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LIBS QUANTITATIVE ANALYSES OF BRONZE OBJECTS FOR CULTURAL HERITAGE APPLICATIONS

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Abstract. The present paper reports analyses made on bronze objects using Laser Induced Breakdown Spectroscopy technique. Where Cultural Heritage is concerned, a very important factor consists in obtaining maximum information with minimum invasiveness. Therefore, the irradiation, acquisition and detection parameters of the current LIBS setup (of INOE) were explored in order to assess the current potential of single pulse 1064 nm LIBS quantitative analyses on artefacts that contain copper. Certified standards (copper based alloys) were used for shaping the calibration curves, taking into consideration Cu, Sn and Pb concentrations. Each set of investigations was acquired using three laser energies (above the ablation threshold). After the proper working regime was established, quantitative LIBS analyses were made on an *Censer*, in order to determine the concentration of the major chemical elements identified. The data processing was made in LabView and MatLAB dedicated applications.

Key words: LIBS, Cultural Heritage, bronze, quantitative analyses.

1. INTRODUCTION

Laser Induced Breakdown Spectroscopy (LIBS) is a fast diagnosis technique based on the analysis of the spectral emission of a plasma plume created by an intense laser beam focused on a target surface. LIBS is quite a flexible technique that does not need sampling or sample preparation, that provides valid results both *in lab* and *in situ* environments [1]. It can be applied in various sceneries such as air [2–3], vacuum [4], fluids [5–6], high temperature/pressure [7] and presently, in outer space explorations [8].

The qualitative, semi-quantitative or quantitative LIBS applications fit right in the Cultural Heritage field, since it is a micro-destructive technique, which ablates tens or hundreds of nano-grams from the investigated material, providing a good sensitivity and a fast response [9]. Thus, there are some important hitches that may affect the semi-quantitative and quantitative LIBS investigations, such as reaching the LTE conditions in the plasma, self-absorption of high concentration elements, the matrix effects, and basically the large number of complex physical-chemical phenomena involved in the processes of ablation and plasma formation,

evolution and interaction with the background ambient etc. that are constantly cracked and unraveled by the LIBS community [10–12].

Double pulse (*dp*) LIBS configuration (orthogonal or collinear) is proven to deliver enhanced emission signal, if the right irradiation and acquisition parameters [13] are selected (energy, inter-pulse delay, spectrometer delay, gate-width etc.).

2. EXPERIMENTAL

The laser irradiation was achieved using a nanosecond Nd:YAG Q-switched laser (Quanta Systems), using the fundamental wavelength – 1064 nm. The laser beam was concentrated on the sample through a focus lens system (focal length 20–70 cm).

The detection and acquisition system consisted in a fiber optic collector and a gated ICCD coupled to an Echelle type spectrometer (Andor). The laser triggering and the gate of the ICCD were interconnected using a delay generator, which also panels the laser frequency at 2 Hz. The type of acquisition, gain, delay and gate width were set using the spectrometer's Andor software.

In order to avoid crater formation issues, each set of the analyses were acquired in previously non- irradiated spots on the objects. All the analyzed items were placed on an *x-y* translation stage, at the same focal length distance, and the irradiation, detection and acquisition parameters were kept constant.

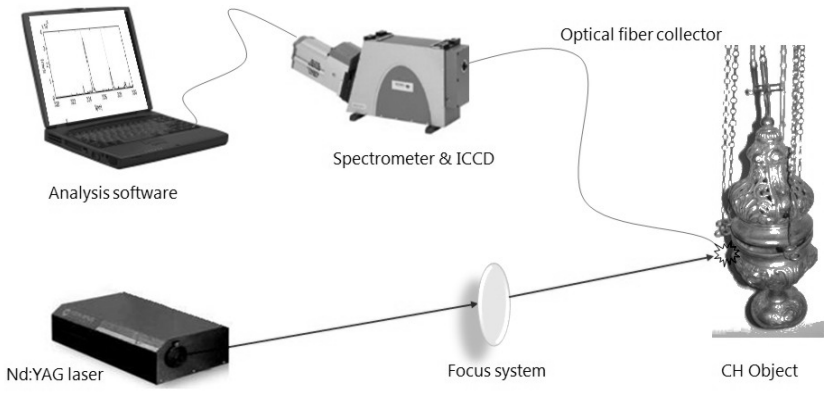

Fig. 1 – LIBS experimental setup.

The object under investigation is a 19th century bronze religious censer, part of a private Romanian collection. The LIBS investigations made on the artefact consisted in quantitative analysis of the spectral lines, in order to determine the concentration of copper and lead, employing a calibration slope acquired from reference samples.

The bronze samples used in the quantitative measurements are three Certified Reference Materials (CRM), with concentrations' range similar to the ones of the bronze Cultural Heritage object investigated. The concentrations of the CRM's are listed in Table 1.

Table 1

Cu and Pb concentrations of the standard bronze samples

CRM	Cu (%)	Pb (%)
LB11	76.97	10.56
LB15	72.52	21.76
7835	69.93	3.15

3. RESULTS AND DISCUSSIONS

In order to find the proper acquisition times, the delay was increased step by step. In Fig. 2 are presented the spectra acquired for each delay value and it can be observed how the quality of the lines (324.7 nm) fluctuates with the delay.

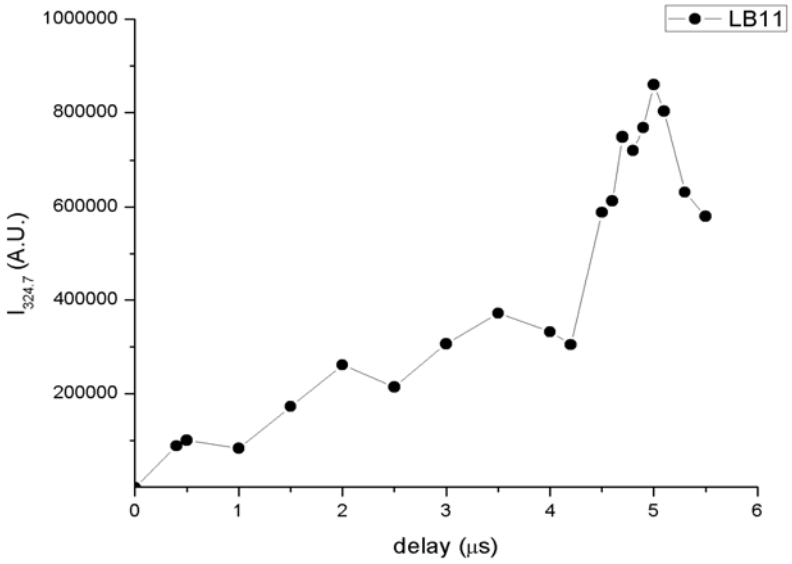

Fig. 2 – Intensity of 324.7 Cu line at different delay values for LB11 reference sample.

Considering the investigations presented above, the delay value was set at 5 μs and the gate width at 8 μs. The gain (signal/noise ration) was set at 220 out of 250 accordingly to previous experiments [14].

Taking into consideration the self-absorption that may affect the 324.7 nm copper lines, several energies above the ablation threshold were assessed, in order to select the proper one [15].

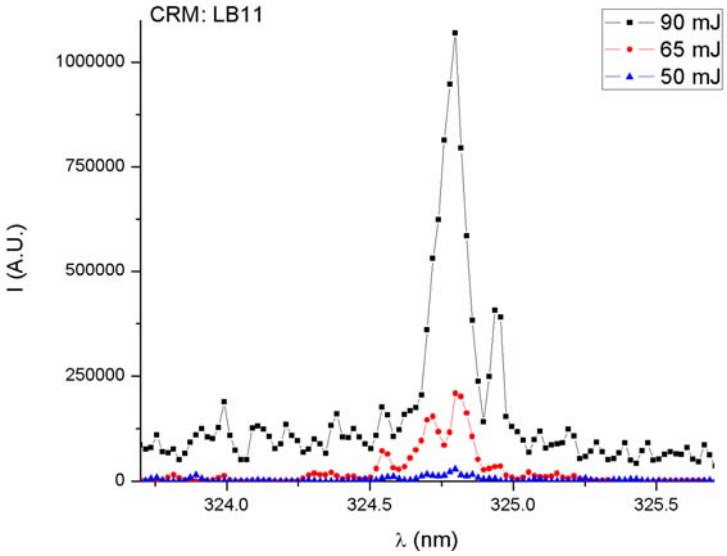

Fig. 3 – Sample LB11.

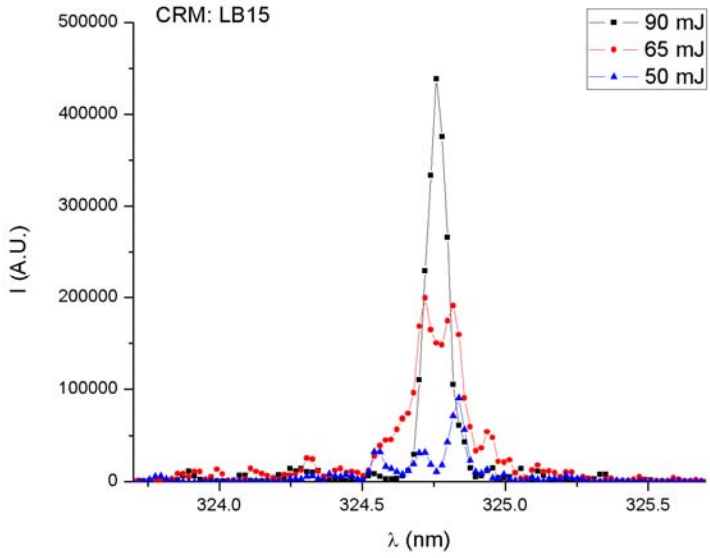

Fig. 4 – Sample LB15.

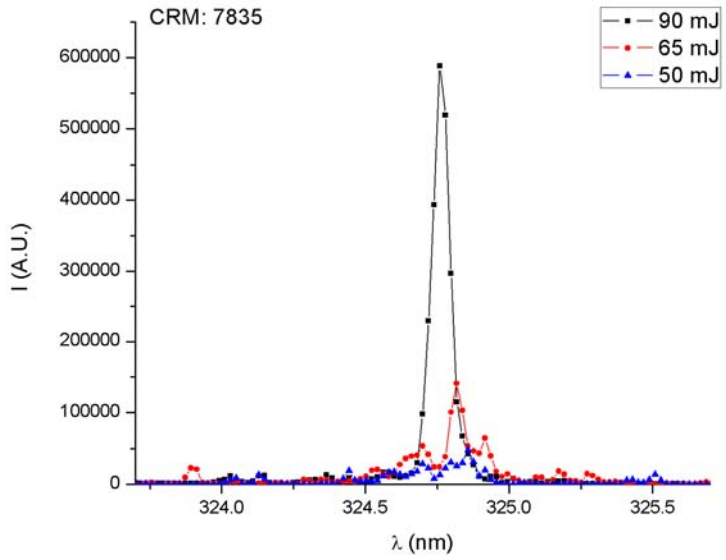

Fig. 5 – Sample 7835.

In Figs. 3, 4 and 5 are presented the spectra acquired for three representative energies applied on each of the reference materials. The changes in the shape of the 324.7 nm copper line while the energy is increased can be observed.

After examining the results obtained from the assessment presented above, the energy that was used in the quantitative analyses was set at 90 mJ. All the samples, as well as the *Censer,* were placed in exactly the same position, in order to have the same irradiation/acquisition geometry. All measurements were done in basic environmental conditions (air pressure, T = 18°C).

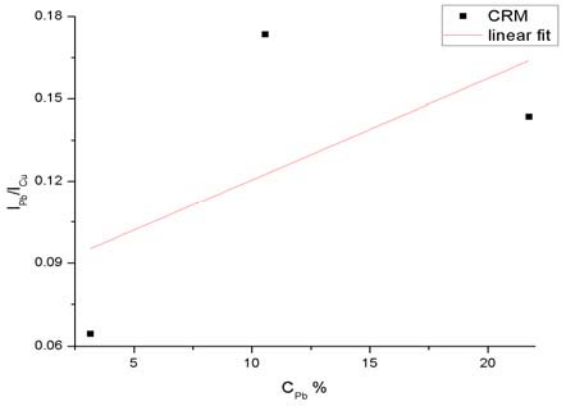

Fig. 6 – CRM calibration slope for Cu, E = 90 mJ.

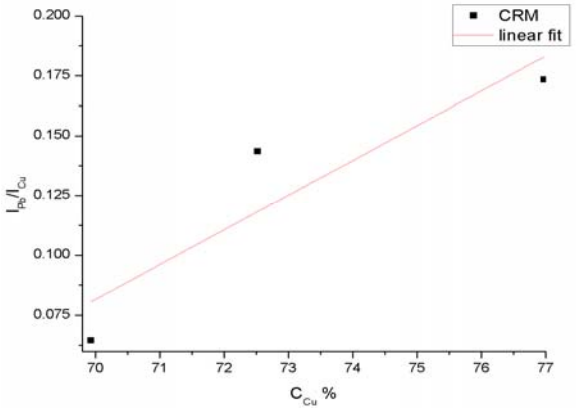

Fig. 7 – CRM calibration slope for Pb, E = 90 mJ.

The spectral data acquired were processed by averaging 20 series of pulses and then charted as described in Figs. 6 and 7. Each set of investigations was preceded by a few laser shots in order to ensure that the surface of the target is representative to the bulk composition and also to remove any surface impurities.

Accordingly to the calibration slopes obtained for the three certified reference materials, the quantitative analysis of the chemical elements present in the *Censer* was accomplished. The results obtained for copper and lead are presented in Table 2.

Table 2

Copper and lead concentrations of the *Censer*

E = 90 mJ	C_{Cu} (%)	C_{Pb} (%)	C_{Sn} (%)
Censer	78.00	16.40	4.2

4. CONCLUSIONS

The quantitative LIBS results reported in this paper were based on the linear dependency of the concentration on the intensity of the spectral lines, obtained with the help of reference standard materials (with certified concentrations). As previously reported, this approach can give us quite fast results, but it is highly influenced by the matrix effect induced by distinct electronegativity and ionizing potentials that have as result nonlinearities in the calibration slope, as reported previously in the literature. In the present study, the standard materials selected had similar ratios as the bronze object investigated, thus the interferences were minimum.

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