SmartNotes

Laser Ablation for ICP-MS – what is it and should I use it?

1. Why would I want to use laser ablation?

Most solid materials presented for elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS) techniques require an initial sample preparation step to bring them into solution. For many sample matrices, a dissolution step is necessary in order to avoid problems of sample inhomogeneity and is often stipulated by the analysis protocol itself (for example US EPA Methods). Depending on the sample matrix, this digestion process may require the use of hot plates, microwaves or fusion assays. 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 sampling in the solid without the need for hazardous chemicals and minimizes the potential for contamination by sample handling. It is capable of sampling almost all solid samples, including conducting samples (e.g. metals and semiconductors), non-conducting samples (e.g. mineral grains, paper and plastics) and biological materials (e.g. tissue sections). It is easily hyphenated with different ICP-MS systems depending on the type of information that is required. Quadrupole based ICP-MS systems, for example the Thermo Scientific™ iCAP™ RQ ICP-MS and iCAP TQ ICP-MS, allow accurate quantification, while sector field instruments, like the Thermo Scientific ELEMENT™ HR-ICP-MS, also provide improved precision for isotope ratio determination. Multicollector ICP-MS systems, for example the Thermo Scientific™ NEPTUNE Plus™ MC-ICP-MS, allow isotope ratio determination with ultimate precisions for geochronology applications.

Detection limits in the range of $ng \cdot g^{-1}$ by LA-ICP-MS can be achieved, which on the first glance may seem high when compared to liquid sample introduction ICP-MS, but in many cases Method Detection Limits (MDL) by LA-ICP-MS can be superior after taking into account the effects of sample preparation and dilution.

2. What is the principle of laser ablation?

Laser Ablation (LA) is a solid sampling technique that uses short pulses of high intensity light to convert a solid sample directly into an aerosol, which is transferred into the ICP ion source for analysis, typically by inductively coupled plasma mass spectrometry (ICP-MS).

The sample is mounted in a dedicated laser cell and the laser beam is focused onto the sample surface. When the laser interacts with the sample, the laser energy is transferred to the bulk (matrix) material, which causes particles to be ejected from the sample surface. These particles are carried away by a 'carrier gas', which is typically helium. Other inert gases can be used, but helium typically gives the best performance.

Combined with the right ICP-MS technique (single quadrupole, triple quadrupole, high resolution or multicollector ICP-MS), laser ablation can be applied to many different application areas, such as bulk analysis of solid materials, isotope fractionation in geosciences and in environmental analysis, elemental imaging in clinical research, or elemental fingerprinting in forensic analysis.

3. What types of laser are available, and which laser type is most useful for me?

There are many laser ablation systems available from industry partners, each with differing wavelengths, energy output levels and pulse durations (summarized in Table 1).

Laser ablation works on the principle of energy transfer, and generally all materials absorb better in the UV (ultraviolet) wavelength range (400 nm and below). Commercial systems are therefore typically offered with wavelengths at 266 nm, 213 nm and 193 nm.

In terms of wavelength, 266 nm lasers generally penetrate deeper into sample matrices, are very effective for opaque materials and are generally used for bulk analysis. A 193 nm laser provides more fine control over depth penetration, is better suited for the analysis of more transparent materials and is often used for profiling, mapping and similar (high end) applications. 213 nm based lasers offer a good compromise in performance and is a good 'general use' laser system for a most sample types. A good general approximation is that the more transparent (or paler) the sample matrix, the more likely a lower wavelength laser will be effective.

An additional important parameter is pulse duration. Solid state (Nd:YAG) based laser systems use a 'Q-Switch' to generate nanosecond duration pulses of energy. These are similar in timescale to thermal transfer and so can cause melting of the sample surface, leading to poor quality ablation and inaccuracies in the analysis of thermally sensitive or conducting materials (e.g. semiconductors and metals). Shortening the pulse width to femtosecond timescales removes the thermal component of the energy transfer allowing for good quality ablation for semiconductors, metals and other thermally sensitive materials.

Table 1. Currently available commercial Laser Ablation Systems, their output characteristics and example materials they ablate effectively.

Laser (wavelength(s))	Pulse width	Example materials	Example system
Q-Switched ArF Excimer (193 nm)	4 – 20 ns	Transparent Glasses Quartz Minerals Rocks Biomaterials	TDY Analyte Excite/Excite HE/G2+ ESL NWR193 ASI RESOlution
Q-Switched Solid State (213 & 266 nm)	4 – 6 ns	Opaque Glasses Rocks Minerals Metals Plastics Biomaterials	TDY LSX-213 G2+ ESL NWR213/NWR266Macro AS J200 LA/J200 Tandem LA-LIBS
Femtosecond Solid State (206 – 1028 nm)	150 – 350 fs	Semiconductors Glasses Rocks Metals Minerals Plastics Biomaterials	TDY Excite Pharos ESL NWRfemto AS J200 Femto QX LA/J200 Femto iX LA

TDY = Teledyne CETAC Technologies; ESL = Elemental Scientific Lasers; ASI = Australian Scientific Instruments; AS = Applied Spectra.

4. What are the most important parameters used in Laser Ablation?

For all laser ablation systems, the most important parameters influencing the ablation process, and hence the analytical result, are spot size, fluence and repetition rate.

- The spot size defines the diameter of the laser beam incident on the sample. Larger spot sizes generate more ablated material, thereby increasing the resulting signal, but reduce spatial resolution.
- Fluence describes the amount of energy delivered to the sample in $J \cdot cm^{-2}$. The fluence should be high enough to achieve an efficient ablation, but not too high to cause melting of the sample surface.
- The repetition rate is the number of laser shots incident on the sample per second, and higher repetition rates generally lead to more ablated material per unit time.

The ideal combination of spot size, fluence and repetition rate are defined by the sample type and/or application.

5. How is the laser system controlled?

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software offers dedicated plug-ins to provide integrated control of laser systems from leading manufacturers*. In addition to simple hardware control, plug-ins allow scan lists laid out on the sample surface using the LA system to populate the Qtegra ISDS Software. In this way, automated scan settings can be synchronized with data acquisition so that unattended acquisition over long periods is feasible, e.g. when analyzing hundreds of mineral grains in geochronology or for elemental mapping.

*Qtegra ISDS Software plug-ins are available for laser ablation systems such as those from Teledyne CETAC Technologies and Elemental Scientific Lasers.

6. Is the ICP-MS system configured differently for Laser Ablation analyses?

Sample delivery with laser ablation is fundamentally different to conventional (solution based) ICP-MS analyses. Since the laser ablation system generates dry particles in a carrier gas stream, nebulizers and spraychambers are not required with the output from the laser cell connected directly to the ICP-MS injector. An argon gas flow is used to buffer the laser carrier gas to maintain plasma stability.

Since one of the main advantages of laser ablation is spatially resolved sampling, data is usually acquired in a time-resolved acquisition.

The Qtegra ISDS Software offers a dedicated feature set for evaluating data derived from laser ablation, trQuant. Switching between optimized analysis modes for specific analytes would lead to loss of spatial information so trQuant based analyses are restricted to a single acquisition mode.

7. How can I optimize my ICP-MS system with a laser system?

There are well-characterized standard reference materials that can be used for tuning and performance verification of a LA-ICP-MS system. For example, NIST reference materials 610, 612 and 614 (trace elements in glass) contain a variety of trace elements and are ideally suited for performance testing. Qtegra ISDS Software includes a dedicated autotune routine for laser ablation that uses NIST 612 to optimize sample introduction system and lens parameters for optimum sensitivity and oxide formation.

The QCell collision/reaction cell system used in both the Thermo Scientific iCAP Q and iCAP Qnova Series ICP-MS allows for interference free analyses across the entire mass range (Li to U) using kinetic energy discrimination (He KED). For specific (generally high mass range) applications, collisional focusing can be used to increase the attainable sensitivity for many elements. A dedicated autotune routine that optimizes the system is provided as part of the default installation of the software.

8. How can laser ablation help me with bulk analysis?

The use of laser ablation for direct sampling of solid samples has the advantage that no sample preparation is required. For conventional ICP-MS analyses, a portion of the sample would need to be dissolved using acids, which imposes a considerable workload, exposure to potential hazardous chemicals and risk of contamination.

Conversely, the sampled area using Laser Ablation is relatively small: maximum spot sizes are typically 200 µm (some systems use specialized optics that can generate spot sizes up to 750 µm). Consequently, there may be potential issues with sample homogeneity so care must be taken to sample enough material to compensate for any sample inhomogeneity. This is typically handled by using large area raster scans as the sampling strategy.

Depending on the application, laser ablation can also provide useful information on depth profiles; however, other techniques like Glow Discharge Mass Spectrometry (GD-MS) may offer significant advantages.

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9. What is the typical spatial resolution one can expect in LA-ICP-MS?

There are two limiting factors for the attainable spatial resolution in laser ablation analyses. The laser spot size determines the area sampled by the laser shot but moving to smaller spot sizes to improve spatial resolution will eventually decrease the amount of ablated material to below the measurable detection range of the ICP-MS system used. For most commercial LA-ICP-MS systems, the minimum spot size is approximately 2 – 5µm.

The second decisive parameter is the wash out time of the ablation cell, since material needs to be transferred quickly and effectively to the ICP-MS system for analysis. If the washout is relatively long, material from one ablation site may not have transferred completely before the next site is ablated. This leads to loss of spatial resolution and 'blurring' of the spatial information. Fast-washout systems are available from industry standard manufacturers to enhance washout performance in routine and specialist applications.

10. What is Elemental Imaging or Mapping?

Elemental images or maps refer to an LA-ICP-MS analysis that provides information on the elemental distribution across a two-dimensional area of a sample, for example across the surface of a mineral grain or 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 (see Figure 1, for example).

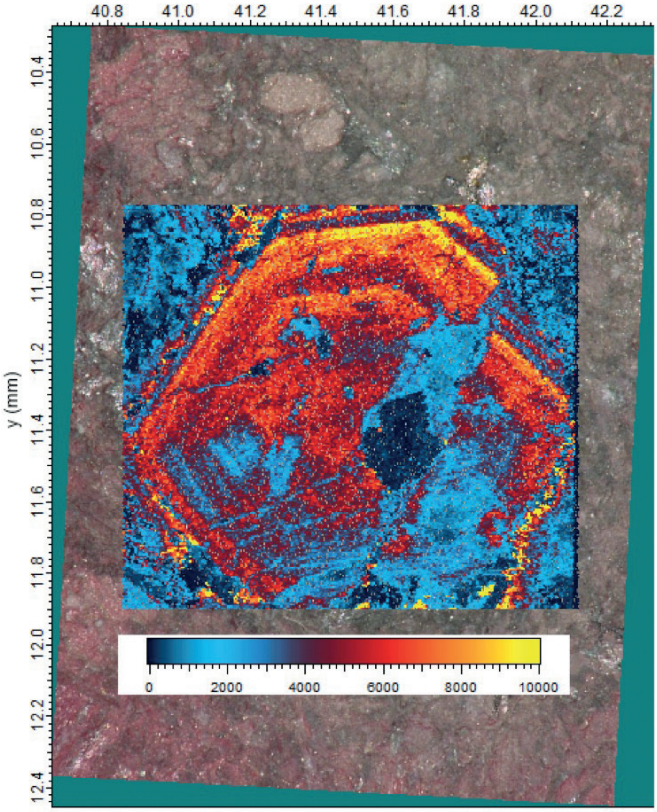

Figure 1. Scandium distribution in a garnet crystal, measured using LA-ICP-MS imaging using a 5 µm laser spot and an iCAP TQ ICP-MS. Scandium was measured in TQ-O_2 mass shift mode as $^{45}Sc.^{16}O$, and the color scale is in counts per second (cps).

Imaging is of particular interest in biological samples, as here the distribution of an element (for example, in stems and leaves of a plant) may give valuable insight on uptake and distribution of essential or toxic trace elements.

Detection sensitivity and interference elimination is crucial for this application, as it translates into an expansion of the achievable dynamic range across the image. Therefore, the use of triple quadrupole ICP-MS offers decisive benefits for this application.

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