeck et al. 0.07488)

With the standard ES interface the Attom ES had similar sensitivity to the Nu Plasma II for the same size ablation spots. The extra sensitivity of using the multiplier for ^{238}U compared to the faraday on the Nu Plasma II improved precision so that both instruments were similar performance for Pb/U ratios. As all Pb isotopes were measured with multipliers on the Nu Plasma II the enhanced precision of multi-collection was evident but the fast peak switching of the Attom ES provided enough reduction in sampling noise that the internal precision difference of ~2x could be accounted for by the difference in signal measurement time (each Pb peak was measured for ~5x longer on the Nu Plasma II compared to Attom ES which only spent ~1/5 of each cycle measuring each isotope).

Method development for U-series isotope ratios

The primary objective with the U-series analyses was to obtain the best precision for low concentrations of uranium so micron to submicron particles of pure uranium could feasibly be analysed. To initially test the method, single shot ratios of NIST 612 and 610 were evaluated using the automated data acquisition and processing methods, Figures 8 and 10 show the trace profiles for 612 and 610 respectively and Figures 9 and 11 show the regression plots to calculate the $^{235}U/^{238}U$ ratios and individual shot precisions over a range of spot sizes from 10 µm to 100 µm. It is worth noting that NIST 610 ablations tended to show a double peak and extended washout so an alternate method was adopted on the laser using 20 individual overlaid spots of one shot each with a 2 second washout between spots. This methodology could still be automated using the Attom ES triggers and simple tools used within the ESI NWR213 software to move all 20 patterns to a new spot location when required.

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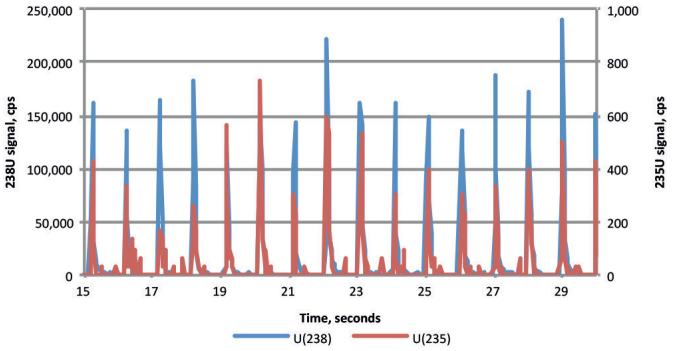

Figure 8: NIST 612 glass - 10 µm single shots at 1 Hz rep rate and 6 J/cm²

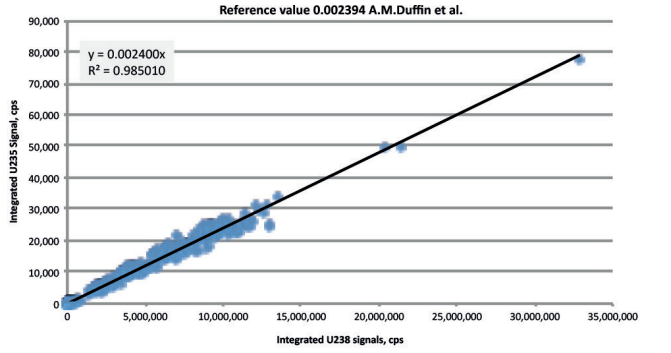

Figure 9: Linear regression plot for NIST 612 single shots over a range of spot sizes. Individual shot ratios with 2 Σ exclusion 0.002422 (10.2% RSD) Reference value 0.002394 A.M.Duffin et al.

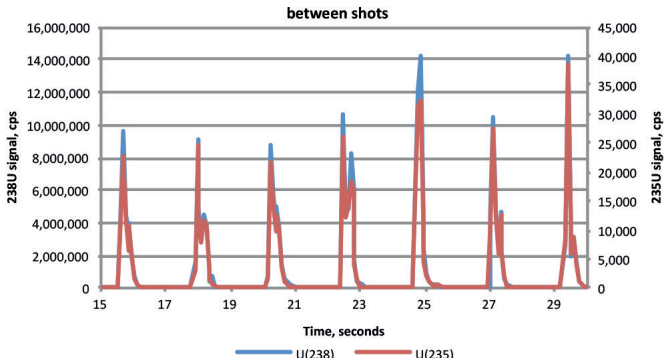

Figure 10: NIST 610 glass – 40 µm 6 J/cm² single shots with 2 second wait between shots

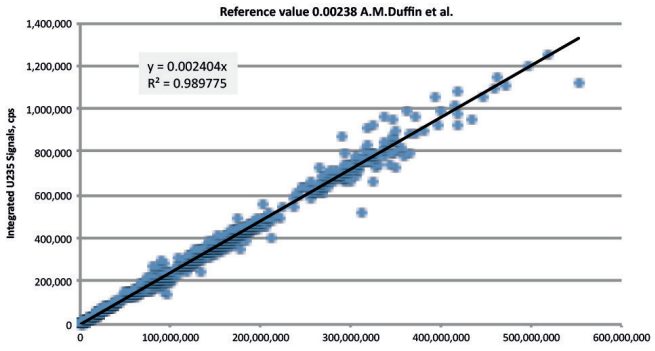

Figure 11: Linear regression plot for NIST 610 single shots over a range of spot sizes. Individual shot ratios with 2 Σ exclusions 0.002411 (6.0% RSD) Reference value 0.00238 A.M.Duffin et al.

Methodology for U-series isotope ratios on small particles.

To examine particulates, aliquots of various uranium series solution standards were added to ground and sieved milligram amounts of either calcium carbonate (approximately 100 µm particles) or silica (3-30 µm particle sizes). The liquid was left to evaporate so the uranium within the solutions would be absorbed into the particle pore structures. Dried particles were then mounted on double sided sticky tape and the individual particles ablated with single shots. The washout between each shot was set to a few seconds to allow the stage to move between particles. A range of count rates were seen indicating different levels of uptake for the uranium spikes but this also showed the linearity of the technique.

Figure 12 shows the trace profiles for ablation of calcium carbonate particles and Figures 13 and 14 show the regression plots for a range of count rates from particles doped with U010 and U050 at 100 ppm. Figure 15 shows the trace profiles for the silica particle ablations and Figures 16 and 17 show the regression plots for U010 and U500 doped particles. Figure 18 shows a screenshot from the ESI software with the image of the mounted silica particles and the defined ablation sites prior to starting a sample run.

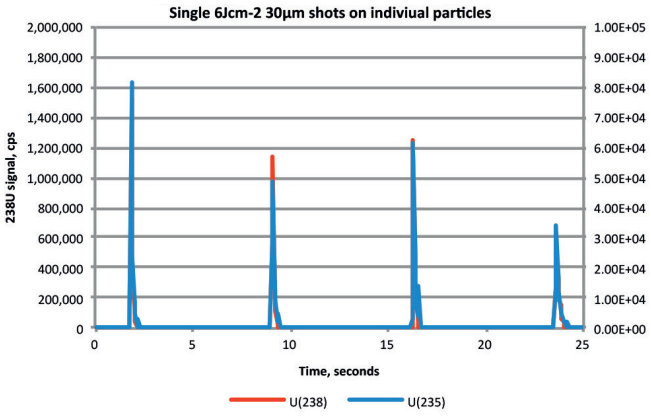

Figure 12: 100 ppm U050 doped ~100 um $CaCO_3$ particles Single 6 Jcm² 30 µm shots on indiviual particles

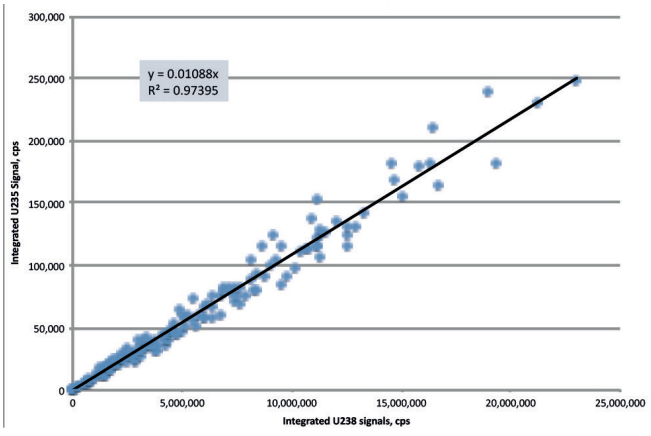

Figure 13: Linear regression plot of 100 ppm U010 doped onto ~100 µm calcium carbonate particles, single shot ablations - ref. 0.01014 Individual shot ratios 0.01069 (11.8% RSD)

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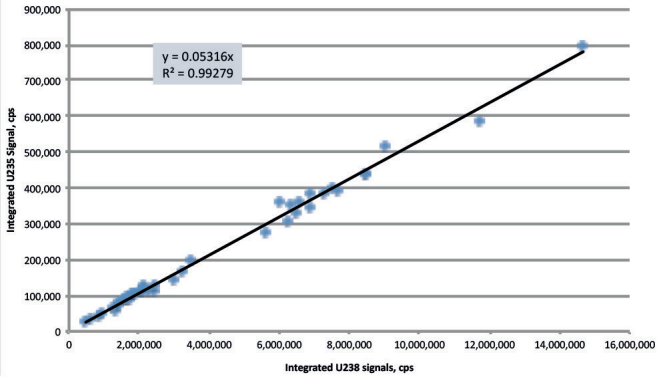

Figure 14: Linear regression plot of 100 ppm U050 doped onto ~100 µm calcium carbonate particles, single shot ablations - ref. 0.052784 Individual shot ratios 0.05401 (6.6% RSD)

The unique attenuated detector mechanism on Attom ES allowed sub-millisecond data to be acquired even when signals were in excess of $1e^8$ cps. This maintained precisions and enabled a wide range of uranium ratios to be measured accurately over a wide range of particle sizes.

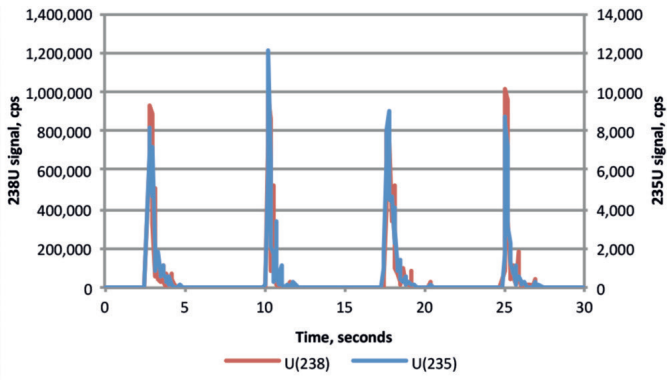

Figure 15: 100 ppm U010 doped onto 3-30 µm silica particles single shots on individual particles

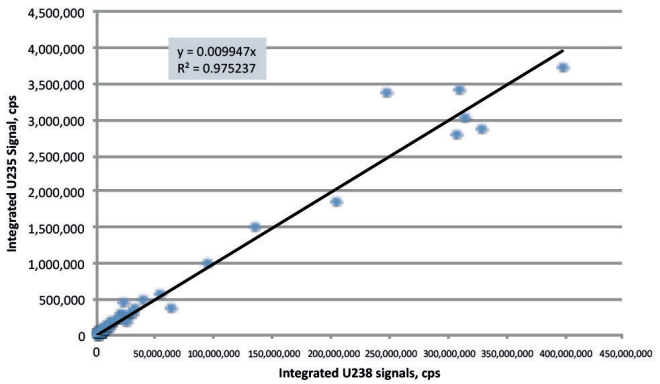

Figure 16: 100 ppm U010 doped onto silica particles 3-30 µm, reference value 0.01014, individual shot ratios 0.01124 (20.9% RSD)

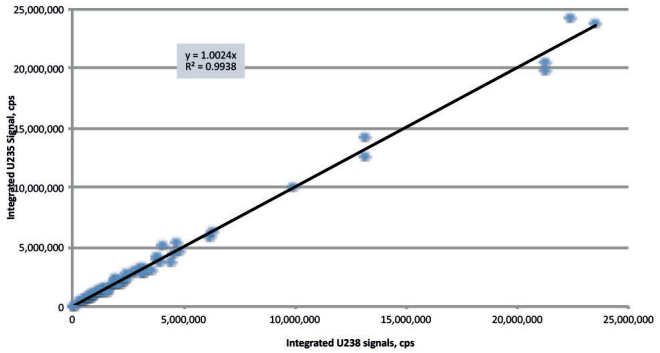

Figure 17: 100 ppm U500 doped onto silica particles 3-30 µm, reference value 0.999698, individual shot ratios 1.0186 (8.44% RSD)

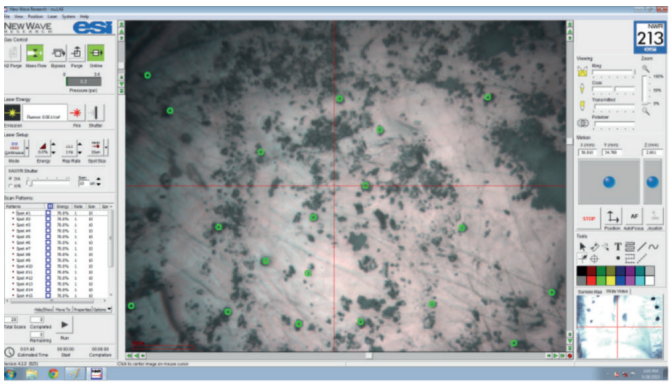

Figure 18: Mounted 3-30 µm silica powder spiked with uranium series standard to ~100 ppm.

Discussion and conclusions.

The sensitivity of both Attom ES and Nu Plasma II allowed accurate and precise ratios with single Figure %RSD to be obtained with very small spots and single shots which consumed significantly less material than the conventional techniques of ablating for several seconds with 10-20 Hz rates. The technique of integrating over the transient ablation peak adequately compensated for the skew seen with Attom ES due to the sequential measurement of peaks or with Nu Plasma II due to the response lag of the faraday detector relative to the multipliers.

The benefit of the narrow compressed signal from the TwoVol2 cell was matched extremely well with the wider dynamic range of Attom ES. Benefits were also seen with the fast data acquisition using 50 µs settling times and an attenuated detector range with up to $1e^9$ cps signal still at 300 µs dwell times to avoid larger skew effects which would make sequential isotope detection too imprecise for this work.

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The peak integration technique proved very helpful in negating the effects of laser coupling for different materials causing double peaks or particle clusters for the different materials. Even the different ablation characteristics seen between NIST 612 and 610 were compensated for with little loss in accuracy or precision.

The automated data processing with NICE in the Attom ES's Nu Quant software dramatically reduced the amount of data manipulation required by the user. Global parameter or method changes could be applied to complete batches of samples which were then processed together improving productivity significantly.

References

[1] John M Cottle, Matthew S A Horstwood & Randall R Parrish A new approach to single shot laser ablation analysis and its application to in situ Pb/U geochronology J. Anal. At. Spectrom. 2009. DOI: 10.1039/b821899d