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Vitesse Time of Flight (TOF) ICP-MS: Live high speed multi-elemental imaging

- **One laser shot per pixel or multiple shots per pixel possible**
- **Total automation to acquire multiple images and calibrations in one session**
- **Live rendering and manipulation of fully processed and quantified images**
- **Automated shutdown and error handling for unattended analysis**

Vitesse - TOF-ICP-MS

Introduction

ICP-MS has proven to be a powerful analytical tool for laser ablation analysis of a variety of sample types. The Vitesse TOF-ICP-MS collects mass spectra at over 39 kHz and stores processed data to disk at up to 12,800 spectra/second meaning multiple data points can be averaged for each laser pulse, even for sub-millisecond washout times using the latest imaging ablation chambers. This note will describe the way in which this huge amount of data is reduced to individual pixels of an image. It will also describe how the data acquisition is automated for supported laser ablation systems and how the image can be calculated and rendered in real-time as it is being acquired. Finally, the note will show the methods available for image display and saving of images for use elsewhere.

Linking ICP-MS Signals to Laser Shots

Images are acquired as a sequence of parallel lines ablated from the surface of a sample where the ablated material is passed to the ICP source, vaporised, ionised and then the ions separated and counted using the time of flight mass spectrometer. To coordinate the measured spectra with the material ablated from the sample surface, a timing signal from the laser for each laser pulse is passed to the timing circuit of the Vitesse. This hardware signal provides the exact knowledge of which data is related to which laser pulse and gaps in the regular pulses from the laser when it stops to move to a different line allow the Vitesse software to separate the data for each line of the image. All data collected between the laser trigger markers (figure 1) is averaged to produce a single spectrum for each laser shot.

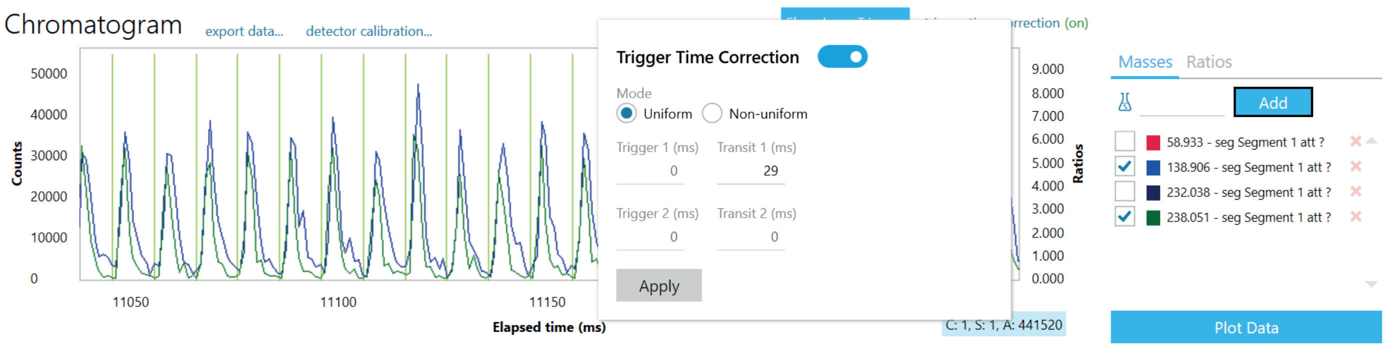

Figure 1: shows the TOF-ICP-MS signals acquired at 1ms per spectrum with the green lines indicating the time corrected laser pulses for a 100Hz ablation rate.

Linking Laser Shots to Pixels and Images

A software link between the Vitesse CoDaq instrument control software and the laser ablation software obtains the name of the image each line is associated with, the starting position of each line, the laser spot size, the spacing between laser shots and the direction of the stage movement for ablation. Images can be acquired as horizontal or vertical lines acquired in either one direction (parallel lines) or both directions (a raster of alternating line directions). If the laser stops firing between each line this allows time for the software to separate the data for each line. The laser only needs to stop for a time that is longer than the time between shots within a line.

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Preventing Aliasing Effects in the Image

Users of quadrupole ICP-MS are familiar with the careful method development required to match the data acquisition rate for the sequentially measured isotopes to the ablation rate of the laser and very often, image clarity and speed of analysis are sacrificed to ensure a stable signal for all isotopes measured. By using an ablation rate that is far faster than the washout of the laser chamber a generally steady signal for homogenous materials can be obtained for a few isotopes where the scan rate of the mass spectra is matched to some multiple of the laser ablation rate, spectra being acquired in a few tens of milliseconds. However, small differences in the acquisition and ablation rates, variation in sample washout from the chamber or drift in the timings between the system controllers of both ICP-MS and laser can become apparent in the final image (figure 2).

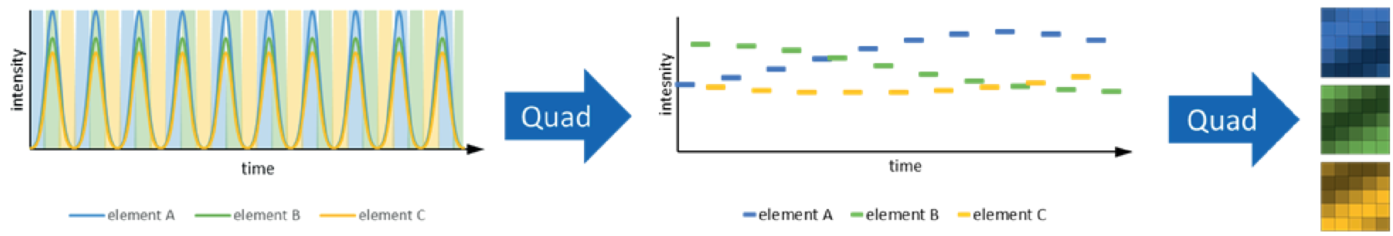

Figure 2: shows a schematic representation of how data for quadrupole ICP-MS is acquired at speeds generally lower than chamber washout rates and the criticality of synchronising the acquisition and ablation rates.

With TOF-ICP-MS, as complete mass spectra are acquired in a few tens of microseconds and summed to produce the stored spectra every 0.1-10 ms, the is no need to consider matching the laser ablation rate to the mass spectra scan speed and laser ablation chambers can be optimised to completely isolate the signals from each laser shot at up to kilohertz speeds (figure 3).

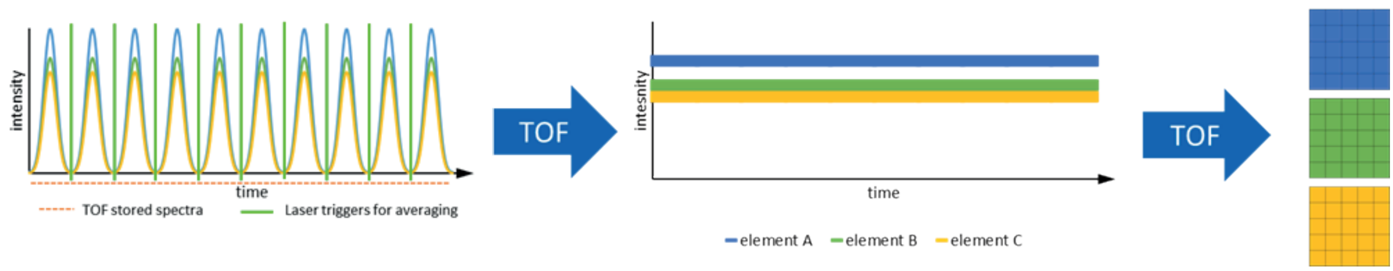

Figure 3: shows a schematic representation of TOF-ICP-MS data being acquired at rates faster than the laser ablation and how this prevents the aliasing effects that can be seen with quadrupole imaging even when the quadrupole uses much slower ablation rates for imaging.

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Calibration

Calibration data can be acquired as part of an automated sequence of patterns using the laser ablation software. By naming each group of lines separately in the laser software, the Nu Quant data processing software can separate all standards and use in built quantitation routines to define sensitivities for each isotope in the standards. Any elements not in the standards can be reported using stored relative sensitivity factors using the general instrument mass response curve calculated from the known elements in the standards (figure 4).

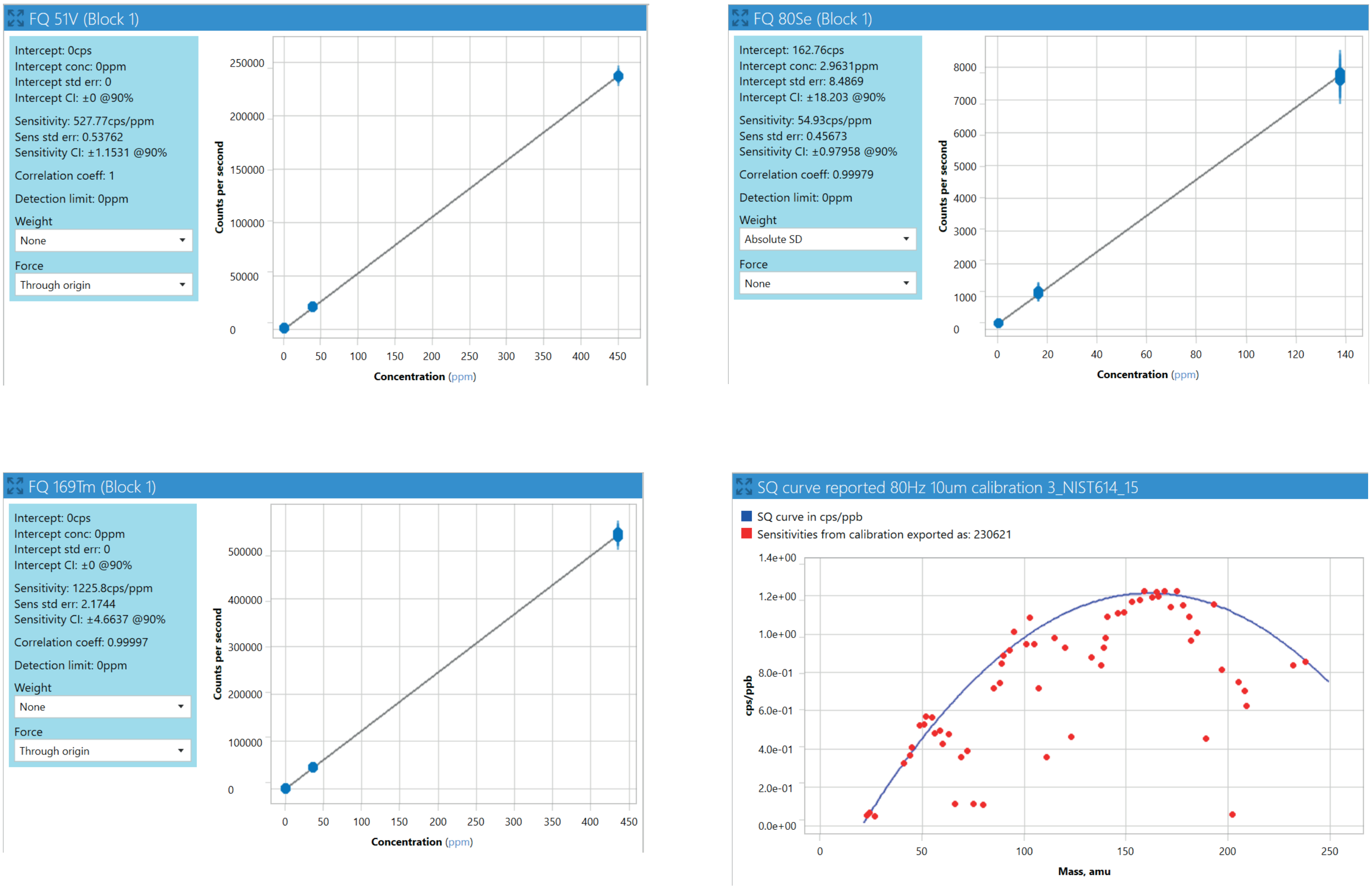

Figure 4: shows representative calibrations using NIST glasses 610, 612 and 614 and the calculation of a semi-quantitative response curve from the data that can be used for elements without reference values.

Techniques to Improve Signal to Background and Image Resolution

As the mass spectra are acquired, processed and stored to disk faster than the time between laser shots, there is a lot of flexibility to improve signal to background by using multiple laser shots for each pixel being represented in the image. Different laser software packages approach the setup of line patterns to establish this according to their own hardware requirements but, for supported systems, Nu Quant will create a pixel of the same size as the laser spot used. The number of shots used for each pixel is taken as the spot size divided by the spacing between each shot. Some ablation modes will specify the spot spacing explicitly but where necessary, CoDaq and Nu Quant can calculate the spot spacing using the ablation rate and the stage movement speed for example:

Spot size = 5 µm
Ablation rate = 80 Hz
Stage speed = 40 µm/sec

- Calculated spot spacing = 0.5 µm/shot
- Calculated shots/pixel = 10

As there are a variety of laser types (Nd:YAG, Excimer and Femto), acquisition modes (laser and stage movement synchronised or asynchronous) and ablation chamber behaviours (single millisecond to sub-second washout) the data handling needs to accommodate a variety of behaviours to ensure accurate image alignment and signal normalisation. For some laser types and ablation modes the initial few shots on each line and the final shots where the stage is accelerating or slowing down can produce signals which are not suitable for the image. During the sample data processing, it is possible to ignore the first few milliseconds of data for each line and then process only a fixed time for each line so any end of line effects are ignored.

The resolution of the image is most sharp when the ablation rate of the laser is matched to the washout time of the laser ablation chamber and each pixel is defined by a single laser shot (figure 5).

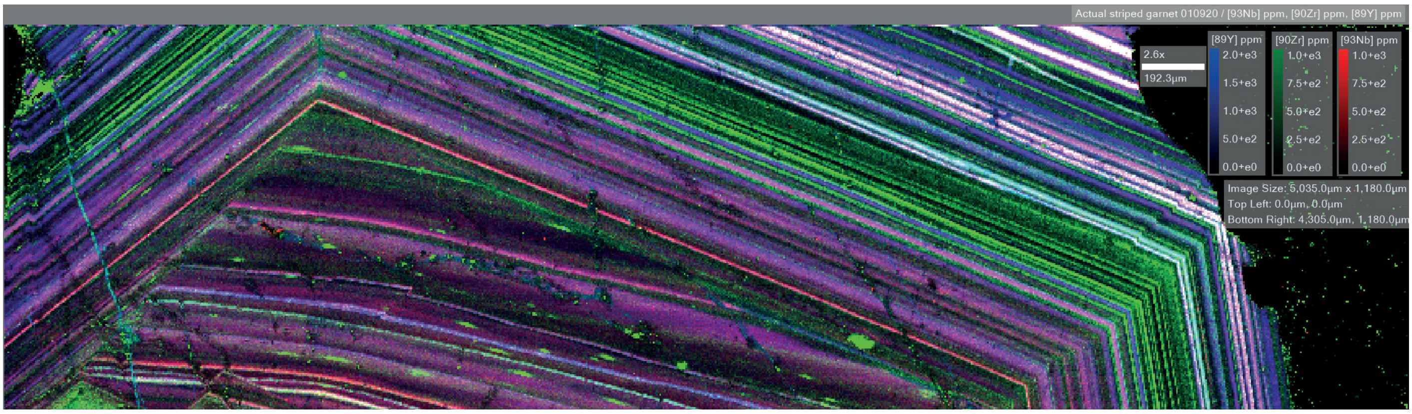

Figure 5: shows a garnet sample with very fine banding features for Y, Zr and Nb. The data was acquired with 5 µm spots, at 80 Hz with one shot per pixel and a sample chamber with <10 ms washout times (sample courtesy of John Cottle at University of California Santa Barbara (UCSB)).

However, signal to background is significantly improved where multiple shots per pixel can be recorded which will be matrix dependant. Similarly, using an ablation rate which is faster than the washout of the ablation chamber can significantly improve analysis speeds with little noticeable smearing of signals between image pixels, again depending on the matrix. By combining multiple shots per pixel and overlapping ablation shots it is possible to achieve a balance between speed of analysis, image quality and a wide dynamic range of element measurements. The flexibility in data acquisition and data processing with Vitesse enables the optimum imaging conditions to be found for each sample.

Dealing with Sample Inhomogeneity

The amount of material removed with each laser shot and some elemental fractionation effects can vary with matrix and laser focus conditions.

In circumstances where the concentration of one element is known for the whole sample, conventional internal standards techniques can compensate easily for laser focus or sample density effects as in the case of imaging porous corals using the 0.4% calcium content by weight as the internal standard (figure 6).

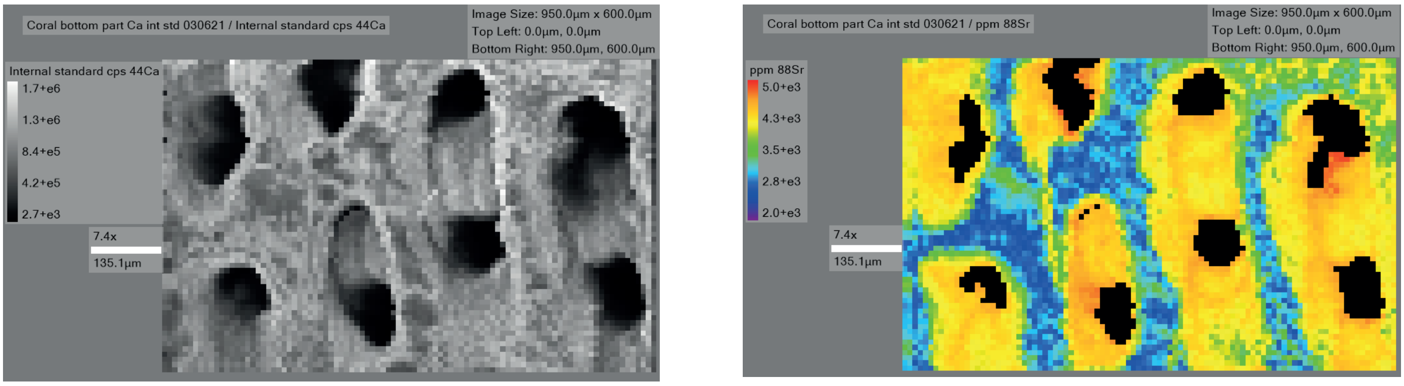

Figure 6: shows a greyscale image of the calcium internal standard signal for a porous Belize coral and the corrected strontium concentrations showing significant elevations around the pores (sample courtesy of Gavin Foster at National Oceanography Centre (NOC), UK)

The advantage of TOF-ICP-MS is that each laser shot is a near complete representation of all elements so with appropriate calibrations (fully quantitative, semi-quantitative or mixed) each pixel can be normalised to the total mass of material ablated providing compensation for laser focus where the sample surface was imperfectly polished or affected by previous ablations (figure 7).

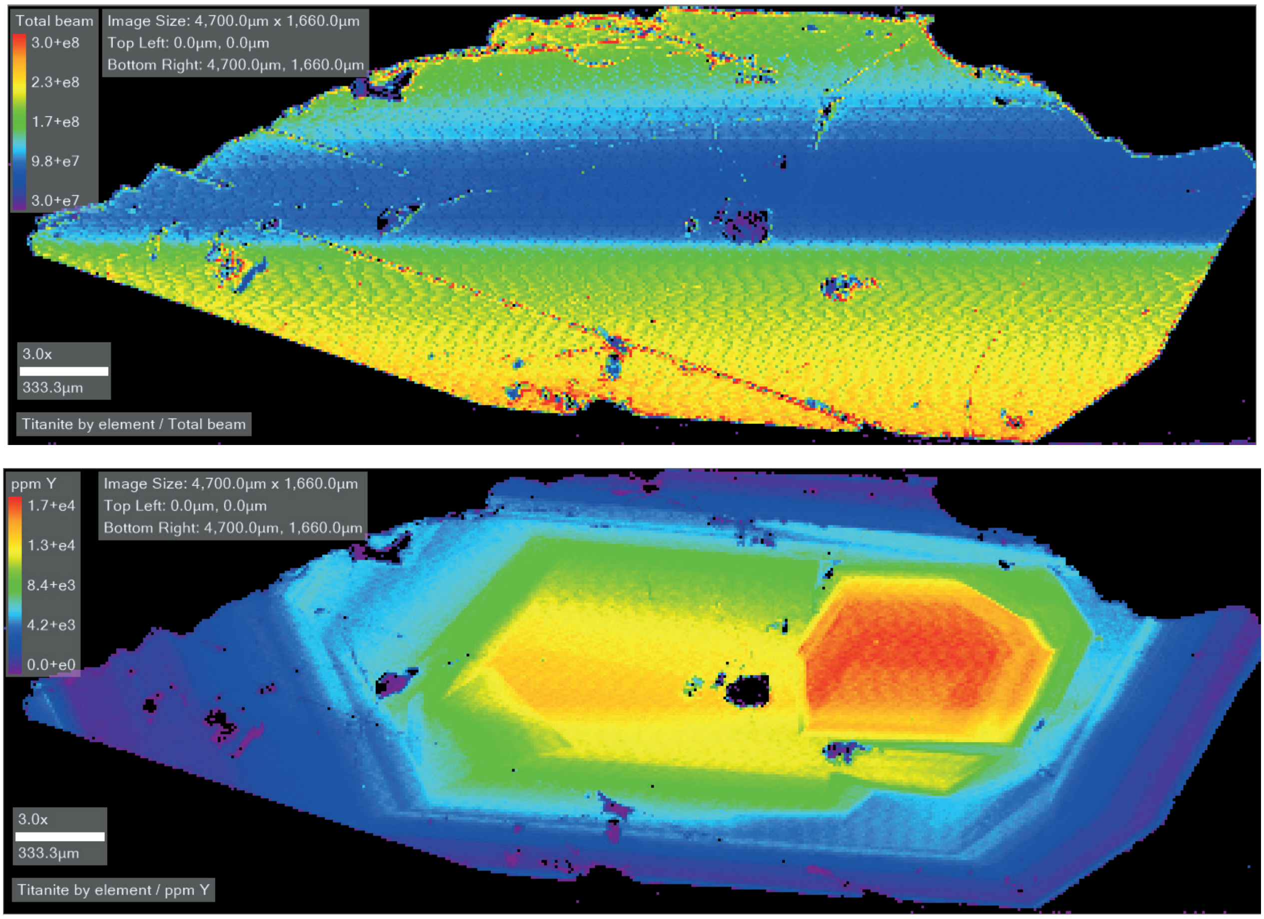

Figure 7: shows a titanite sample where the laser focus was not perfectly maintained over the complete range of patterns ablated. The total element concentrations for each pixel corrected for the differing amounts of material ablated and provided element maps such as this one shown for Y (sample courtesy of John Cottle at UCSB)

Biological materials are particularly problematic for quantitative analysis as the material for different tissue types ablates at different rates but also the concentration for any single element which might be used as an internal standard cannot often be determined for every part of the sample (figure 8).

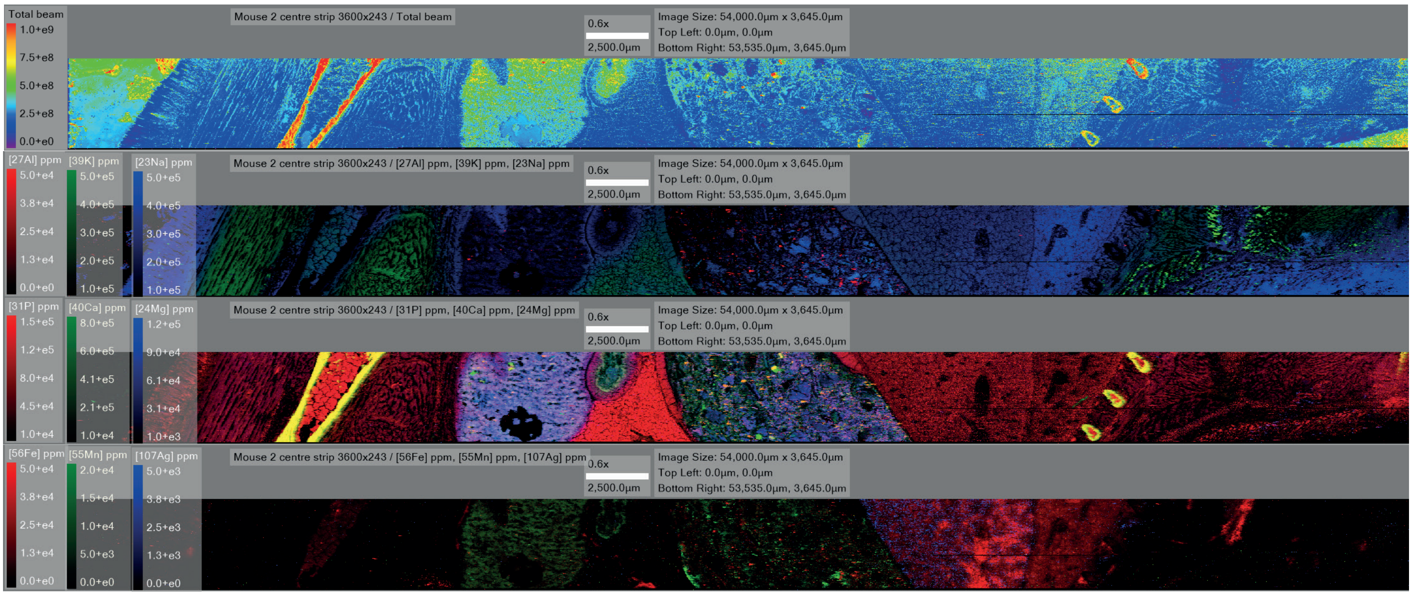

Figure 8: shows the ablation of part of a whole mouse sample, 15µm spots were used and the total sum of element concentrations showed a 20 fold variation in the total material released from each shot due to the sample matrix changes. Correction of the total amount for each pixel allowed high quality element overlay maps to be generated for a range of elements (sample courtesy of Meng Wang of the Institute of High Energy Physics, Beijing)

Improving Productivity

The most common approach to generating an image with laser ablation is to define an ablation line at one edge of the sampled area and then duplicate that line to produce a rectangle covering the area of interest. As image data collection can take many minutes and often hours, techniques that can improve image acquisition times are valuable. The use of TOF-ICP-MS and fast washout laser chambers with high repetition rate ablations will obviously improve productivity but the Vitesse has the ability to acquire data from irregular laser ablation patterns and renders the image using any starting point for the laser line and any length of line (figure 9).

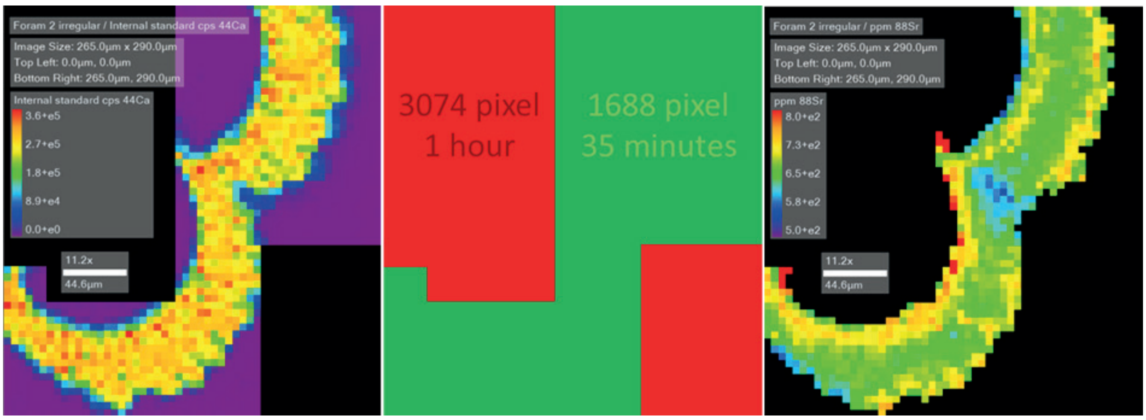

Figure 9: shows a foraminifera image where much of the ablated sample would be the mounting resin which is of no interest. By creating the image as four sections in one ablation run where all lines are defined as the same image (illustrated with the red and green sections in the schematic), it was possible to reduce the data acquisition time from 1 hour to 35 minutes with the fully quantified final image being produced in real time as the image was acquired. Strontium shows the growth banding and other simultaneously acquired elements show various growth effects from the creature's life cycle which can disrupt the climatic information obtained unless corrected on the micron scale (sample courtesy of Gavin Foster at NOC).

Image Management Tools

The Vitesse image rendering software, Nu Quant, can display images in whatever units have been defined in the processing scripts. The scripts are flexible to allow local naming conventions and calculation methods to be implemented with ease. To make it easier to manage larger images, areas of the image can be saved as “favourites” (figure 10) so the display conditions and particular images of interest can be easily recalled (figure 11):

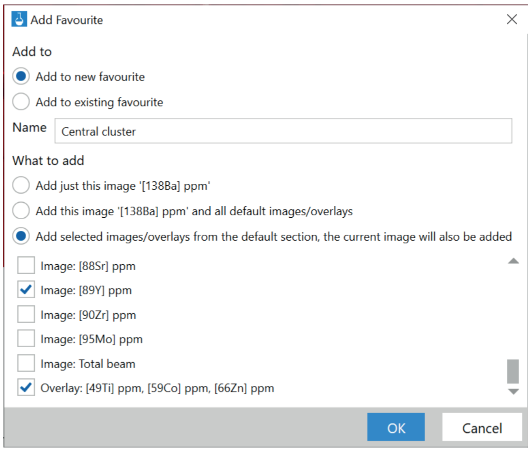

Figure 10: shows the dialog to create a region of interest and add images saved as a favourite.

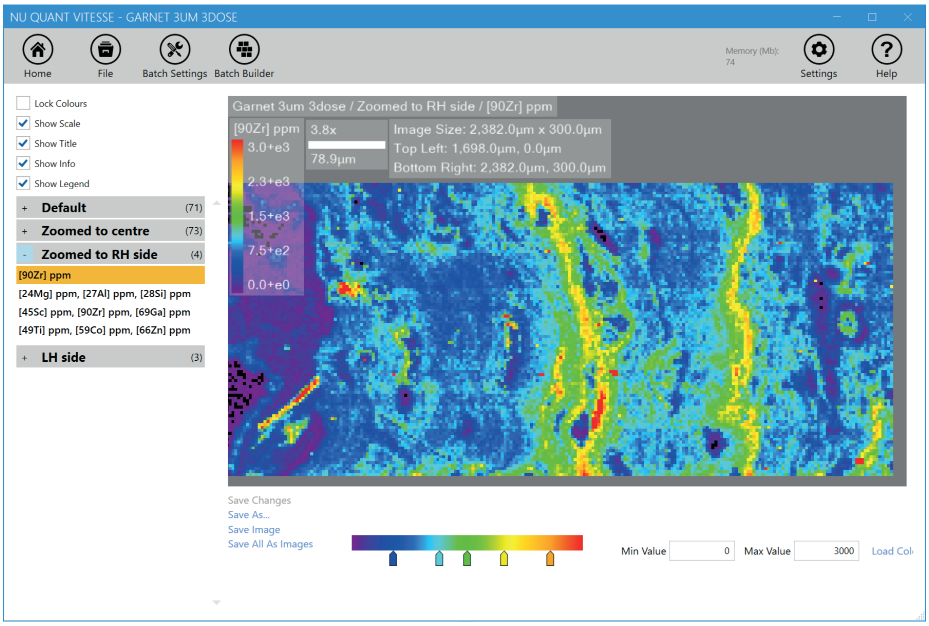

Figure 11: hows one small part of a complete sample saved as a favourite with a few images added of particular interest (sample courtesy of John Cottle UCSB).

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To compare images for different elements or ratios, creating overlays with each image being scaled as red, green or blue is easy to do (figure 12).

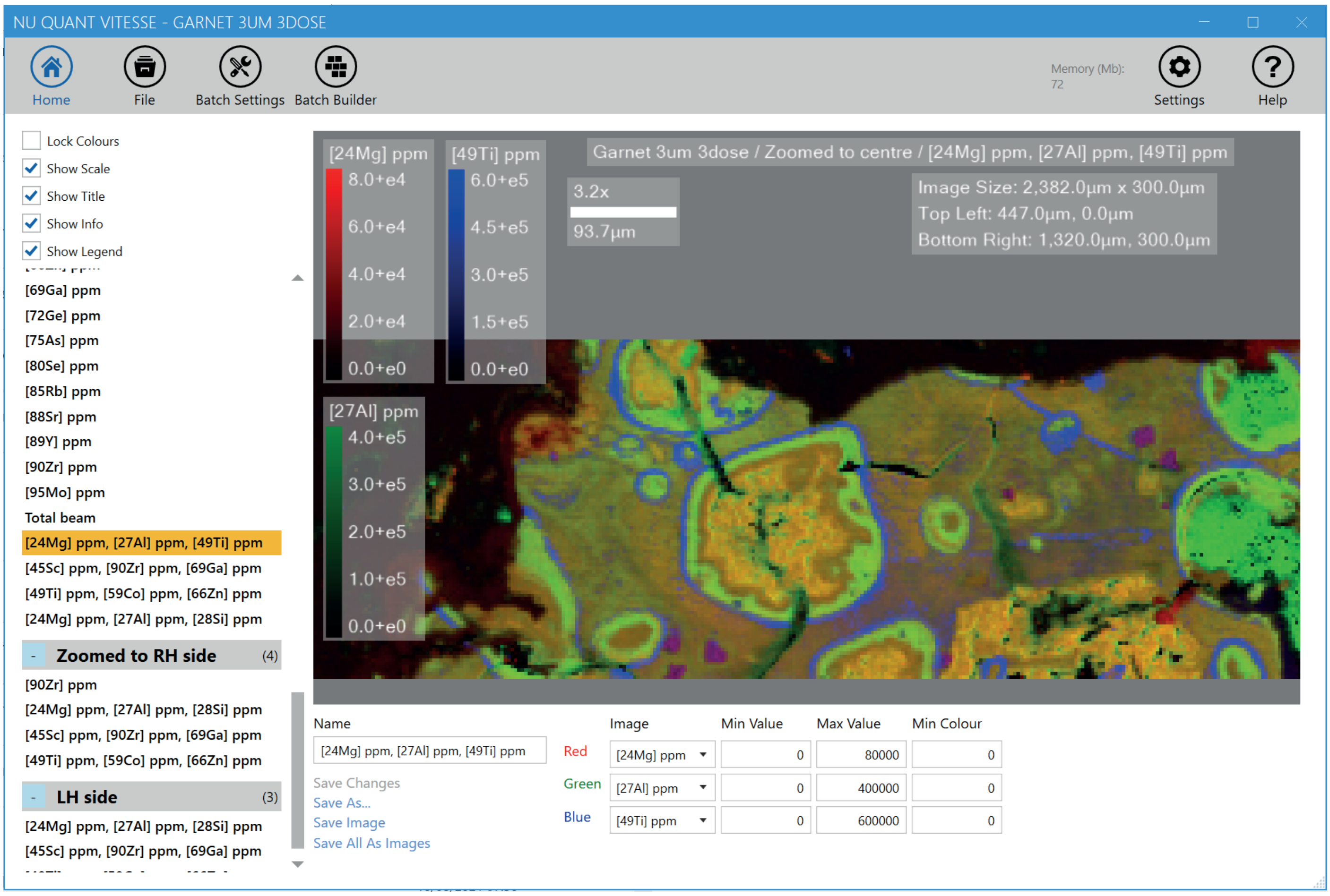

Figure 12: shows the simple workflow required to create quick, editable RGB overlays (sample courtesy of John Cottle at UCSB)

Individual images can be saved or all images saved as a batch with the option to save the whole image with a scaling factor or any favourite part as displayed on screen. The user can also choose which information panels to display and whether the minima values should be displayed as black or transparent to allow overlays on camera images of the same sample.

Unattended Analysis

As multiple calibrations and images can be defined and acquired automatically, productivity is further improved with the use of an automated shutdown process once the data collection is completed. Using the software communication between the Vitesse and laser system, the ICP-MS expects to run a set number of acquisitions. Once those acquisitions are complete, the Vitesse will request the laser to shut down the gas flows and then shutdown the plasma, saving power and consumables.
The Vitesse can also safely shutdown the plasma and laser if any error messages are received from the laser that prevent data collection or the laser does not respond to information requests from the Vitesse. Similarly, if the Vitesse shuts down for any reason such as an interruption in the cooling water or gas supplies, a gas shutdown message is sent to the laser and no further ablations take place preserving the precious samples for analysis once the fault is corrected.

Summary

The Vitesse demonstrates how images can be collected for the majority of elements in the periodic table at high pixel speeds with live rendering of fully processed quantitative images. High levels of automation with tools to improve productivity and data quality compliment the high speed and near full element coverage.