thermoscientific

Hyphenation of a high-speed laser ablation system to Quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for imaging applications

Mike Mourgas[1], Dhinesh Asogan[2], Petr Chrást[3], Daniel Kutscher[2]; Thermo Fisher Scientific (1: West Palm Beach, FL, 33407; 2: Bremen, Germany, 28199; 3: Brno, Czech Republic, 62700)

ABSTRACT

Purpose: Demonstrate the capabilities and limitations of the combination of a new laser-ablation systems dedicated to high-speed mapping with quadrupole based ICP-MS systems.

Methods: An Elemental Scientific Lasers imageGEO193 Laser Ablation system fitted with a TwoVol3 Ablation chamber was directly coupled with a Thermo Scientific™ iCAP™ TQ ICP-MS using a compatible Dual Concentric Injector. Data was acquired using Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software and processed using Iolite™ Laser Ablation Data Reduction Software.

Results: A series of tooth samples containing a range of elements in localized phases was analyzed to demonstrate the ease of coupling to a commercially available high-speed mapping laser ablation system, ease of dwell-time optimization for best signal-to-background ratio and image contrast across all scanned elements, and finally fast analysis times from sampling to image

Figure 1. Thermo Scientific iCAP TQ ICP-MS Instrument, Elemental Scientific Lasers imageGEO193 Laser Ablation System with TwoVol3 Cell, and the ESL Dual Concentric Injector (DCI) for Thermo Scientific iCAP Qnova Series ICP-MS and Thermo Scientific Neoma Multicollector ICP-MS Systems

INTRODUCTION

Laser Ablation (LA) coupled with ICP-MS is a well-established way to directly analyze solid samples. The main advantages of laser ablation include the ability to avoid lengthy and potentially contamination prone sample preparation protocols and the ability to obtain information about the spatial resolution of an analyte in a sample.

The interest in so-called mapping techniques has increased in recent years, calling for laser ablation systems to develop methods to improve sample transfer and therefore speed of mapping experiments. New laser-ablation systems dedicated to high-speed mapping are commercially available and can be easily coupled to quadrupole ICP-MS for such applications.

With the improvement in sample transfer and washout times from laser ablation systems, the time available to analyze discrete packets of sample from a laser pulse is drastically reduced. The limit for lateral resolution using a sequential ICP-MS, such as a quadrupole ICP-MS, is dependent on the dwell times chosen for each measured m/z channel. This has a direct impact on the signal-to-background ratio achievable for each m/z channel; therefore, a direct impact on the final image contrast for each mapped m/z channel.

MATERIALS AND METHODS

Sample Preparation

A human tooth was embedded in a 1-inch round epoxy resin mount and sectioned. The exposed surface was polished flat using diamond paste and cleaned before placing in the laser ablation chamber ready for analysis

Instrumentation

The choice of appropriate method settings (e.g. triple quad vs. single quad operation, reactive gas used and product ions to be analyzed in Q3) was accomplished using the Reaction Finder method development assistant in the Qtegra ISDS Software. Reaction Finder selects optimum analysis conditions despite the many available options inherent when using a triple quadrupole ICP-MS, but also leaves flexibility for testing different settings for a particular analyte.

Intelligent Mass Selection (iMS) was used on Q1 in all analyses to efficiently remove other ions potentially interfering on the product ion mass whilst maintaining highest detection sensitivity.

Method settings are summarized in Table 1.

Table 1. Instrument Configuration and Operating Parameters

Thermo Scientific iCAP TQ ICP-MS	
Injector	2.0 mm i.d., quartz
Interface	Ni Cones using a High Sensitivity (2.8 mm) Skimmer insert
RF Power	1300 W
Make-Up Flow	0.66 L·min^{-1}
CRC Flow	0.320 mL min^{-1} O_2
Elemental Scientific Lasers imageGEO193 Laser Ablation System	
Total Cell Flow	0.800 L·min^{-1} (Analytical Cup)
Spot Size	25 µm Square
Scan Type	Image Lasso Scan
Laser Energy	~3.0 J·cm^{-2}
Repetition Rate	250 Hz
Overlap / Scan Rate	20 µm / 1,250 µm sec^{-1}

Data Analysis

Data acquisition was accomplished using Qtegra ISDS Software, dwell time optimization was performed using the Precognition™ plugin of Elemental Scientific Lasers ActiveView™ 2 Software and image generation was accomplished using Iolite Laser Ablation Data Reduction Software.

For high-speed imaging applications, after tuning and optimizing the ICP-MS Instrument and laser energy for the sample matrix, the imaging workflow is as follows:

RESULTS

Washout Measurement and Optimization

For low-dispersion laser ablation set-ups, it is vitally important to assess the washout performance and peak shape of the laser pulses to determine the maximum scanning rate that can be used for a particular number of m/z channels without introducing blurring effects.

To do this, a low repetition rate line was ablated on the sample surface and a matrix element was measured at 1 ms dwell time (44Ca as 44Ca.16O in this case).

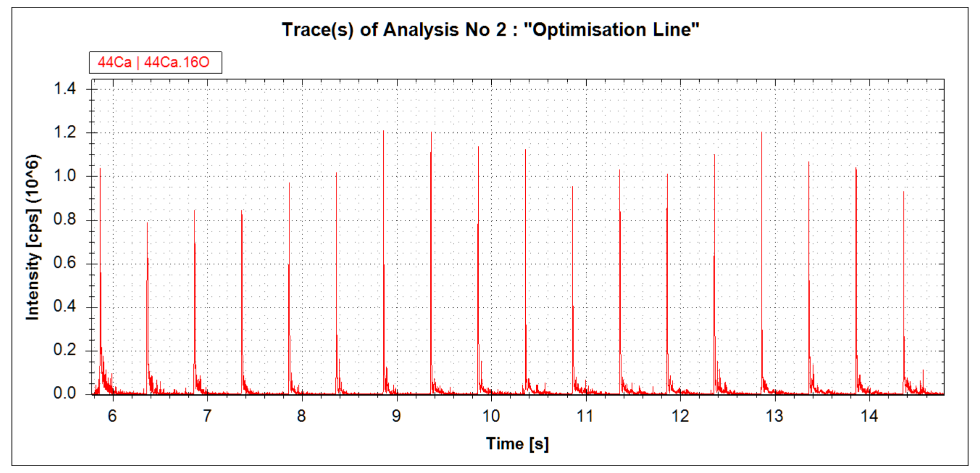

Figure 2. Example Washout Optimization Trace from Qtegra ISDS Software

The data were transferred to Microsoft Excel, using the Laser Data Reduction Export functionality in Qtegra ISDS Software, each peak was extracted, peak heights normalized to the first peak height and then all peaks were averaged. The peak width was then measured as the width of the peak at 10% peak height. Using this method, the measures peak width was 27 milliseconds, which was then used as a time constraint for subsequent dwell time optimization.

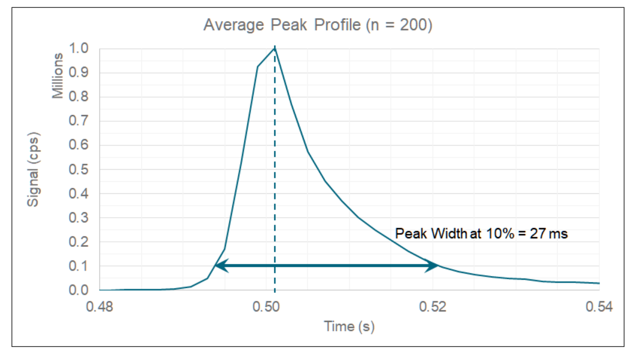

Figure 3. Average Normalized Peak Shape for the Laser Ablation Imaging Experiment using the ESL TwoVol3 Analytical Cup and DCI injector coupled to the iCAP TQ ICP-MS Instrument

Table 2. Optimized Dwell Times for Tooth Imaging using the Iolite Precognition Add-On for ActiveView2 with the Van Malderen Method

Identifier	Dwell Time (s)	Q1 Resolution
44Ca | 44Ca.16O	0.0005	Normal
88Sr | 88Sr.16O	0.0006	Normal
138Ba | 138Ba.16O	0.001	Normal
31P | 31P.16O	0.0005	High
55Mn | 55Mn	0.0036	Normal
24Mg | 24Mg	0.0004	Normal
66Zn | 66Zn	0.0007	Normal
111Cd | 111Cd	0.0031	Normal
208Pb | 208Pb	0.002	Normal
238U | 238U.16O2	0.004	Normal
45Sc | 45Sc.16O	0.0004	Normal
89Y | 89Y.16O	0.0006	Normal

Optimization of the Dwell Times was performed using the Precognition Add-On from Iolite Software available for ActiveView2 Laser Ablation Software.

Human Tooth Images

The following selected images were generated using an imaging lasso scan measuring 12,871.2 × 15,500 µm (Figure 6). At a scan rate of 1,250 µm/sec, the entire map was collected in just over 2 hours. The images show certain elements are found preferentially in the crown of the tooth vs the dentine. Various elements can be stacked to show phase separation and/or co-localization as can be seen in the example image below (Figure 5).

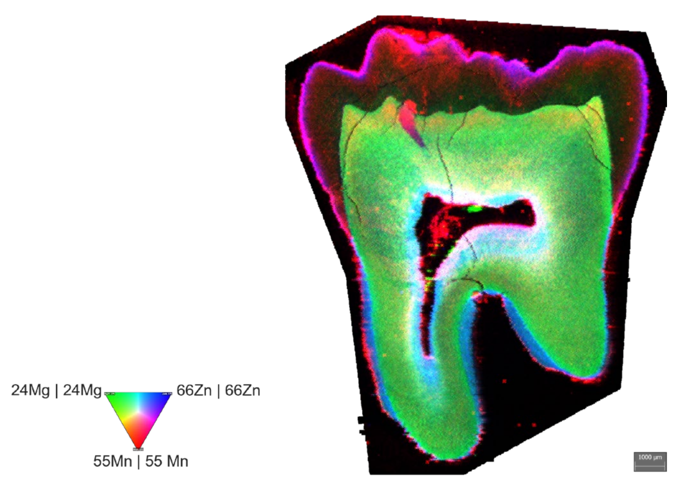

Figure 5. Three-element RGB image showing separation of Mg from Mn and Zn, and some co-localization of Mn and Zn in the tooth crown.

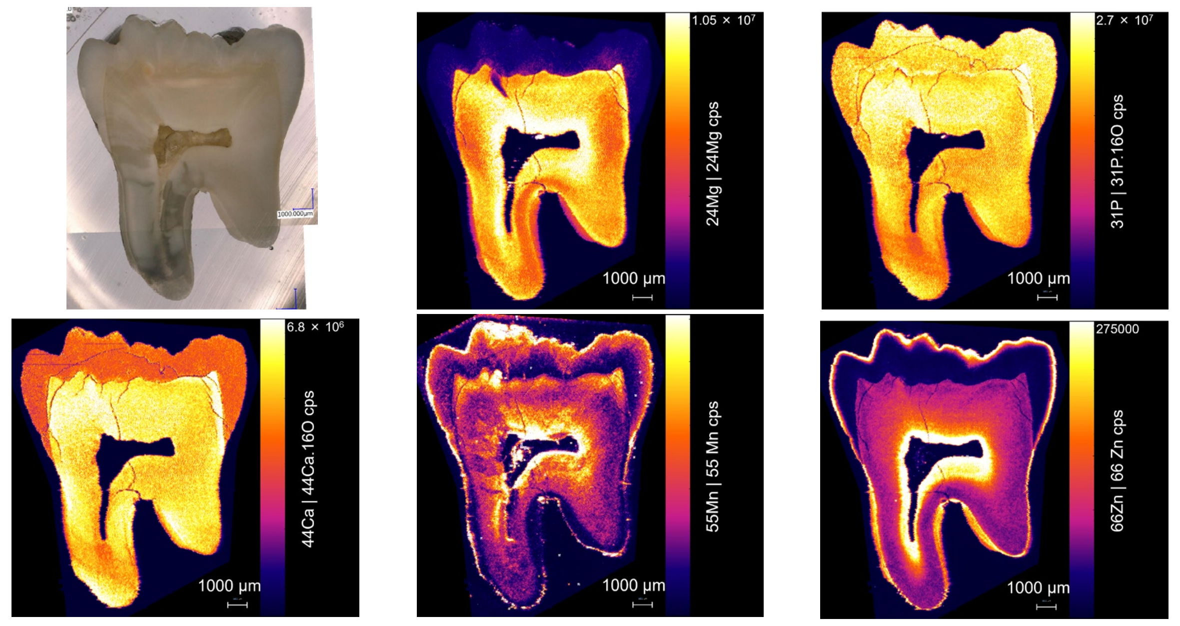

Figure 6. Selected Single Elements distributions within a human molar tooth

CONCLUSIONS

Through careful optimization of laser ablation and ICP-MS parameters, it is possible to generate high quality multi-elemental images at a fast rate. The use of new low-dispersion laser ablation cells and aerosol transfer technology is not limited to simultaneous mass spectrometers and is also applicable to sequential scanning mass spectrometers such as Quadrupole ICP-MS.

The major limitation of coupling low-dispersion Laser Ablation systems to sequential mass spectrometers is the limited number of elements that can be scanned; however, this is offset by the sensitivity and the specificity of, especially, triple quadrupole ICP-MS systems for the reduction of interferences on select analytes.

Most imaging experiments can be reduced to three or four analytes of interest, and in these cases LA-ICP-MS coupled to Triple Quadrupole ICP-MS using a low-dispersion, fast imaging setup can provide the analytical data quality required to answer challenging research questions.

REFERENCES

1. S. J. M. Van Malderen *et al.*, *Spectrochim. Acta, Part B*, 2018, 140, 29-34

ACKNOWLEDGEMENTS

The authors would like to thank the team at Elemental Scientific Lasers for providing the ESL imageGEO193 Laser Ablation System, Iolite Laser Data Reduction Software and Precognition to perform this work.

TRADEMARKS/LICENSING

© 2024 Thermo Fisher Scientific Inc. All rights reserved. Excel is a registerd trademark of Microsoft Inc. Elemental Scientific Lasers, imageGEO193, ActiveView Precognition and Iolite are trademarks of Elemental Scientific Inc. All other trademarks are the property of Thermo Fisher Scientific and its subsidiaries unless otherwise specified. This information is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others.

ThermoFisher SCIENTIFIC