

# Application of Double-Pulse micro-LIBS 3D Compositional Mapping to the Analysis of Ceramics

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**Abstract** – We developed a new Laser-Induced Breakdown Spectroscopy (LIBS) instrument for 3D compositional mappings of archaeological objects. The system, based on the Modi double-pulse instrument, allows the reconstruction of maps with lateral resolution up to 20 microns and sub-micron depth resolution.

Keywords: LIBS, Compositional Mapping, Archaeometry, Ceramics.

## I. INTRODUCTION

The analysis of ceramic samples is of paramount in Archaeology. Many different techniques has been developed for the study of the composition of ceramic findings; the information gathered from these techniques, in many cases, does not help in reconstructing the compositional changes occurring at microscopic scale that, in the majority of the cases, must be recovered through visual analysis at the optical microscope after a proper treatment of the sample.

In this communication, we report on the development of an instrument, based on Laser-Induced Breakdown Spectroscopy (LIBS) technique [1], which allows a multi-elemental depth-resolved compositional mapping of ceramic samples, with sub-micron depth resolution and lateral resolution up to 20 micron. The method of analysis does not require any treatment of the ceramic samples; quantitative results, if needed, may be obtained through the application of standardless methods (Calibration-free approach) [2]. Laser-Induced Breakdown Spectroscopy has been already proposed, in the past, for elemental mapping of materials, with interesting results [3,4]. Most of the applications proposed, however, were based on the use of a single-pulse laser as plasma source. One of the most important improvements in LIBS research of the last decade has been the introduction of the Double Pulse LIBS technique; in its simplest and more effective configuration, two collinear laser pulses are sent on the

sample, with a delay in the order of one microsecond. The plasma produced by the second pulse on the sample is brighter, more stable and its optical emission is characterized by a signal over background ratio more favourable with respect to the LIBS signal obtained using a single laser pulse of the same total energy [1].

## II. THE INSTRUMENT

The instrument we used for micro-LIBS 3D compositional imaging is based on our MODI' (Mobile Dual-Pulse Instrument) LIBS spectrometer [5] (see figure 1). The laser (a double-pulse Nd:YAG laser, emitting two collinear pulses at 1064 nm, in 20 ns FWHM pulses, at the maximum repetition rate of 10 pulses per second, with energy up to 60 mJ per pulse) is coupled to an optical microscope (Zeiss Axio Scope) through the MODI' 5-joint articulated arm.



Fig. 1- The micro-MODI' instrument.

The microscope 10x objective has a focal distance of 10 mm; the sample is placed on a motorized plate which realize the 2D scanning of the sample surface, with a maximum lateral resolution of about 30 nm. The actual resolution of the instrument, however, depends on the size of the laser-induced crater, which can be made as small as a few microns in diameter. According to material analyzed and the energy of the laser, the in-depth resolution of the instrument can range from a few hundreds of nanometers up to several microns.

The optical signal from the laser-induced plasma is collected by an optical fiber, placed at an angle of about 45 degrees and at a distance of 10 mm from the laser spot, and then sent to a broadband spectrometer (AvaSpec-2048-2 from Avantes) covering the spectral range from 180 to 900 nm with a spectral resolution of 0.1 nm in the range between 180 and 450 nm and 0.3 nm from 450 to 900 nm.

The synchronization between laser, spectrometer and x-y movement is done using a dedicated Labview® software. The reconstruction of the compositional images and the standardless quantitative analysis of the spectra is done by the LIBS++ software of the MODI' instrument [5].

In previous applications of micro-LIBS, the use of double-pulse laser was not considered as a viable option, because of the larger size of the laser-induced crater on the sample with respect to single-pulse LIBS. On the other hand, the marginal increase in the crater size is largely compensated by the improvement in readability obtained using the Double-Pulse LIBS technique. In figure 2 are compared portions of a LIBS spectra obtained on a brass sample using a double-pulse LIBS (2 mJ per pulse), a single pulse of 2 mJ and a single pulse of 20 mJ (in all the cases, the acquisition delay was 260 ns after the (second) laser pulse).

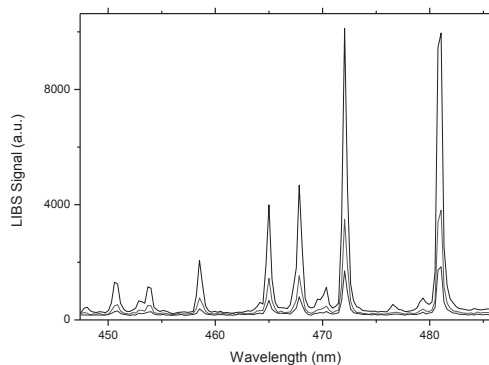


Fig. 2 – Comparison of the LIBS spectra obtained using the double pulse (2 mJ per pulse), and single pulse (20 mJ, 2 mJ) techniques.

While the Double-Pulse signal is about 10 times higher than the one obtained with single pulse at 2 mJ and about three times higher than the one obtained with single pulse at 20 mJ, the size of the crater is only marginally larger than the one obtained with single pulse at 2 mJ, and of the same order of the one generated by a single pulse of 20 mJ (figure 3).

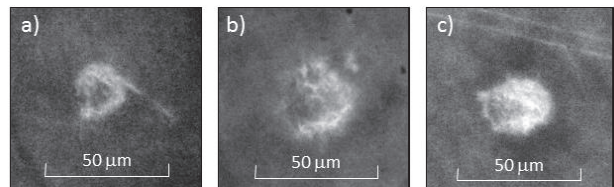


Fig. 3 – Laser-induced crater on a brass sample. a) Single pulse, 2 mJ; b) Single pulse, 20 mJ; c) Double pulse, 2 + 2 mJ.

The use of Double-Pulse micro-LIBS for elemental mapping can thus be considered as a viable method for obtaining well-defined spectra without degrading the spatial resolution of the map. An example is given in the next section.

### III. EXPERIMENTAL RESULTS

The sample studied for testing the micro-LIBS instrument is a fragment of (modern) ceramics (see figure 4). In the upper part of the picture, a defect can be detected, characterized by a small yellowish spot. Three consecutive laser (couples of) pulses were shot at each point, on a 100 x 100 grid, with a 50 micron lateral resolution (5 mm x 5 mm), for a total of 30,000 LIBS spectra. In the lower region, we acquired the LIBS spectra in a 100 x 100 grid (10,000 spectra), with a 50 μm lateral resolution (5 mm x 5 mm). We performed a micro-LIBS 3D scanning in these regions: each map corresponds to about 5 micron in depth, as determined by microscopic inspection of the ablated layers.

The emission lines of the elements considered are shown in table I.

In figure 5 are shown the compositional maps obtained with the first, second and third laser shots on the sample surface. The analysis of the maps allows to determine that the blue is a cobalt-based pigment.

Table I – Emission lines of the elements considered for the mapping

Element	Wavelength (nm)
Al	309.27
B	208.89
Ca	422.67
Co	345.35
Fe	385.99
H	656.30
K	670.78
Li	766.49
Mg	279.55
N	746.83
Na	588.99
O	777.42
Si	288.16
Zn	330.26
Zr	360.12

The glaze is done with zirconium (in the correspondence of the defect, the zirconium concentration is strongly reduced); at the same position, an anomalous increase in the concentration of Pb, Sb and Sn is evidenced. The visible defect is thus determined by a clump of lead antimonate (also known as Naples yellow or Antimony Yellow) and lead-tin yellow under the surface. The size of the clump is smaller in the first 5 microns under the surface (first laser shot), and then reaches its maximum size in the next 10/15 microns (second and third laser shot).

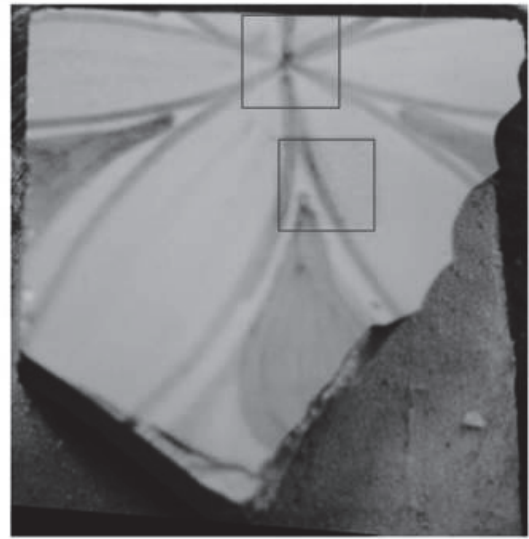


Fig. 4- The ceramic sample analyzed: the two zones analyzed were marked in squares.

The compositional maps obtained on the lower region of the sample evidence that the blue pigment used for the decoration is cobalt-based; the maps of the other elements show a uniform distribution.

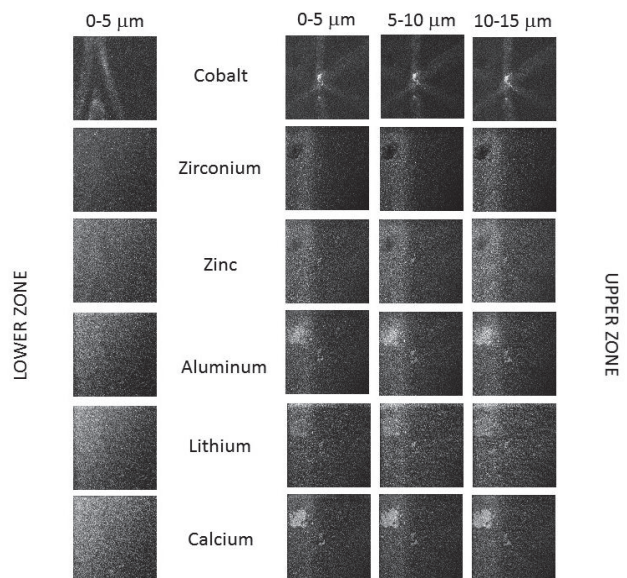


Fig. 5 - Compositional maps of several elements in the Lower (left) and Upper (right) zones analyzed by micro-LIBS. The three maps obtained at 5 μm intervals under the surface are shown for the upper zone.

We can observe that the zone underlying the yellowish defect is larger than the visible spot on the surface; this zone is characterized by a reduction of the zirconium and zinc line emission (roughly proportional to their concentrations) and an anomalous increase in the concentration of Al, Li, Ca, sodium, potassium and titanium (these last three elements are not shown in the figure). The concentration of other elements, such as Fe, B, Si, H, O and N, is basically constant (not shown). The intensity of the emission lines of all the elements considered is almost constant within the first 15/20 microns under the surface.

### III. CONCLUSION

Double-pulse micro-LIBS has been demonstrated to be a very effective technique for high-resolution and fast 3D compositional mapping of ceramic materials. The technique can be applied without any treatment, it is able to detect elements of low atomic weight and does not suffer from limitations that plague the LA-ICP-MS technique, for example the double-ionization interferences. Using a calibration-free approach, the LIBS spectra can be analyzed quantitatively without the need

for reference samples. Double-Pulse micro-LIBS mapping is thus particularly suited for the analysis of ceramic materials in Cultural Heritage and Archeology.

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