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Mass spectrometry

Direct quantitative analysis and imaging of solid samples using laser equipped Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

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Introduction

Typical samples analyzed by inductively coupled plasma mass spectrometry (ICP-MS) require an initial sample preparation step to convert them into a solution. These procedures are normally labor and cost intensive, often requiring the use of hazardous chemicals such as concentrated acids that may lead to loss of certain analytes during the procedure and increase the potential for contamination.

Laser ablation (LA) enables direct analysis of solid materials and is capable of sampling a wide range of sample types, including conducting samples (e.g., metals and semiconductors), non-conducting samples (e.g., glass, mineral grains, paper, and plastics), and biological materials (e.g., tissue sections). Laser ablation can be used for localized analysis, including forensic applications like age and origin determination using elemental and isotopic composition, or bulk analysis of solid materials. It can also provide spatially resolved distribution patterns of trace elements, important for research applications in the life sciences, or an examination of geological structures. This spatially resolved analysis is essential for understanding their composition, formation history, and the geological processes that rocks, sediments, or other geological materials have undergone.[1] Laser ablation achieves typical resolution in the low μm range combined with the sensitivity and multi-element detection capabilities of ICP-MS, thus making it an indispensable tool for detailed geochemical investigations.

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This study illustrates the setup and optimization of critical parameters for LA-ICP-MS. After an initial evaluation of performance using well-established materials (glasses), the LA-ICP-MS setup was used to generate high-resolution images of the elemental distribution in a geological sample. The data allowed an opportunity to match visible structures within the sample with the concentration of different trace elements.

Experimental

Instrumentation

A Thermo Scientific™ iCAP™ MTX ICP-MS was coupled to an imageGEO193 Laser Ablation System (Elemental Scientific Lasers, Bozeman, MT, USA) for comprehensive quantitative analysis and imaging. The ablated particles were transported via a PFA tubing (4 mm i.d.) directly into the ICP-MS injector using helium gas, controlled by the laser system. The default injector (2.5 mm i.d., quartz) was used for quantitative analysis, while a dual concentric injector (DCI) was employed for imaging due to its advantage of rapid washout. Both configurations are easy to change and can be set up within minutes thanks to the user-friendly design of the instrument's sample introduction system area. Table 1 summarizes the instrument configuration and analytical parameters.

Table 1. Instrument configuration and operating parameters.

iCAP MX series ICP-MS		Laser system	
Injector	Dual Concentric Injector (DCI)	Total He flow	0.75 L·min⁻¹
RF power	1,250 W	Laser fluence	4 J·cm⁻²
Nebulizer gas	0.55 L·min⁻¹	Spot size	25 μm
Dwell time per m/z	0.5 to 4.2 ms for 15 analytes	Repetition rate	100 Hz
Total duration time	2,214 sec	Scan speed	285 μm·s⁻¹

Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used for controlling instrument parameters and data acquisition on the iCAP MTX ICP-MS. By using a dedicated plug in to control and synchronize data acquisition between the ICP-MS and the laser system, operation of the combined system was seamless, both for tuning and method optimization, as well as for unattended data acquisition across a larger area of the sample. This integration offers a significant advantage by enabling laser patterns (samples) modified in the imageGEO193 laser software, ActiveView2, to be directly imported into the sample list of Qtegra software without any additional manual input. Data acquisition was accomplished using a dedicated module (trQuant), specifically developed for laser ablation. Iolite™ software (ESL) was used for exporting and processing data to create detailed elemental and isotopic maps.

Tuning and performance checks of the instrument can be accomplished using well characterized standards, such as the NIST 610/612 glasses (National Institute of Standards and Technology, MD, USA). Figure 1 provides an overview of the process inside the main window of Qtegra ISDS software. The instrument's performance over time can be tracked using the performance monitoring tool set that is part of the Thermo Scientific™ Hawk™ Consumables and Maintenance Assistant.
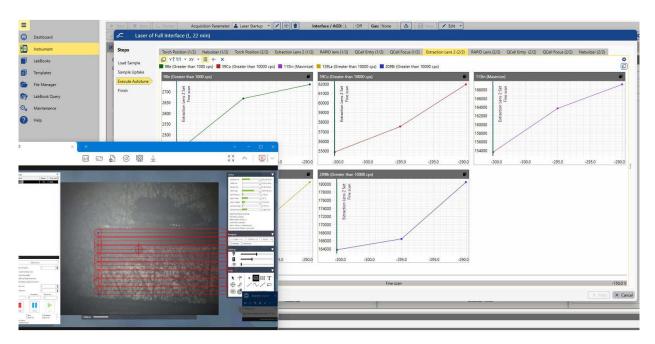
Figure 1. Screenshot of autotune with NIST 612 glass standard for LA-ICP-MS by Qtegra ISDS software.

Results and discussion

Sensitivity comparison using different analysis modes

In contrast to conventional ICP-MS analysis, which is usually performing peak-to-peak jumps on a steady state signal, switching between different modes of operation is not feasible during time resolved analysis. All analytes under investigation must therefore be monitored in a single mode, which may lead to compromises in performance (interference removal and sensitivity) for some analytes. The iCAP MTX ICP-MS offers full flexibility for leveraging different reactive gases inside the QCell collision/reaction cell (CRC) as well as different gas flow and resolution settings for both Q1 and Q3.

In this study, the sensitivity for selected analytes was compared across five different analysis modes: standard or no gas mode (STD) as baseline, kinetic energy discrimination using helium as collision gas (He KED), collisional focusing using high helium flow rates (He CCT), and triple quadrupole using either oxygen or ammonia as reactive gases (TQ-O_2 and TQ-NH_3, respectively). The elements analyzed ranged from low mass (^{39}K) to high mass (^{238}U), providing a comprehensive understanding of sensitivity differences across the mass spectrum. Results are displayed in Figure 2.

The use of kinetic energy discrimination with helium is a well-known option in conventional ICP-MS analyses, as it helps to significantly reduce the impact of polyatomic interferences. Whereas typical sensitivity is slightly reduced compared to no-gas mode, signal-to-noise ratios for elements such as arsenic (As) and selenium (Se) are often significantly improved. However, He KED is unable to eliminate other types of interferences, such as doubly charged species or isobaric overlaps.

The use of helium as an inert collision gas in the QCell also leads to collisional focusing, a phenomenon that reduces the inherited spread of the ion beam as positively charged ions repel each other. Collisional focusing leads to a signal increase (versus standard mode) for analytes with higher mass (here ^{140}Ce, ^{175}Lu, and ^{238}U), and can be an effective tool to boost sensitivity if spectral interferences are not expected. Please note that this mode (contrary to KED mode) utilizes a positive bias potential between the QCell CRC and the analyzing quadrupole of the system, so that potential interferences are not actively removed.

The use of oxygen (O_2) as a reactive gas is a powerful tool to enable sensitive and interference-free detection for elements suffering from polyatomic and isobaric overlaps. Due to the reactive nature of the gas, effective mass filtration before the CRC is required to avoid unwanted side reactions of other ions generated from a sample. TQ-O_2 mode provided moderate sensitivity improvements across most elements, with previous research highlighting its high sensitivity for rare earth elements (REEs).[2] In the context of this work, the use of TQ-O_2 can help improve the performance of critical elements, such as the lanthanide series (La-Lu). It can also be used to remove isobaric overlaps of, for example, ^{87}Rb on ^{87}Sr.

The use of ammonia (NH_3) as a reactive gas can be beneficial for some analytes. Ammonia induces a series of highly selective ion-molecule reactions and may lead to the formation of multiple product ions for a given analyte. This may lead to lower sensitivity for the analytes investigated here (i.e., ^{89}Y, ^{140}Ce, and ^{175}Lu), but also leads to unmatched interference removal in certain cases (i.e., removal of isobaric ^{176}Lu from ^{176}Hf).[3]
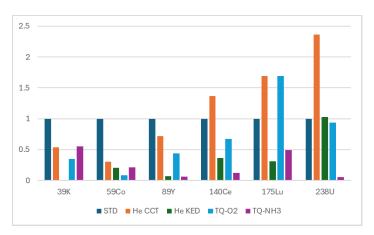
Figure 2. The sensitivity comparison between five different analysis modes using LA-ICP-MS. U was analyzed as $^{238}U^{16}O^{16}O$ in TQ-O$_2$ mode.

In summary, the choice of analysis mode in LA-ICP-MS impacts the achievable sensitivity for different elements. Standard or no gas mode may be more applicable when using laser ablation instead of conventional liquid sample analysis because the resulting dry plasma conditions generally lead to a lower formation of polyatomic interferences. However, KED mode often remains the default choice to suppress potential false positive results. The use of helium as a collision gas combined with a negative bias potential between the collision cell and the analyzing quadrupole can be a way to significantly improve sensitivity for elements in the mid- and high-mass range because collisional focusing occurs and reduces the natural dispersion of the ion beam. To combine sensitivity increases with interference removal, the use of TQ-O$_2$ is an ideal choice. This mode allows for comprehensive removal of a wide range of interferences while providing excellent sensitivity. The advanced interference removal can help with overcoming otherwise challenging isobaric overlaps.

TQ-NH$_3$ mode, although lower in sensitivity, effectively eliminates complex interferences, enabling the removal of ^{204}Hg from ^{204}Pb, a critical interference for uranium/lead dating. Since reactions with ammonia may lead to a wide range of potential product ions from a series of elements, prefiltration of the ion beam in Q1 is mandatory

to obtain unbiased and correct results. Understanding these differences is crucial for selecting the appropriate mode based on the specific analytical requirements and the elements of interest.

Mapping of the elemental distribution across the surface of a sample

Elemental images or maps refer to an LA-ICP-MS analysis that provides information on the spatial distribution of one or multiple elements across a two-dimensional area of a sample, like a mineral grain or a biological tissue section. As the laser is fired at the sample surface, the sample is moved at a defined and constant rate. This means that the time profile of a line scan can be translated into a distance profile. Gathering multiple profiles across the sample generates a 2D image of the elemental distribution in the sample (3D after moving the laser sampling point in the vertical axis), where signal intensity is directly proportional to concentration. However, the quality of the resulting image depends on a series of factors. While small spot sizes and overlapping of single shots increase the resolution of an image, the reduced amount of ablated material may cause signals for individual analytes to be only detectable slightly above background. At the same time, small spot sizes along with low repetition rates lead to a substantial duration of the time required to map or image a small area of a sample. The use of laser systems with high repetition rates is a solution to the above-mentioned limitations, but parameters need to be carefully optimized to avoid artifacts limiting the image quality.

This section explains the workflow of how to implement a procedure using LA-ICP-MS for imaging an area within an agate (donated by an agate collector), a banded chalcedony known for its wide variety of colors and patterns, resulting from its unique formation process (Figure 3). This technique provides comprehensive elemental analysis and distribution mapping across layers with high spatial resolution and precise depth profiling. By eliminating the need for extensive sample preparation, it is particularly suited for the investigation of complex geological structures. LA-ICP-MS serves as a powerful tool for the detailed exploration of the spatial distribution of the elemental composition.
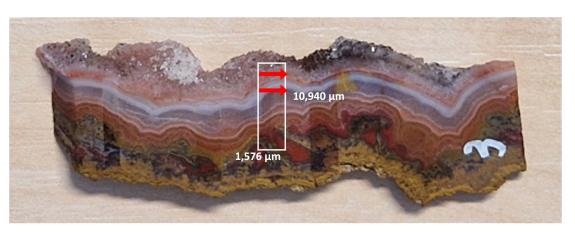

Figure 3. Photographic image of the sample. The white rectangle indicates the area that was selected for image generation, whereas the red arrows show the direction of line scans that were conducted during the analysis.

Optimization of parameters for laser ablation and data acquisition

The optimization of measurement parameters for imaging applications needs to focus on two important outcomes even though resolution of individual features of a sample ideally requires the use of small laser spot sizes. There are different approaches to reduce the (incremental) sampled area, however, a reduction in the amount of ablated material reduces the observed signal in the ICP-MS and increases the time needed to completely scan a previously identified area. For efficient transfer of ablated material and fast analysis of a large area, the use of laser systems with high repetition rates and specially designed ablation cells that allow complete transfer of the material ablated in a single laser shot have become the default choice.

Lateral smearing is a potential artifact that can affect image quality for images acquired at high repetition rates caused by incomplete washout from the ablation cell. Figure 4 shows a comparison of the peak shape of the signal of ^{238}U for individual laser pulses generated with a repetition rate of 1 Hz using two different helium gas flows. The data demonstrates that the higher helium gas flow rate of 750 mL·min^{-1} results in complete and fast washout and therefore generates symmetrical peaks with high signal intensity. The lower flow rate (450 mL·min^{-1}) leads to an asymmetrical peak shape prone to increased lateral smearing in a resulting image.
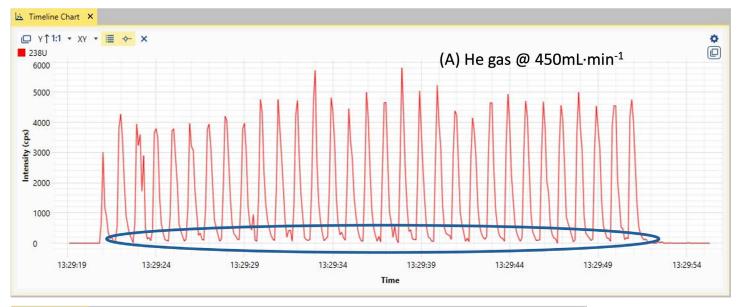

Figure 4. Comparison of washout time and peak shape between two different helium gas flow rates.

Optimization of data acquisition parameters

All quadrupole-based ICP-MS systems sequentially scan different m/z ratios. For short transient signals, this means that a compromise must be found between the available duration of a signal, and the individual measurement time and total number of analytes. Individual dwell times may depend on the analytes of interest and the expected signal intensity in the sample. To determine the optimized dwell time settings for all analytes, a pre-screening using a line pattern was conducted to identify the elements present, utilizing a 500 μs integration time per analyte.

Subsequently, the final integration times, along with laser settings such as repetition rate, spot size, and scan speed,

were thoroughly reassessed based on the pre-screening results of Excel calculations, which analyzed both the intensities and background signals.

Conversion of raw data to an image

All raw data gathered in the analysis were automatically exported to the imageGEO193 laser software, ActiveView2. Importing the LAX file from ActiveView2 into the Iolite™ software generates elemental maps data with different steps conducted automatically during data processing (i.e., subtraction of the gas blank from the ablation area). Figure 5 illustrates how the data collected in the entire analysis reflects the individual line scans conducted.
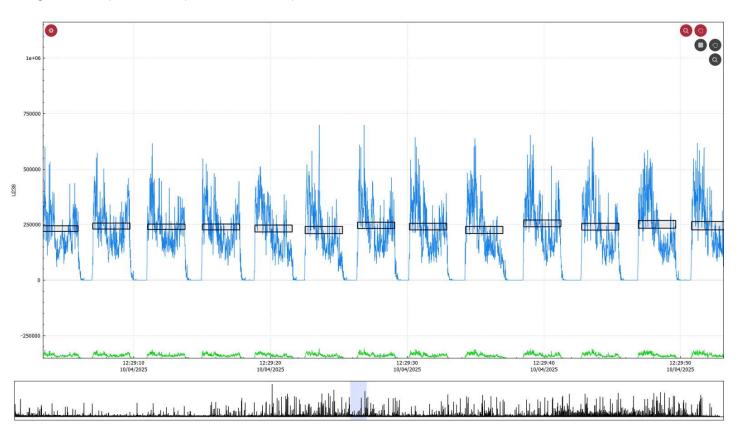

Figure 5. Example of TRA results in Iolite™ software. Bottom window: Signal acquired during the entire duration of the analysis. Shown here is the data for ^{238}U, which is visible to be distributed homogenously across the sample surface. Top image: Zoom into a previously selected part of the data set.

The images created for a selected panel of elements are shown in Figure 6, together with an optical image of the visible structures. The color coding reflects the relative intensity distribution over the sampled area with the maximum observed intensity value for each analyte displayed as well. The obtained relative results can be converted into quantitative concentrations if suitable calibration standards are available.

The data reveals distinct spatial distribution patterns of multiple elements (Al, Si, Fe, Ce, Pb, and U) within the analyzed sample. The elemental maps display varying concentrations represented by a color gradient from blue (low concentration) to red (high concentration).

Aluminum (Al) and Silicon (Si) show similar distribution patterns, which are consistent with the fundamental silica-rich nature of agate. The banding patterns visible in these elements reflect the characteristic concentric structure of agate formation, where silica-rich solutions precipitated rhythmically during diagenesis. The heterogeneous distribution of aluminum suggests its incorporation as a trace element during silica crystallization phases.

Iron (Fe) exhibits a striking heterogeneous distribution with a particular zone showing a high concentration that correlates well with a visible band in the bottom part of the sampled area. These Fe-rich zones likely contribute to the characteristic color variations in the agate where iron exists in different oxidation

states (Fe^{2+} and Fe^{3+}) within the silica matrix. The observed pattern for Fe again supports the sequential precipitation model of agate formation.[4]

Notably, the rare earth element Cerium (Ce) shows a distinct pattern as opposed to Fe, as it is abundantly observed in zones where the concentration of iron is low. This suggests possible co-precipitation or absorption mechanisms during agate formation and may provide evidence for the geochemical conditions during crystallization phases.

The distribution of lead (Pb) appears more localized, with discrete high-concentration zones that might represent either primary mineralization during agate formation or secondary enrichment processes through later fluid interactions. The irregular distribution pattern suggests multiple episodes of incorporation of this element.

Uranium (U) displays a unique distribution pattern with well-defined zones of enrichments that don't completely mirror other elements' patterns. This suggests discrete U-bearing phases or specific geochemical conditions controlling mobility and fixation of this element during formation.

The observed elemental associations and spatial relationships indicate complex mineralogical and geochemical processes during agate genesis. The heterogeneous distribution of elements, particularly heavy metals and rare earth elements, points to multiple episodes of mineral formation or alteration, providing new insights into the conditions and mechanisms of agate formation. These patterns could be attributed to variations in fluid chemistry, pH conditions, and redox states during the prolonged process of agate crystallization.
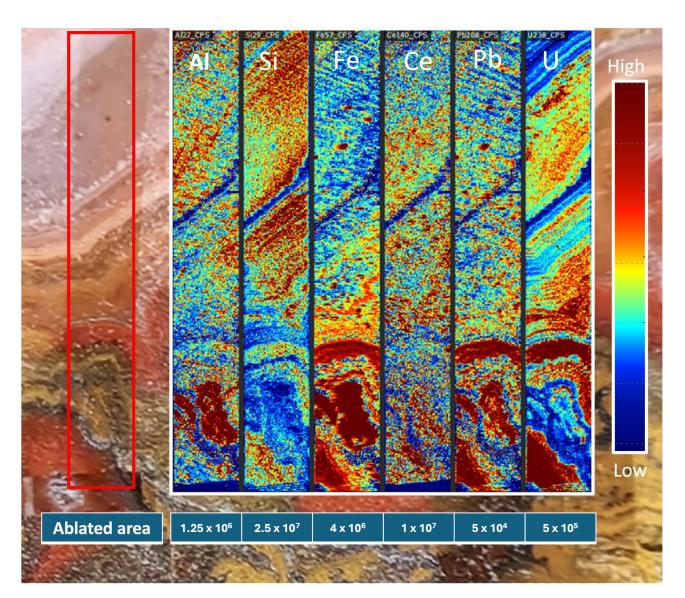

Figure 6. Element distribution maps for ^{27}Al, ^{29}Si, ^{57}Fe, ^{140}Ce, ^{208}Pb, and ^{238}U were generated using iolite™ software. The shape outlined with red is the original sample image. The color bar shows red indicating higher signals and blue indicating lower signals. The maximum intensity numbers are shown under the mapping images.

Conclusions

This study demonstrated the efficacy of LA-ICP-MS for direct solid sample analysis and high-resolution imaging of multi-layered stones. The iCAP MTX ICP-MS and the imageGEO193 laser system coupled together allow for high sensitivity, low background, and high-speed integration capabilities for elemental imaging and mapping. The combination allows for direct analysis without extensive sample preparation, saving time and reducing contamination risks for bulk analysis. LA-ICP-MS can also be applied for comprehensive elemental analysis and mapping, enhancing our understanding of geological history and stone composition, and providing insights into its formation and elemental incorporation mechanisms of geological structures.

References

1. Steiger, R. H. & Jäger, E. Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett.* 36, 359–362 (1977).

2. Application Note AN 44479, Thermo Fisher Scientific.

3. Application Note AN 44387, Thermo Fisher Scientific.

4. Park et al. Journal of Analytical Science and Technology (2015) 6:37.

Acknowledgments

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