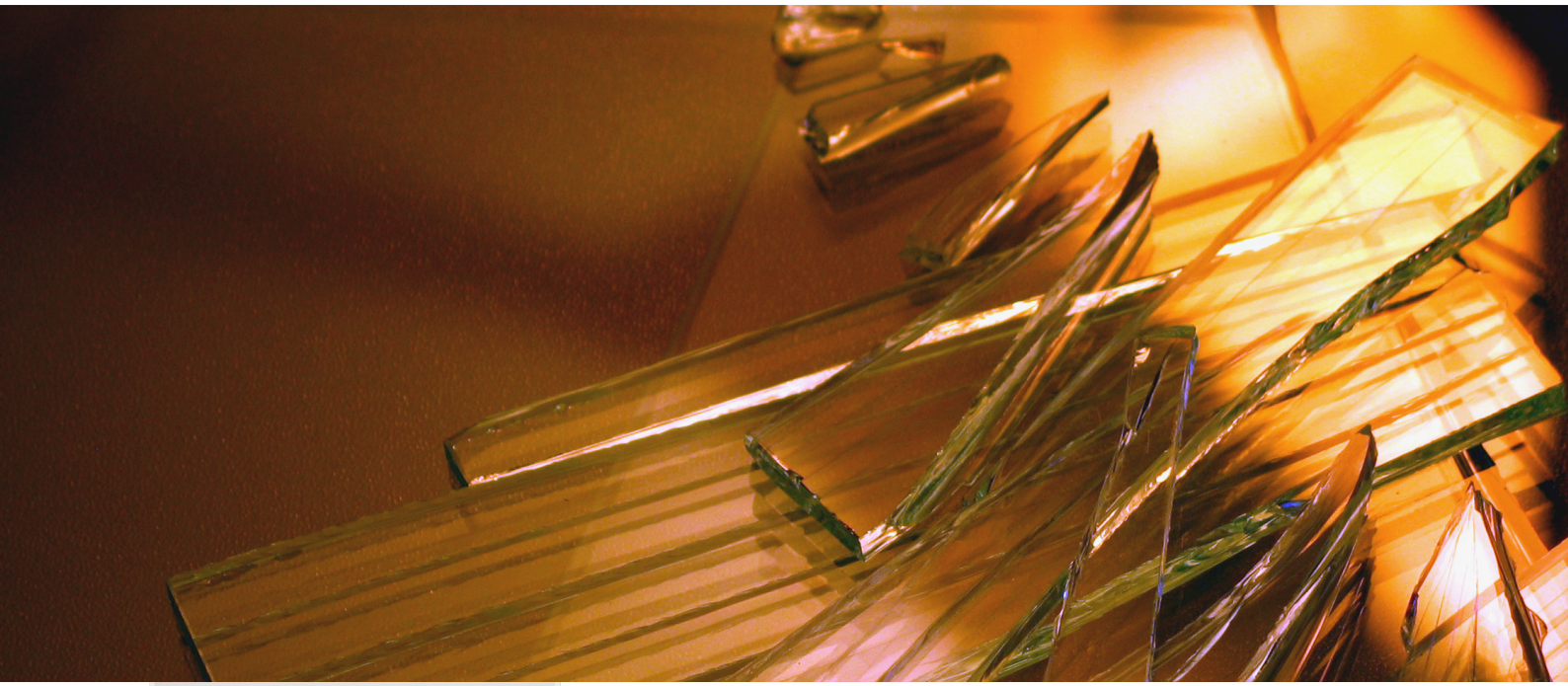

Achieving Ultra-Sensitive Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) Analysis with the J200 LA Instrument: A Glass Sample Study

Challenge

Determination of the absolute mass in solid samples and detection limits using on a glass sample study.

Solution

High-precision analysis of solid samples with superior sensitivity (down to ppb levels) and little to no sample preparation using LIBS and LA-ICP-MS.

Introduction

Laser ablation (LA) is a direct solid sampling technique that uses a laser pulse to remove small amounts of mass (pg – fg scale) from a sample of interest. Combining LA with inductively coupled plasma – mass spectrometry (ICP-MS) offers very attractive technical benefits for the analysis of solid samples, which include little to no sample preparation, high precision measurements, and superior sensitivity (down to ppb levels) with respect to other atomic spectroscopy methods. LA-ICP-MS analysis also offers both elemental and isotopic information. Depending on the laser sampling method deployed, LA-ICP-MS can be used for traditional bulk analysis, as well as for spatially-resolved analysis such as elemental/isotopic mapping and depth profiling.

Applied Spectra Inc.'s J200 LA Instrument

The following application describes the analysis of glass samples (NIST SRM, trace elements in glass) to determine the absolute mass that can be detected and the limits of detection (LODs) when interfacing an Analytik Jena PlasmaQuant MS Elite ICP-MS and Applied Spectra Inc.'s J200 LA instrument.

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Instrumentation

Operating Parameters Analytik Jena PlasmaQuant MS Elite

- Time resolved data acquisition
- High sensitivity optimization
- Peak hopping mode: $^{7}Li^{+}$, $^{47}Ti^{+}$, $^{59}Co^{+}$, $^{88}Sr^{+}$, $^{121}Sb^{+}$, $^{140}Ce^{+}$,$^{177}Hf^{+}$, $^{195}Pt^{+}$, $^{197}Au^{+}$, $^{208}Pb^{+}$, $^{232}Th^{+}$, and $^{238}U^{+}$
- Synchronized instrument triggering with J200 LA instrument

Operating Parameters Applied Spectra J200 LA Instrument

- 266 nm Nd:YAG laser (ns)
- Flex sample chamber with helium or argon gas flow
- NIST SRM 612 glass sample
- LA transient data analyzed with Applied Spectra Data Analysis Software package

Sample Analysis

The glass sample (NIST SRM 612) was placed into the J200 LA instrument Flex sample chamber. The Flex chamber can be purged with either helium or argon so that when the laser pulse removes a tiny portion of the sample in the form of fine particles, the particles are swept out of the LA chamber into the ICP-MS. The particles enter the plasma where they are vaporized, atomized, and ionized. The ions are detected according to their mass-to-charge ratios. The NIST glass was analyzed with increasing 266 nm laser pulses (5, 10, 15, 20, 25, and 50) to introduce increasing amounts of mass into the ICP-MS PlasmaQuant® MS Elite. An example of the crater profile from 25 laser pulses can be seen in Figure 1.

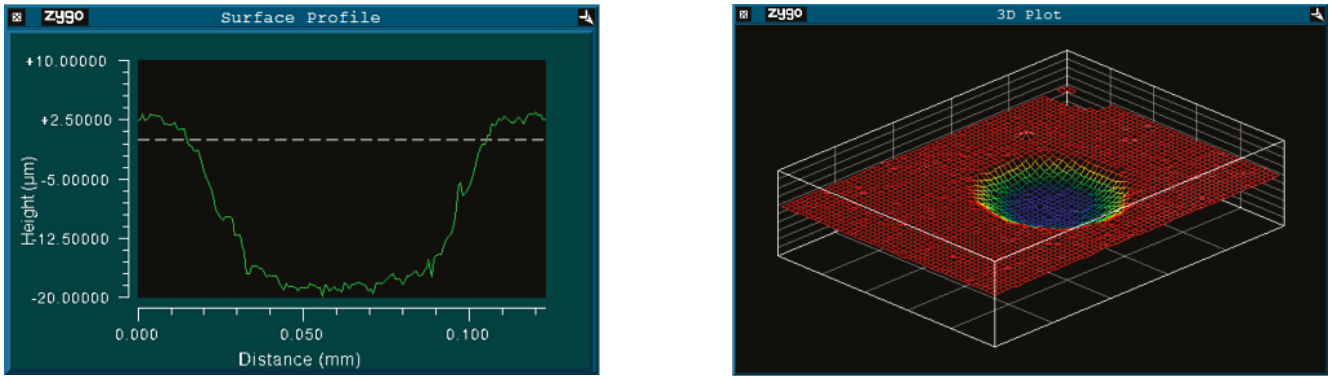

Figure 1. Laser ablation crater (60 µm spot) displayed using a white-light interferometric microscope (Zygo). The crater is a result of 25 laser pulses from a 266 nm laser at 0.57 ± 0.01 mJ

The sample was analyzed in triplicate for each set of laser pulses. With Applied Spectra Inc.'s integrated data analysis software transient peaks can be processed and integrated with ease. The analyst does not have to create own software codes or use 3rd party software that may not be optimized for robust LA-ICP-MS analysis. An example of ASI's LA data analysis software can be seen in Figure 2. The ICP-MS data files from the PlasmaQuant® MS Elite can be easily loaded into the data analysis software, where transient peaks can be integrated and converted into tables of numerical values or into a full mass spectrum.

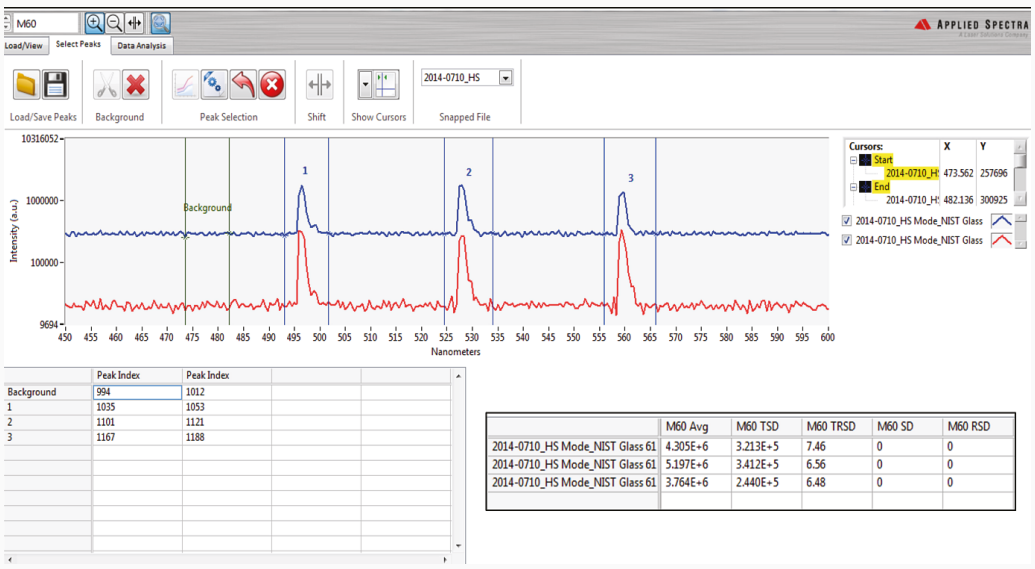

Figure 2. ASI LA data analysis software screen shot illustrating how transient data can be integrated. Any ICP-MS data files can be loaded into the data analysis program, allowing the J200 LA instrument to be coupled with any ICP-MS instruments. An example of the integrated data is displayed for 60Ni in the bottom right of the screen shot (All elements are integrated and saved into the data file, but 60Ni shown above for simplicity).

The craters from the 5, 10, 15, 20, 25, and 50 laser pulses on the surface of the NIST 612 glass sample were measured using the Zygo microscope to determine the volume (μm^3) ablated. These volumes were then converted into mass (using density of glass = 2.3 g/cm^3), and plotted against the response for each element in Figure 3. The amount of material ablated had a linear response in relation to each element. Figure 3 shows examples of intensity response curves for Li, Co, Ce and U. The other measured elements in this study showed similar behavior.

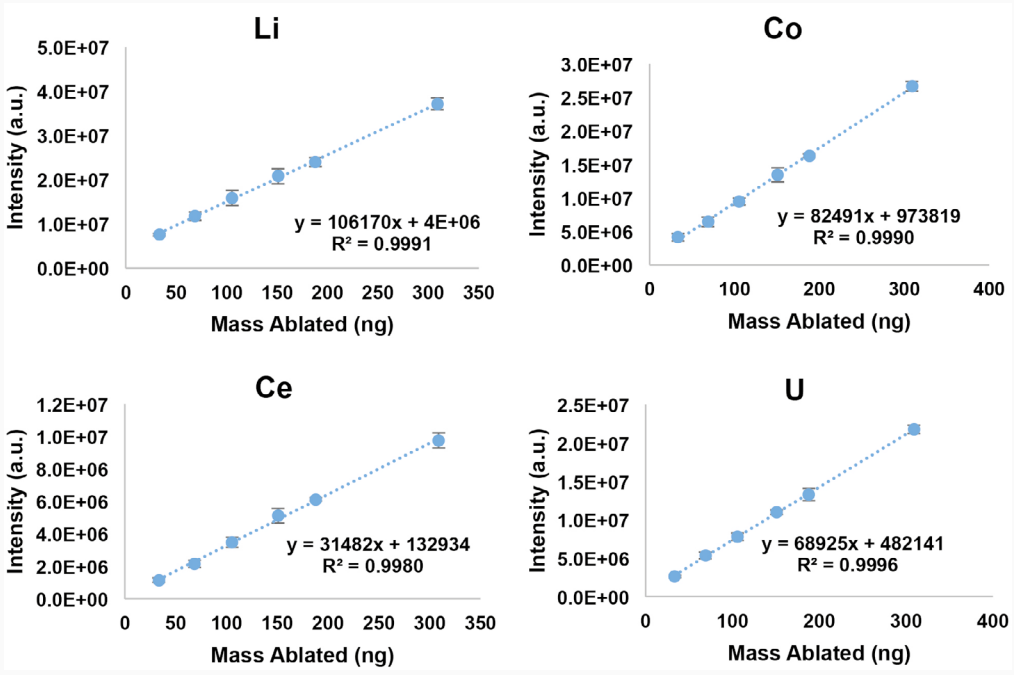

Figure 3. LIBS elemental maps based on C, H, Ti, and Sr signals obtained from the J200 (CCD detector)

The slopes determined from plotting intensity vs. mass ablated were used to determine the absolute mass detectable for each element listed in Table 1. The absolute mass detected using the J200 LA instrument in combination with the Analytik Jena PlasmaQuant MS Elite ICP-MS was in the range of 0.92 – 133 pg. The limit of detection (LOD) was determined for all of the elements listed in Table 1. The LODs ranged from 0.11 – 10 ppb. Titanium was the exception with an absolute mass of 961 pg and LOD of 125 ppb, this results from not being able to use the major isotope for titanium (^{48}Ti = 73.8% abundant) since it has an interference with Ca at mass 48 (calcium is a matrix element in the NIST 612 glass). Since a collision or reaction cell was not used for these experiments, mass 47 was used for titanium (^{47}Ti = 7.3 % abundant) analysis.

Table 1. Absolute mass detected and LODs for NIST 612 (trace elements in glass) using the J200 LA + Analytik Jena PlasmaQuant® MS Elite ICP-MS combination.

Isotope	Absolute Mass (pg)	LOD (ppb)
^{7}Li	81	9.3
^{47}Ti	961	125
^{59}Co	57	10
^{88}Sr	6.2	1.6
^{121}Sb	19	2.1
^{140}Ce	5.5	0.69
^{177}Hf	11	1.0
^{195}Pt	133	1.4
^{197}Au	37	0.54
^{208}Pb	3.9	0.45
^{232}Th	3.6	0.45
^{238}U	0.92	0.11

LOD = (3 x Noise x Concentration)/(Intensity)

Conclusions

Applied Spectra's J200 LA instrument offers the ability to analyze solid samples with little to no sample preparation. When coupled with Analytik Jena's PlasmaQuant MS Elite, this technique offers detection limits in the ppb to sub-ppb range with excellent absolute mass detection limits in the pg to sub-pg range.

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