DOI: 10.19276/plinius.2019.01008

μ-LIBS-SCAN FOR CULTURAL HERITAGE GEOMATERIALS

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INTRODUCTION

This article reports the experimental results obtained with the Micro-Laser-Induced-Breakdown Spectroscopy Scanning (μ-LIBS-Scan) technique and the optimization parameters obtained in the analysis of geological materials of interest for cultural heritage. The main improvements regard the use of a microscope with at least a 10X objective and a software-operated sample holder. In particular, the control software and a specific routine for the data processing were developed. An optimized routine using MATLAB® was developed for the LIBS technique applied to Cultural Heritage geomaterials. In particular, the work focused on the analysis of highly inhomogeneous materials, such as mortars and archaeological pottery with the aim of overcoming the measurement uncertainties. The followed strategy aimed to realize the elementary maps of representative portions of materials. Moreover, the use of different statistical methods for the data processing allowed overcoming the intrinsic drawbacks. The main results of this work were the capability to obtain virtual elemental cross-section of the analyzed samples and the possibility to carry out in a fast way quantitative information with proper precision and accuracy. There are still several aspects to be improved and carried out. For instance, a possible improvement could be the realization of a more compact and lightweight instrument, with a tunable laser and a 20X objective. Finally, the analysis code in a multiplatform software able to work on IOs, Android and Windows devices would be compiled.

MOBILE DUAL PULSE INSTRUMENT (MODÌ)

One of the greatest advantages of LIBS technique is the possibility to realize in situ measurements with a transportable instrument. The idea behind the Mobile Dual Pulse Instrument (MODÌ; Fig. 1), manufactured by Marwan Technology, is to take advantage of a dual pulse laser (Bertolini *et al.*, 2006) coupled with standardless methods for elemental quantification (CF-LIBS method; Bulajic *et al.*, 2002; Tognoni *et al.*, 2002; Corsi *et al.*, 2006; Yaroshchyk *et al.*, 2006; Tognoni et al., 2007; Tognoni *et al.*, 2010).

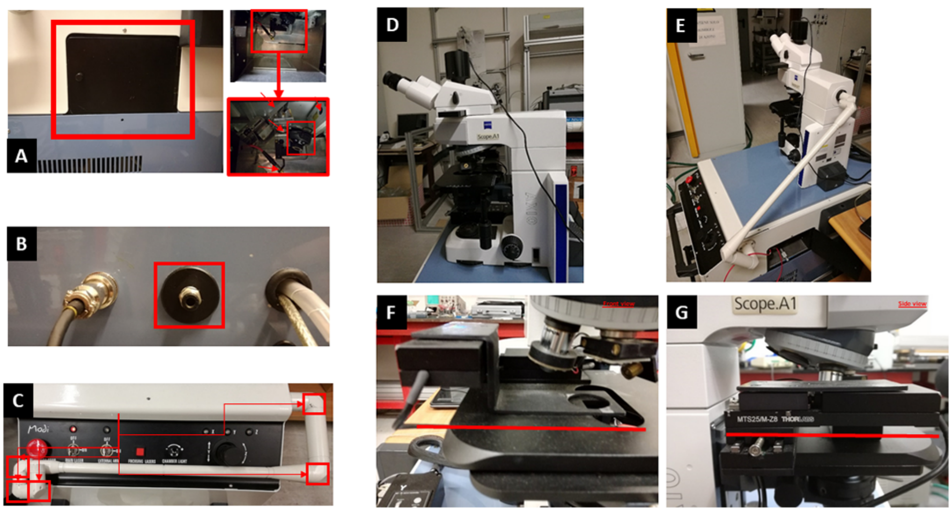


Fig. 1 - The different part of the MODÌ instrument. A) Main analysis chamber with some details; B) backpanel with airflow nozzle; C) external articulated arm with the indication of reflecting mirror positioning; D) the microscope with digital camera; E) the microscope attached to the instrument by mean of the articulated arm; F) scanning system X axis; G) scanning system Y axis.

The system (Fig. 1) is equipped with a CCD spectrometer that covers a range from 200 to 900 nm with a resolution of 0.1 nm in the UV region (190-420 nm) and 0.3 nm in the VIS-IR region (410-900 nm).

The single components of the instrument are relatively small (main body; W=0.50 m x L=1 m x H=0.70 m and with microscope H=1.30 m) offering the possibility to compact the instrument in a small volume. The instrument includes an analysis chamber, where an inert gas can be flushed through an insert nozzle, and an external arm which allow to perform analysis directly on the object (Fig. 1A-C). The instrument was coupled with a commercial microscope Zeiss AxioPlan A1 equipped with a dedicated 10X magnification objective (coated for λ = 1064 nm laser wavelength; Fig. 1D-E). Two Thorlabs slits mounted on the sample stage assure the scanning movement (Fig. 1F-G).

The instrument is capable of ablate the materials shot after shot in order to obtain a chemical depth profile. The performance of depth profiling were estimated using the method proposed by Borisov *et al.* (2000): two pieces of gypsum with flat surfaces were coupled with a tape and the analysis performed on the junction. After the measurements, the two pieces were separated showing the profile of the LIBS craters. The Fig. 2 shows the craters after 25, 50 and 100 shots.

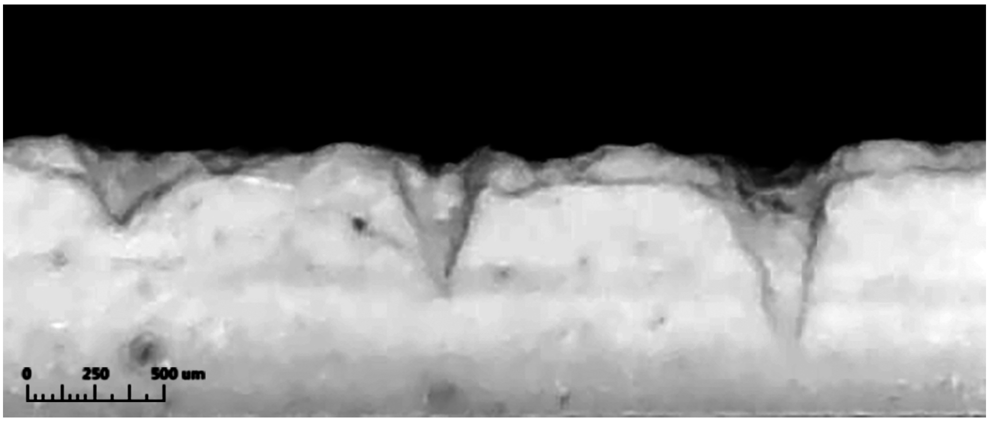


Fig. 2 - Craters made by laser in the analytical chamber. From left to right: after 25, 50 and 100 laser shots.

Plotting the approximate depth for each craters *versus* number of laser pulses an exponential curve were obtained (Fig. 3).

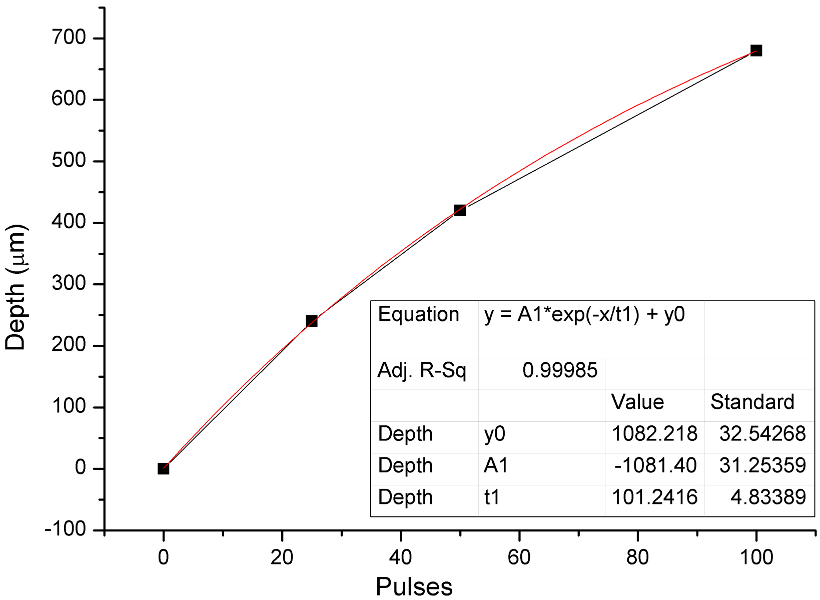
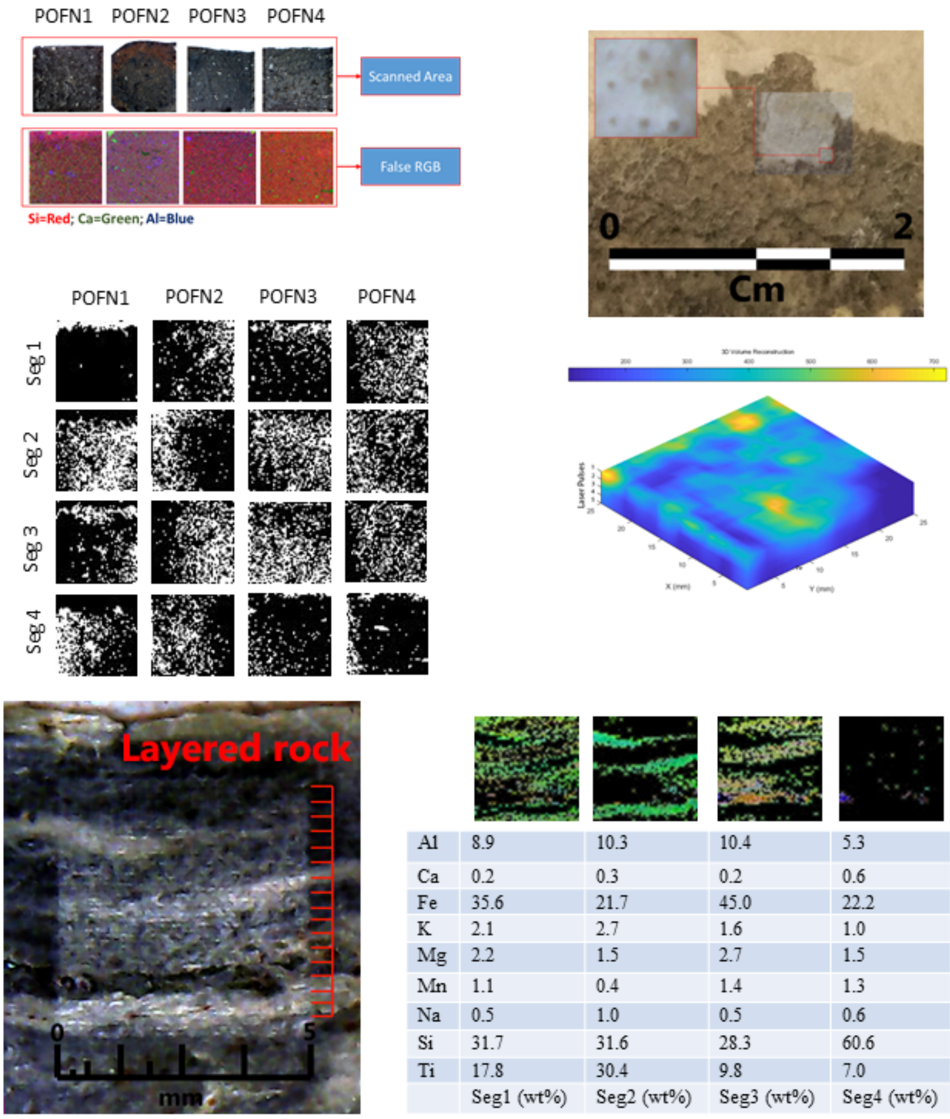


Fig. 3 - Depth of craters (µm) *vs.* number of laser pulses. The depth of craters follow approximatively an exponential curve.

The depth of focus (DOF) with a 10X magnification with 0.25 numerical aperture can be estimated in 8.5 µm (Sheppard, 1988).

THE APPLICATIONS

Although the strength of the technique is the analysis of inhomogeneous materials using mappings, homogeneous materials such as geostandard pellets were also tested with the instrument. The instrument showed its capabilities in the analysis of negative of thin sections (from ancient potsherds), of ancient mortars and stratified rocks (Fig. 4).



	Seg1 (wt%)	Seg2 (wt%)	Seg3 (wt%)	Seg4 (wt%)
Al	8.9	10.3	10.4	5.3
Ca	0.2	0.3	0.2	0.6
Fe	35.6	21.7	45.0	22.2
K	2.1	2.7	1.6	1.0
Mg	2.2	1.5	2.7	1.5
Mn	1.1	0.4	1.4	1.3
Na	0.5	1.0	0.5	0.6
Si	31.7	31.6	28.3	60.6
Ti	17.8	30.4	9.8	7.0

Fig. 4 - Some examples of the capability of the system: elemental maps, false color map (combining different maps), Artificial Inteligence segmentation of the map features and 3D reconstruction of the ablated surfaces.

After obtaining the elementary maps, they can be elaborated with methods coming from the field of multispectral imaging to *i*) obtain maps in false colors, *ii*) process images with the principal component analysis or *iii*) to segment the main elementary characteristics within the area scanned using neural networks. From the segmented map an average spectrum can be obtained which, once processed trough calibration-free LIBS methods, allow to obtain a quantitative analysis.

CONCLUSION

The μ-LIBS-Scan elementary mapping of the materials, in case of inhomogeneous materials, allows fast analysis without any sample preparation. The instrument does not require gas flows (argon or helium), which are very expensive. A further advantage is the possibility of using standardless quantitative methods that reduce analysis time, once automated, to a few seconds. The coupling with neural networks allows to segment the areas investigated in sections with similar elementary characteristics and then to obtain a quantitative analysis. In case of multilayer analysis, the capability of carry out a VECS (Virtual Elemental Cross Section) is a powerful tool for multi-layered materials in order to visualize the depth profile.

To improve the accuracy of the quantitative results, the ANN can supply for the construction of multivariate calibration curves, in a fraction of second.

A precise analysis protocol were established which allowed to provide certain map sizes with a well-defined spot and lateral resolution optimized for the analysis of geomaterials in Cultural Heritage.

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