

Imaging with fast washout laser ablation systems using Vitesse Time of Flight ICP-MS

- **Multi-element analysis of individual laser shots**
- **Microsecond timed individual laser pulses mark peak integrations**
- **Flexible data manipulation and re-evaluation**
- **Data compatible with all popular imaging software**

Introduction

ICP-MS has proven to be a powerful analytical tool for laser ablation analysis of a variety of sample types. Historically, laser ablation systems have created transient sample signals of a few hundred milliseconds from a single shot which has been useful to obtain multi-element analysis of sample surfaces. To create multi-element images of samples, it has usually required spot sizes to be relatively large due to the dilution of the signal with time. Also, analysis times have been long as the repetition rate of the laser needed to be reduced to avoid blurring of data for one pixel into another. As laser ablation cells have developed, the washout times have reduced to a few tens of milliseconds, this has improved the sensitivity as the same amount of sample is compressed into shorter time and improved productivity as laser repetition rates have been able to be increased. However, the shorter transient signal has meant that sequential quadrupole and magnetic sector ICP-MS systems have had to restrict the number of elements being measured and take particular measures to avoid data skew such as matching laser repetition rates with data acquisition times and applying mathematical deconvolutions. Laser ablation is developing still with sample cells now being demonstrated with single figure millisecond washouts down to baseline between pulses. Sequential ICP-MS system can only realistically be used in single element mode with these new cells which means that much of the useful information on correlating elements at a particular sample position is lost.

The only realistic technique to provide multi-element analysis on millisecond timescales is Time of Flight ICP-MS. This technical note will describe how the Vitesse from Nu Instruments is designed to match the latest laser ablation technology to give high resolution multi-element images at dozens to hundreds of pixels per second.

Data acquisition considerations

The only technique capable of capturing spectra for a wide range of elements with sub-millisecond data acquisition rates is Time of Flight mass spectrometry (TOF). A TOF can acquire a near full mass spectrum in under 30 μ s but the amount of data collected can overwhelm the ability of a PC to process the spectra into counts per second values for individual isotopes unless many spectra are summed before calculating isotope counts. This has traditionally meant that TOF instruments have reported multi-element data every 3-20 ms and required data acquisition to be triggered by the pulse signal from the laser with an associated delay.

The Vitesse uses a novel data acquisition and peak processing method where ion signals are acquired at between 5 and 30 μ s per spectra but then the data is transferred directly to the Graphics Processing Unit (GPU) installed on the same PC bus as the data acquisition card. The acquired data can be transferred at 6 GB per second which is considerably faster than it is possible to write data to a hard drive. The GPU then can process the TOF data in real time to produce integrated counts per second for each isotope measured. Using this technique, it is possible to write integrated isotope count data to a Solid State Hard Drive (SSD) as it is acquired at between 0.05 and 10 ms per spectrum.

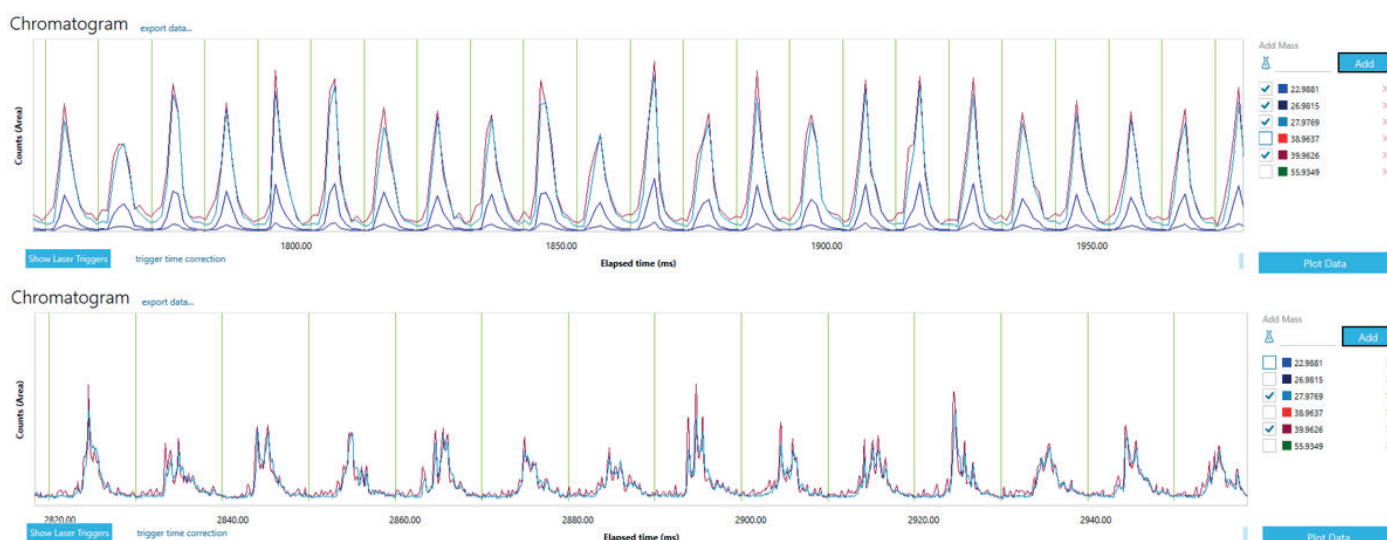


Figure 1: An ultra-low volume laser ablation sample cup with a single diameter PEEK capillary line directly through to the injector of the ICP torch was used with the Vitesse. Individual 3 μ m spots were ablated at 100Hz repetition on NIST 610 glass. The first figure shows data acquired at 1ms per spectrum and the second figure shows a second line of spots acquired at 75 μ s per spectrum. The green lines indicate the laser triggers with a delay implemented for the time between the laser striking the sample surface and the time for the signal to reach the ICP-MS detector.

Data reduction

Large amounts of data are acquired by the ICP-MS when imaging samples, this data is reduced using the measured laser triggers to demark times between which the data is averaged. The gas background is determined from data collected before the first laser trigger and subtracted from the averages between the laser markers. This integrated data is essentially the measured signal for each element in each pixel and can be associated with the X and Y laser stage positions to produce elemental maps with high levels of precision and no blurring between pixels.

The Nu Instruments Calculations Editor (NICE) scripts in Nu Quant can then be used to process the elemental signal data to get elemental concentrations in either mass or molarity using a variety of techniques. The flexibility of NICE allows the data to easily be manipulated to match the established workflows of a laboratory and format the data outputs to suit whichever image rendering software package is preferred by the user.

Image generation

Image data can be converted by NICE with examples of images for different packages shown below:

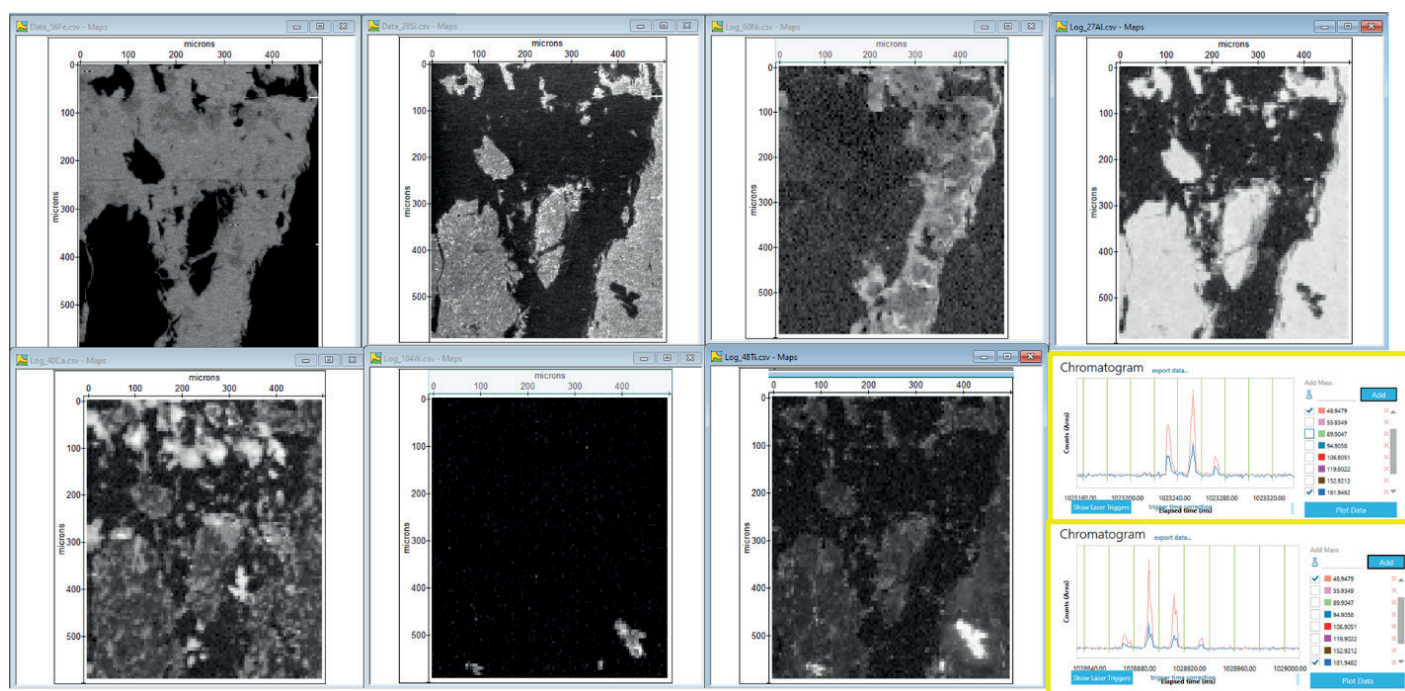


Figure 2: Image of 500 µm x 600 µm geological thin section showing linear greyscale images for 56Fe and 28Si and log greyscale images for 60 Ni, 27Al, 40 Ca, 182 W and 48 Ti. The individual 3 µm, 4J/cm² and 50 Hz laser shots are measured using 1ms mass spectra which are shown for a small tungsten feature demonstrating the high pixel resolution and absence of blurring between pixels possible using the Vitesse with the latest laser ablation cell technology. The data was collected in 18 minutes and is displayed in 3DField, an inexpensive package available from <http://www.3dfmaps.com>.

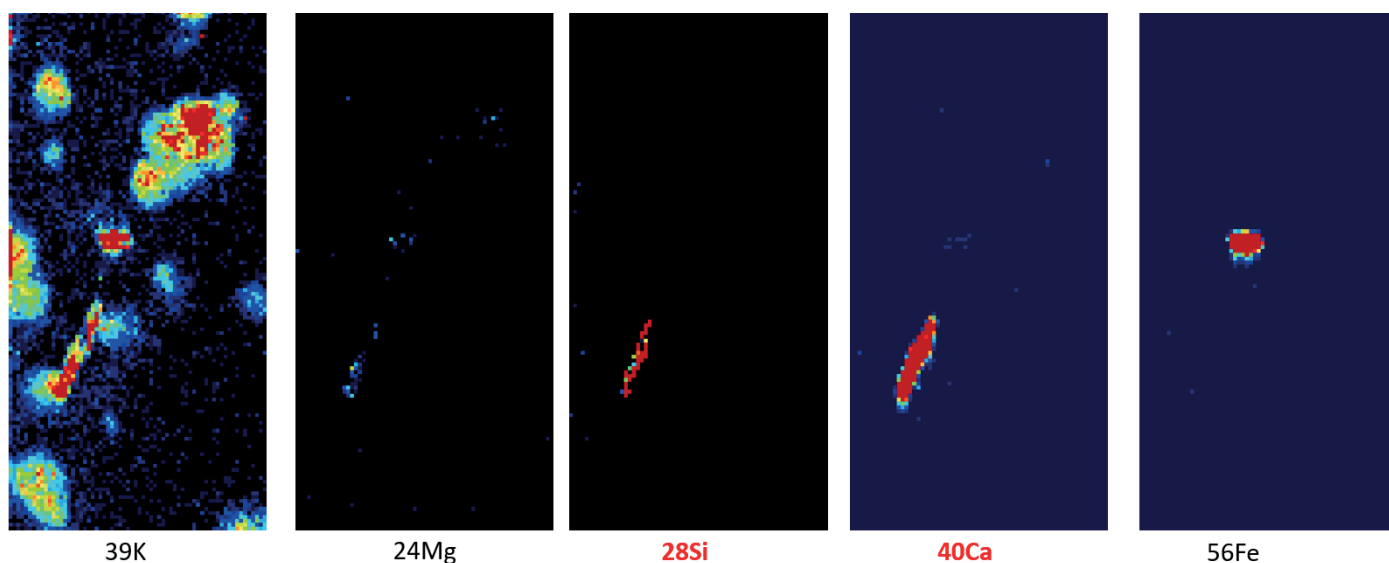


Figure 3: Images (200 x 400µm) of lung cells with embedded fibres using data collected at 10 minutes per sample (3 µm spots, 50 Hz ablation, 4J/cm², 1 ms acquisition per spectra). The multi-element analysis at high pixel resolution allows identification of the mineral composition of the fibre for disease research. This particular fibre is Wollastonite which has silicon (41.3%) and calcium (34.5%) as major components. The images were created in ImageTool v1.7 developed at Loughborough University (J. Anal. At. Spectrom., 2019,34, 1369-1373).

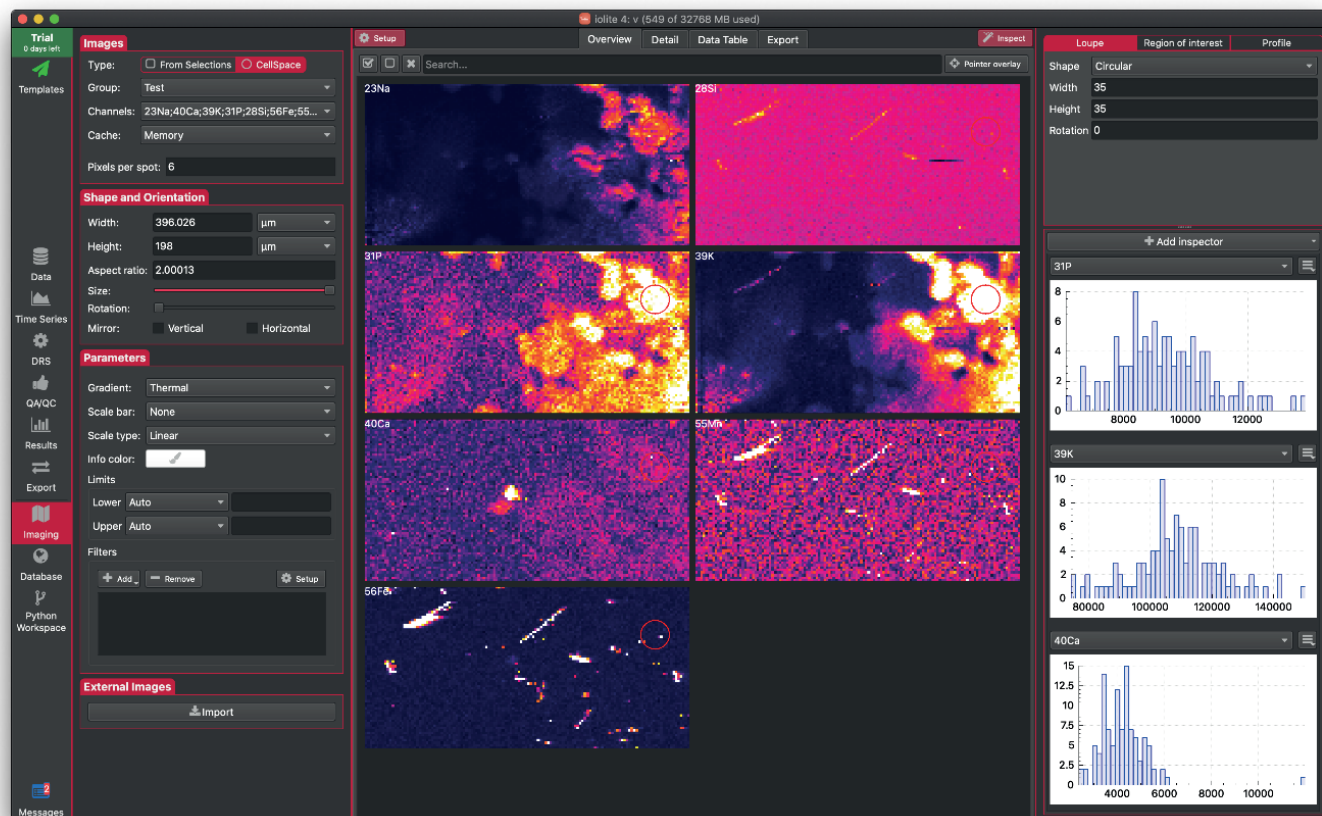


Figure 4: Lung cells with embedded fibres of actinolite using the same conditions as figure 3 (Mg 9.71%, Al 1.39%, Si 25.64%, Mn 1.3% and Fe 8.58%). The images are displayed in Iolite v4 developed at Melbourne University (<https://iolite.xyz/page-about.php>).

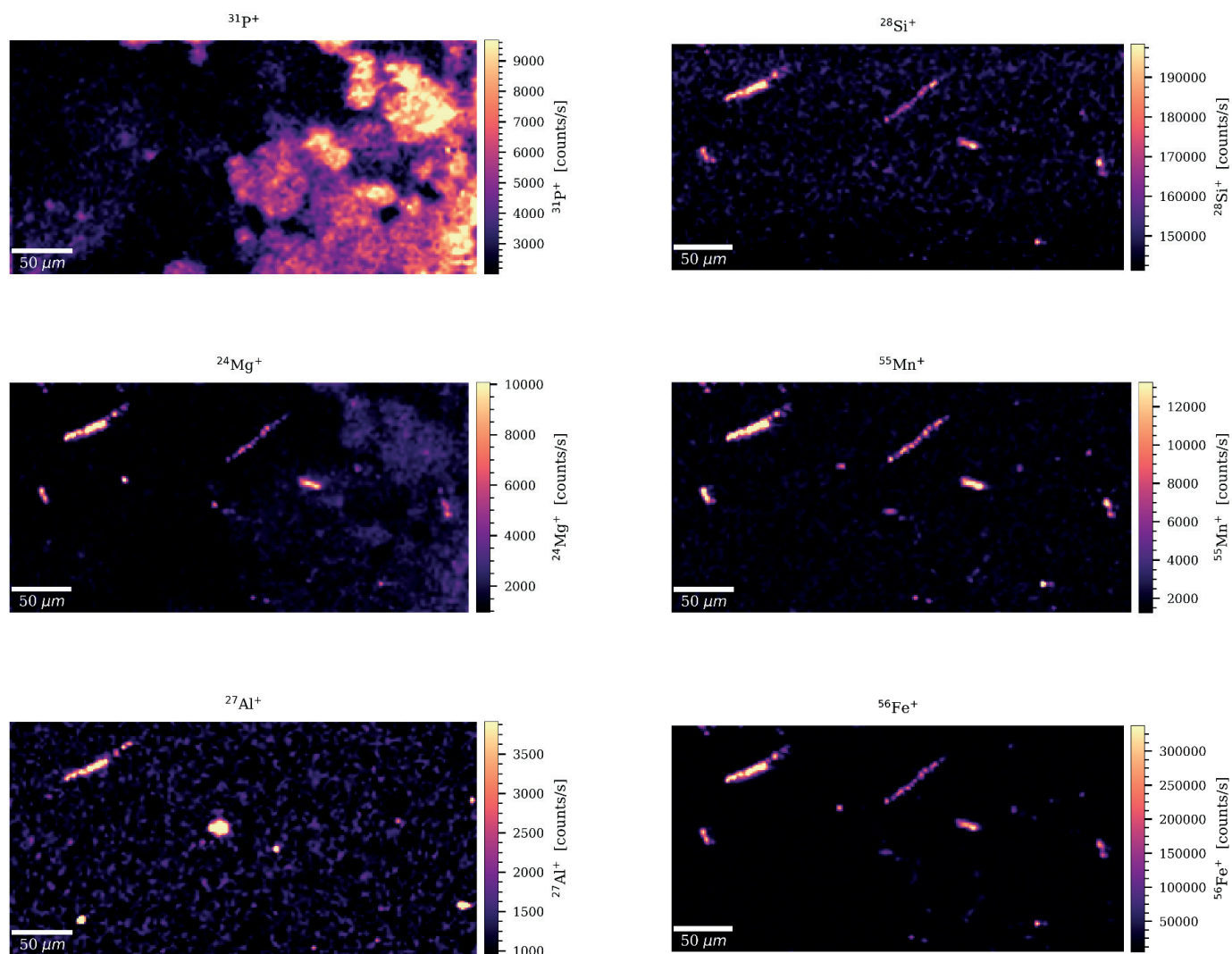


Figure 5: Lung cells with embedded fibres of actinolite, the same data used in figure 4. The images are displayed in HDIP developed at Gent University (<http://www.teledynecetac.com/products/laser-ablation/hdip-imaging-software>).

Summary

Nu Vitesse is proven to be a powerful and flexible ICP-MS with data acquisition and processing capabilities for multi-element data every 0.05-10 ms matched to the latest laser ablation cell designs. Fast, high resolution, multi-element images can be created in minutes.

The use of Nu Quant gives the flexibility to match the data processing methods to the workflows of different users and output image data in a variety of formats compatible with different image rendering software packages.