

# EAG Laboratories



# Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) Services

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (<u>LA-ICP-MS</u>) is an analytical technique that uses direct micro-scale sampling to provide high precision elemental and stable isotope analyses of solid materials.

LA-ICP-MS is a microanalytical technique for direct elemental and isotopic analysis. In laser ablation, material is removed from a solid sample using a pulsed laser. This contrasts with the more common solution Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) in which a liquid sample is turned into an aerosol by a nebulizer to facilitate introduction to the mass spectrometer. The most commonly used types of laser for this technique feature either a solid-state Nd:YAG or gaseous Excimer laser source with ultraviolet wavelength and nanosecond pulse width (duration). The pulsed laser induces heating, evaporation, and ionization of the sample (Figure 1); the plume of ablated material subsequently recondenses into nanoparticles which are swept into the ICP-MS by a carrier gas stream. The argon plasma in the ICP-MS acts as a secondary energy source that ionizes the sample atoms for discrimination and measurement according to the mass to charge (m/z) ratio of the positively charged ions.



Figure 1: In situ plasma formed by laser ablation of a clay mineral sample with a 100 micron spot, 10 Hz repetition rate, and 5 mJ energy.

As a microanalytical technique, laser ablation requires substantially less sample mass than

solution ICP-MS. Picograms to femtograms of material are removed by laser ablation, making this a true minimally destructive approach to elemental analysis. In contrast to solution ICP-MS, LA-ICP-MS requires no chemical preparation of samples such as leaching, digestion, fusion, or liquid dilution. Many samples can be analyzed as received, while some may require mechanical preparation to ensure that the sample fits in the laser ablation cell and presents as smooth and flat a surface as possible to the laser. In addition to facilitating analysis of samples too small for solution ICP-MS (or too valuable for destructive analysis), laser ablation is ideally suited to analysis of difficult to digest materials like refractory minerals, metals, and alloys.

LA-ICP-MS yields a transient analytical signal, in contrast to the steady-state signal produced by solution ICP-MS. The signal, represented as counts per second versus time in Figure 2, can either be treated as time-resolved (for spatially targeted analyses of specific features or chemical imaging) or as a pseudo-steady-state signal for bulk analyses of homogeneous materials.



Figure 2: Time-resolved signal for potassium, strontium, and barium isotopes in the FEBS-1 fish otolith powder reference material, ablated as a pressed pellet.

## Types of Laser Ablation Patterns

Laser ablation pattern refers to the shape of the laser "spot" focused on the sample and the area ablated by that spot as the sample is kept fixed or moved under the pulsing laser. Laser spots are most typically circular, with square and cruciform spots available on some systems. Patterns fall into three categories: 1) spot ablation, 2) scan line ablation, and 3) raster ablation (Figure 3).



Figure 3: Examples of laser ablation patterns on high-purity tantalum. From left to right, three scan lines using a 100 micron diameter laser spot, four fixed spots ablation using 200, 150, 100, and 50 micron spots, and a raster ablation using a 75 micron spot.

Spot ablation is carried out at a fixed location; the laser pulses for a set duration and ablates down into the sample until the laser pulses cease or focus is lost (middle of Figure 3). Fixed spots are mostly used for targeting features like defects and inclusions, or small particles. Scan lines are typically used to generate a pseudo-steady-state signal for bulk analysis of homogeneous samples (left of Figure 3). As the laser fires at a known rate, the sample is moved at a known rate. This permits the analyst to control dosage (number of laser pulses per location), prevent the laser from losing focus, and generate a longer duration signal that reduces instrumental uncertainty. Lastly, raster ablation is similar to a scan line except that the pattern features switchbacks to continuously ablate a larger area (right of Figure 3). Raster patterns are useful for generating long duration signals for high-precision analyses or continuous coverage of a sample for chemical imaging.

#### Strengths

- Trace, minor, and major elements can be measured during the same analysis.
- Microanalytical technique: Sample features

 $200 - 40 \ \mu m$  in size are routinely ablated, while features as small as 5  $\mu m$  may be analyzed under some circumstances.

- Qualitative, semi-quantitative, or fully quantitative data as needed.
- Not limited by sample electrical conductivity, vacuum stability, inorganic/organic composition, or optical transparency/opacity.
- Fast no chemical preparation, clean fewer opportunities for contamination, and green no hazardous waste generated and minimal consumables used.
- Polyatomic interferences caused by acid reagents and issues caused by the instability of some elements in dilute acid solution are both avoided.

#### Limitations

- Requires matrix-matched, solid reference materials for quantitative analyses.
- Not measurable: unstable radioisotopes, H, N, O, F, and noble gasses.
- Internal standard element for data normalization cannot be added to most samples; a matrix element measured by a secondary technique or a pseudo-internal standard such as a gold sputter coating are required for most quantitative analyses.
- Large and/or irregular samples may need mechanical preparation to fit in the laser cell.
- Requires samples stable at room temperature and free of liquids for most applications.

#### **Common Applications**

- Qualitative analysis to identify elemental signal intensity differences between "good" and "bad" samples, or between defects/inclusions and unaffected areas.
- Qualitative survey analysis, with tandem Laser Induced Breakdown Spectroscopy (<u>LIBS</u>), to identify major and minor elements present in truly unknown samples.
- Semi-quantitative analysis yielding ratio data (*e.g.*, Element X concentration/Matrix element



concentration) suitable for provenience (*i.e.*, sourcing or traceability) studies.

- Semi-quantitative analysis to compare elemental concentrations between samples of the same matrix or measure gradients within a sample.
- Fully quantitative analysis to measure total metallic impurities (TMI) in samples too small for bulk analysis or resistant to acid digestion.
- Fully quantitative measurement of specific analytes for RoHS compliance and other health and safety regulations.

#### **Industry Sectors and Technologies**

- Semiconductors and printed circuit boards
- Lithium-ion batteries and other advanced energy storage
- Photovoltaic solar, nuclear reactors, and other alternative energy
- Medical devices, pharmaceutical packaging, and personal care
- Industrial coatings and films
- High-performance alloys, ceramics, and glasses
- Mining and related extractive industries
- Forensics, archaeology, biological anthropology, and paleontology

### Case Study: Characterization of an Inclusion Defect in High Purity Fused Quartz Glass

A manufacturer of a high-purity  $SiO_2$  glass for the semiconductor and photovoltaic industries detected a series of opaque inclusions approximately 500  $\mu$ m in size in a batch of glass. They suspected the inclusions were metal debris from the manufacturing process but needed to rule out mineral impurities in the source quartz sand such as pyrite (FeS<sub>2</sub>) or uraninite (UO<sub>2</sub>). Eurofins EAG scientists carefully cut and sequentially polished blocks of glass to expose visible defects.

LA-ICP-MS was used to analyze unaffected glass adjacent to each defect to obtain reference data before the defect itself was analyzed with a fixed



Figure 4: Example of opaque defects in glass.

spot ablation. The LA-ICP-MS analysis found an elevated Fe signal in multiple defects relative to their associated unaffected glass reference areas. The signals for both S and U were lower in the defects than in the reference areas, ruling out mineral impurities and supporting the metal debris hypothesis.

#### Case Study: RoHS Compliance Testing of an Implantable Medical Device

A medical device manufacturer, planning to bring a new product to market in Europe, needed to demonstrate compliance with the Restriction of Hazardous Substances (RoHS) Directive. A component of the device produced by a third-party was too small for sampling and bulk analysis of Cr,



Figure 5: Illustration of implanted medical device.

Cd, Pb, and Hg by solution ICP-MS. The device component was analyzed using LA-ICP-MS to target specific features. One such feature, a ring holding another component in place, was supposed

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to be composed of bismuth oxide. Semi-quantitative data calibrated with a glass certified reference material and fully quantitative data calibrated with a bismuth reference material were both collected. Although not required for RoHS testing, Bi was measured for LA-ICP-MS data standardization. However, Bi was only found at low part per million concentrations when it was anticipated to be the major element present. Instead, Pb was found to occur in the ~30–90% weight range. EAG's analysis alerted the device manufacturer to a potentially major hazard in the form of a component not made of the advertised material but instead a dangerous, regulated alternative.

### Case Study: Measurement of Major Element Ratio Gradients in Sputter Targets

A company that produces metallic oxide sputter targets received a complaint from a customer about variation in the ratio of major elements being deposited over the use-life of a target. The manufacturer suspected that segregation of elements during the sintering process may be at fault.

The client provided cross-sectioned sputter targets embedded in epoxy and polished. EAG scientists used LA-ICP-MS in two ways to analyze compositional variation over each cross-section. First, a single scan line was ablated at a right angle to the top and bottom surfaces over the entire crosssection and used to collect qualitative intensity data. Second, a series of scan lines parallel to the top and bottom surfaces were evenly staggered over the cross-section to collect semi-quantitative concentration data.

LA-ICP-MS analysis found no significant variation in the ratios of the three major elements present in the sputter targets through the cross-section. This allowed the manufacturer to determine that the sintering process was not at fault and that the targets were functionally homogeneous.

# LA-ICP-MS at EAG

As a microanalytical technique for solid samples, LA-ICP-MS is complementary to many other instrumental techniques offered by EAG.

Glow Discharge Mass Spectrometry (GDMS) is an ideal survey technique for full scan analysis of many solid samples; LA-ICP-MS can subsequently be applied to quantify specific analytes of interest and provide finer spatial resolution than GDMS.

Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy (<u>SEM-EDS</u>) can be used for rapid imaging of discrete surface features and preliminary characterization of major and minor element composition; following up with LA-ICP-MS permits quantification with lower detection limits than SEM-EDS.

EAG uniquely offers tandem LA-ICP-MS and Laser Induced Breakdown Spectroscopy (LIBS), simultaneously measuring analytes of interest with high precision and low detection limits using mass spectrometry and rapidly surveying all elements present with optical spectroscopy.

Lastly, EAG's depth of experience analyzing diverse sample matrices and morphologies provides analysts and scientists with a wealth of knowledge, validated procedures, and reference materials for successfully applying LA-ICP-MS to routine and non-traditional samples from industry, government, and academic clients.

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