attom ES

Combining high sensitivity and fast full mass range scanning capability for imaging by laser ablation ICP-MS with the Attom ES

Introduction

Over the past decade, interest in elemental imaging by laser ablation coupled with ICP-MS (LA-ICP-MS) has grown in several areas such as geology, biomedicine and pharmacology. LA-ICP-MS has proven to be an interesting tool for imaging due to the reduced requirement for sample preparation, high throughput, wide dynamic range, microscopic resolution and isotopic and elemental capability. Though this tool has been used more over the past few years notably, for the analysis of biological tissues, it still suffers from several disadvantages that prevent it to be routinely used. The commonly used sample cells for laser ablation systems have washouts of a few hundred milliseconds meaning that ICP-MS data acquisition rates of about 10 Hz are required to extract the optimum spatial resolution. The speed of data acquisition by quadrupole ICP-MS would then need to limit the number of elements to 5 to 15 to match this requirement. Time of Flight ICP-MS would provide data acquisition at even faster rates but this has an even greater disadvantage of sensitivity, relevant to a quadrupole ICP-MS. The sensitivity of ICP-MS is critical when considering the spatial resolution, with each halving of the spot size the signal generated per ablation is reduced by 4x. Compromises of spatial resolution or detection limit must therefore be considered along with the speed of data acquisition.

High resolution or magnetic sector ICP-MS is well established as being significantly more sensitive for laser ablation with sensitivities 5-20x greater than quadrupole ICP-MS and 20-100x greater than Time of Flight ICP-MS. Recent changes to the Attom ES have improved speed of analysis for the “Linkscan” mode enabling the acquisition of spectra from lithium to uranium in <105 ms leading to acquisition rates at the optimum for spatial resolution with established laser ablation systems.

This work will demonstrate how the use of “Linkscan” mode allows the generation of images of all ICP-MS measurable elements in one run for a 3 mm by 3 mm sample area in 4 h with a resolution of 10 µm.

Instrumental Setup

The NWR193 laser ablation system with a TwoVol[2] cell was coupled to the Attom ES with the argon make-up provided from a Cetac Aridus II so mass calibration and tuning could be done with solutions. The argon was mixed with the helium output from the laser using a t-piece close to the base of the torch. 73 elements were selected using a “LinkScan” method (Figure 1). The sample analysed was a geological thin section sample. A calibration curve was generated using the same parameters on a NIST 612. The laser parameters are presented in Table 1.

Laser Parameters	
Fluence:	8 J/cm^2
Spot size:	10 µm × 10 µm
Repetition rate:	20 Hz
Scan speed:	100 µm/s
Length of the scan:	3 mm
Number of scans:	300
Total analysis time:	3h 58 min

Table 1: Laser parameters

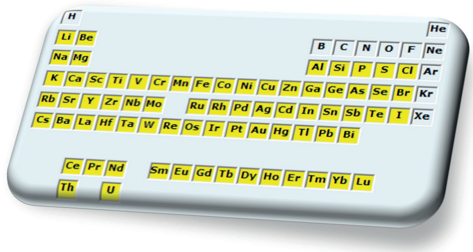

Figure 1: 73 elements measured in the method

Principles of Linkscan

Normally, the field generated by the magnet in a high-resolution ICP-MS is precisely maintained by closed loop control using the measurement from a temperature stabilised Hall Probe. The time taken to change from one field position to another will vary from a few milliseconds to tens of milliseconds with a notable hysteresis effect if the pattern of magnetic field changes (isotopes in the method).

Recent changes to the Nu Attom ES have improved the speed for the closed loop control and a more powerful 200 V power supply provides a faster hysteresis loop of 400-800 ms. This method of data collection is still too slow for the needs of full mass spectrum laser ablation. An alternative operation method is to put the magnet into a constant cycle between zero field and the maximum. This overcomes the hysteresis effect as the magnet is cycling through the same fields and there is no closed loop control, the speed is ~100 ms when driven at 200 V. A full mass spectrum can be obtained but, as the magnetic sector provides a constant resolution (M/**Δ**M), the duty cycle is not optimum. Combining the stable cycling magnet field with the fast deflector scanning provides the ability to track the ions with the deflectors in the OPPOSITE direction of the changing magnetic field and thus remain on the peak top for longer and improve the measurement duty cycle.

Data Processing

All the data were acquired in time resolved analysis (TRA) mode with the laser triggering the start of the analysis for each transect. After the analysis all the transects were imported in NuQuant. The use of a “NICE” script allows for automatic data reduction for each transect as shown in Figure 2:

•Automatic selection of baselines (based on timings from the trigger)
•Automatic selection of transect (based on signal change relative to the baseline for selected elements)
•Normalisation of each isotope to the total ion beam signal (by mass, abundance and relative sensitivity factor (RSF))

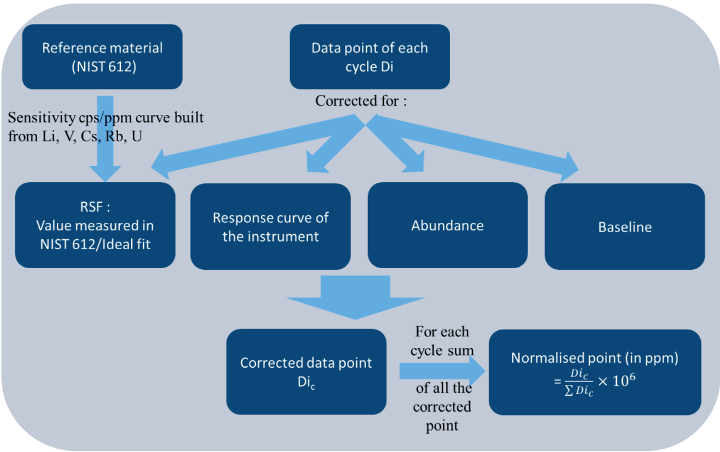

Figure 2: Schematics of the data reduction logic in NuQuant after data reduction, CSV files were exported and 3DField software (http://3dfmaps.com) was used to generate the images for each element.

Methodology

The same location on the thin section was ablated twice with different repetition rates (10 Hz and 20 Hz) to verify the reproducibility and the robustness of the method. Images generated for both ablations were similar as can be seen in the Figure 3. With the short cycle time of 102 ms combined with stage movement speeds of 100 µm/s, a spatial resolution of 10 µm can be achieved. Small clusters of few tens of micrometres can be defined with certainty which is not be the case when using the larger spot sizes needed to get enough sample signal on a quadrupole ICP-MS.

Table 2 shows the detection limits determined from the gas blanks before each transect in this data:

	LOD (ppm)		LOD (ppm)		LOD (ppm)		LOD (ppm)		LOD (ppm)		LOD (ppm)
^{107}Ag	9	^{35}Cl	99	^{178}Hf	36	^{95}Mo	108	^{185}Re	81	^{159}Tb	8
^{27}Al	411	^{59}Co	33	^{202}Hg	2	^{23}Na	2047	^{103}Rh	7	^{124}Te	124
^{75}As	151	^{52}Cr	814	^{165}Ho	8	^{93}Nb	31	^{99}Ru	82	^{232}Th	10
^{197}Au	10	^{133}Cs	10	^{127}I	49	^{146}Nd	40	^{33}S	20607	^{49}Ti	396
^{11}B	86	^{63}Cu	41	^{115}In	5	^{60}Ni	200	^{121}Sb	29	^{205}Tl	22
^{137}Ba	58	^{163}Dy	31	^{193}Ir	10	^{189}Os	13	^{45}Sc	74	^{169}Tm	15
^{9}Be	77	^{166}Er	25	^{39}K	9884	^{31}P	113	^{77}Se	20	^{238}U	5
^{209}Bi	9	^{153}Eu	11	^{139}La	8	^{208}Pb	21	^{29}Si	10378	^{51}V	17
^{79}Br	14	^{57}Fe	2868	^{7}Li	27	^{105}Pd	37	^{147}Sm	51	^{182}W	35
^{44}Ca	20545	^{69}Ga	69	^{175}Lu	9	^{141}Pr	6	^{120}Sn	80	^{89}Y	24
^{111}Cd	68	^{157}Gd	55	^{24}Mg	73	^{195}Pt	25	^{88}Sr	28	^{172}Yb	35
^{140}Ce	7	^{72}Ge	176	^{55}Mn	69	^{85}Rb	43	^{181}Ta	19	^{66}Zn	51
										^{90}Zr	28

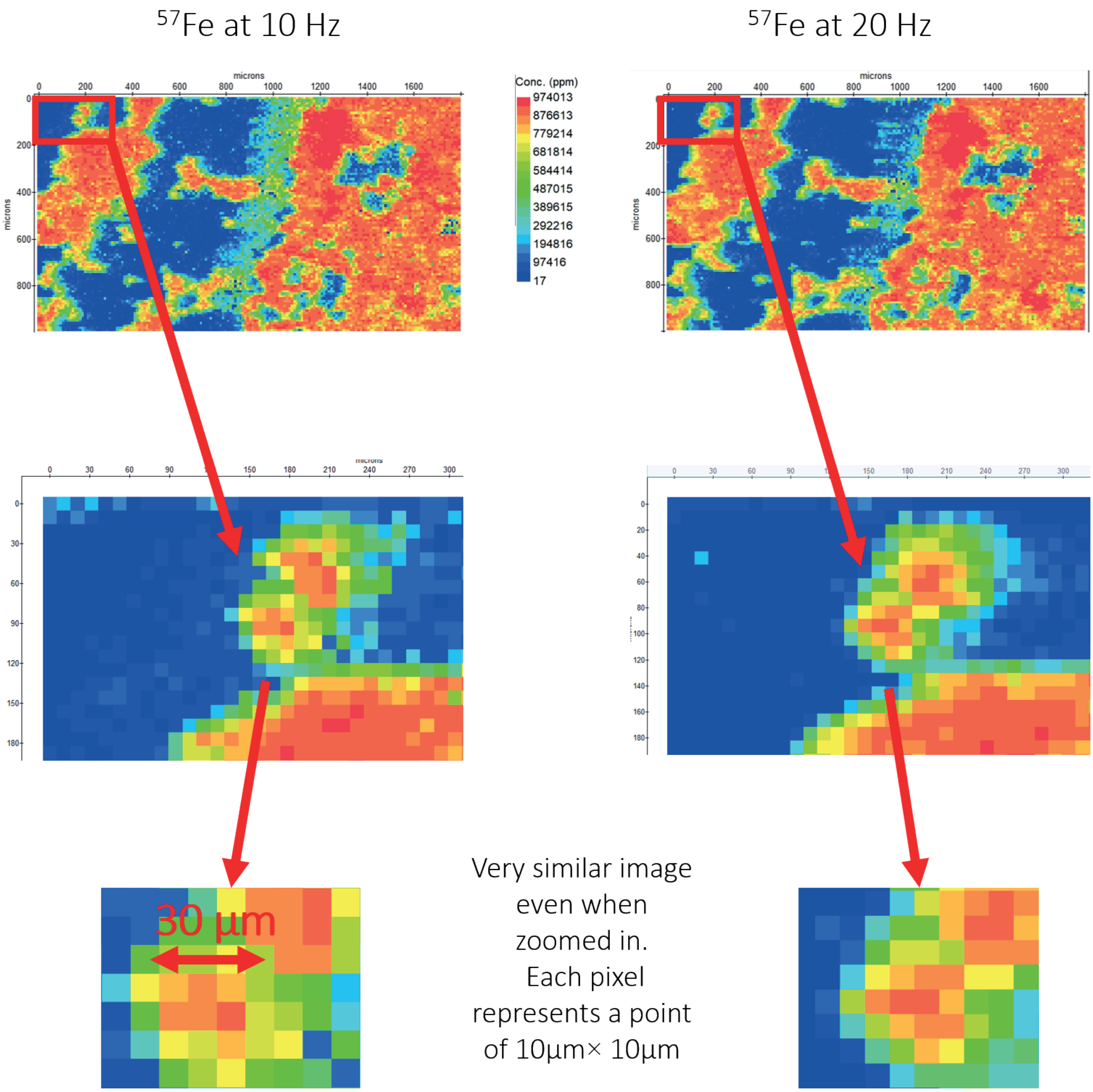

Figure 3: Images of ^{57}Fe at 10 Hz and 20 Hz

Results

Using the “LinkScan” mode with a cycle time of 102 ms, images of total mass concentration for 73 elements on a surface of 3 mm by 3 mm was generated in less than 4 hours. The wide dynamic range of the Attom ES allowed for the determination of the elements of the matrix as well as the trace elements to low ppm values. Figure 4 shows some of the images created from the 73 elements measured in this single analysis session.

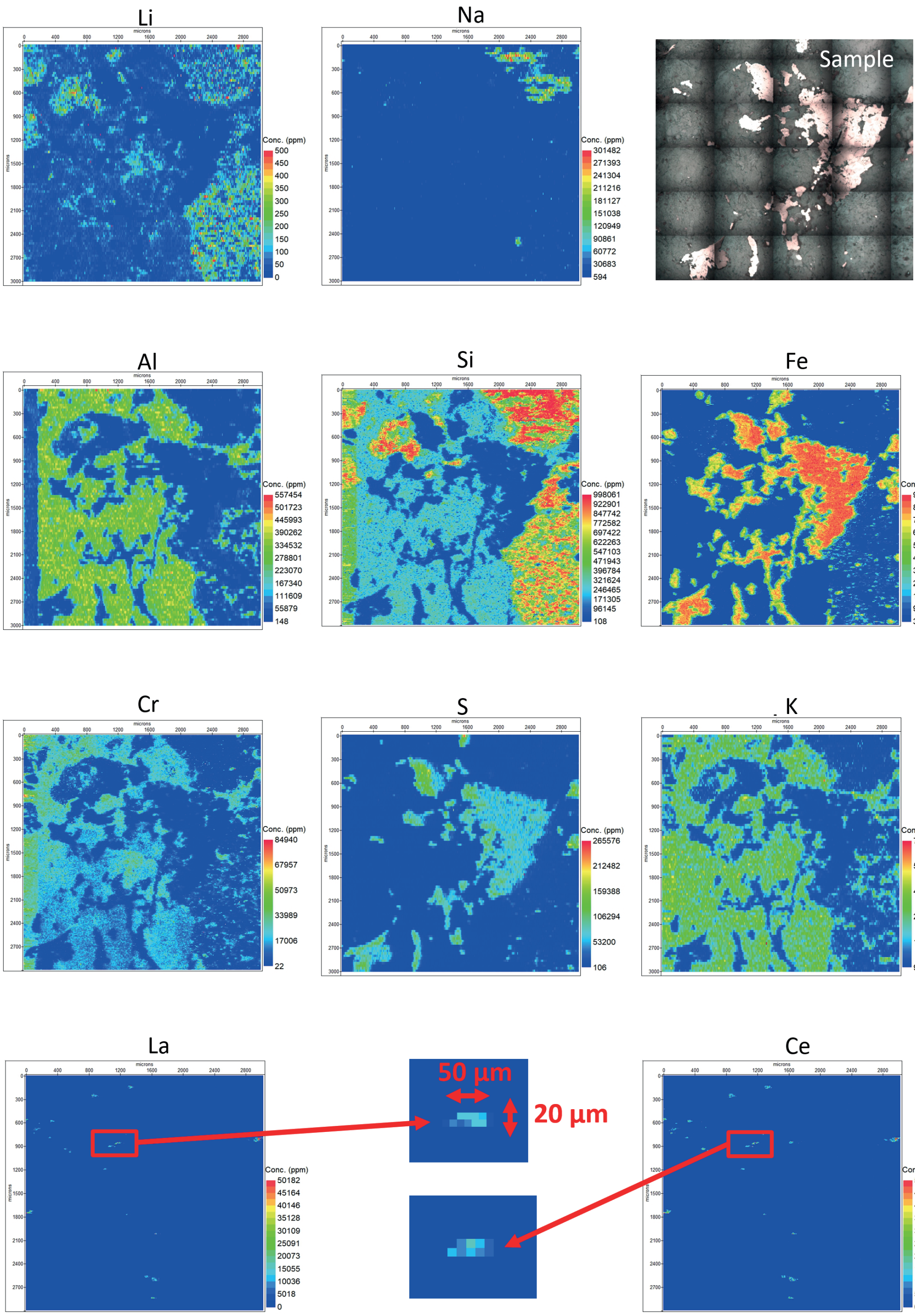

Figure 4: Examples of images generated for different elements (10 out of the 73 recorded) and zoom in a small cluster of rare earth elements.

Use of Iolite

The data is processable in Iolite (https://iolite-software.com/). The data were first opened in NuQuant to automatically isolate the required data from the baseline as NICE had more flexibility in searching for the start and end of the transect using selected isotopes. The files were then imported into Iolite.

In this example the data reduction scheme that was used was Baseline_ Substract. An example of the image generated for ^{57}Fe is presented in Figure 5.

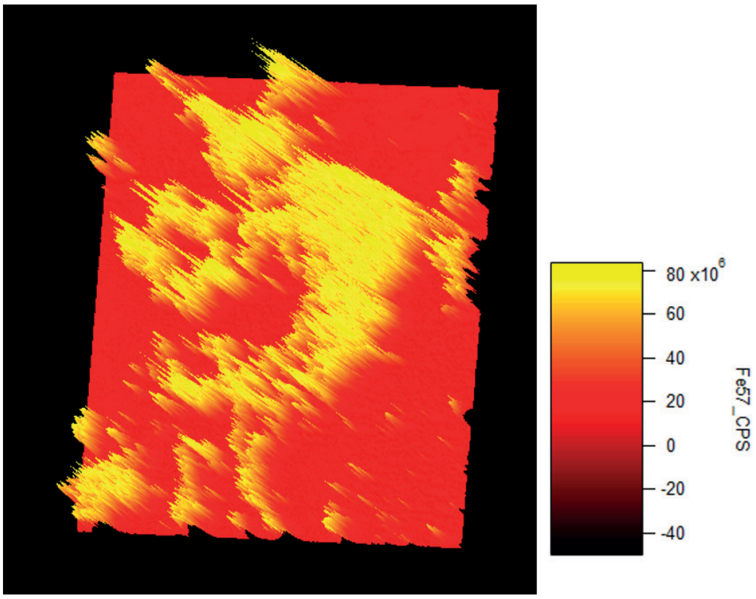

Figure 5: Image of ^{57}Fe in Iolite

Conclusion

The innovative measurement technique of "LinkScan" provided a faster and more sensitive method for imaging with the Attom ES compared to quadrupole ICP-MS. The short cycle time of 102 ms allowed for measurements of the whole mass range from low ppm to high percent levels whilst imaging at >2.3 mm^2/hr.