

Comparative study of mono and double pulse LIBS configurations analyses for *on-site* transportable set-up optimization

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The present paper presents a comparative study on the experimental results collected applying LIBS on three certified reference material samples with different copper concentration. The main interest of the study is the tuning of the LIBS set-up for onsite operation, as well as elaboration of documentation for future calibration protocols. The quality of the spectra and the accuracy of the results are evaluated and discussed for different irradiation and detection parameters: the gate width and the gain – from the detection system and the sp (355 nm or 1064 nm) and dp LIBS configuration.

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1. Introduction

In the conservation field, the quantity of the consumed material for artworks' investigation and diagnosis is the major concern and the current research is going towards new methods and equipments that can provide high accuracy results on site (without sampling), that can offer the possibility of remote investigations. Laser Induced Breakdown Spectroscopy (LIBS) is one of the most appreciated methods that are used in the identification and characterization of the diverse materials encountered in the Cultural Heritage conservation, but not only, e.g. the detection of material mix-ups, analysis of inclusions in alloys, ceramics [1], analysis of biological layers/deposits, etc. LIBS is an analytical technique that can be used in a wide variety of applications, giving us the possibility of qualitative, semi-quantitative and quantitative high-accuracy analyses, that don't require sampling or pre-processing of the piece investigated [2]. It consists on the determination of the elemental composition of the materials on the basis of the characteristic ionic and/or atomic emission from a micro-plasma produced by focusing a high-power laser on the investigated surface. LIBS is a reliable micro-destructive technique that presents us a fast and stand-off detection and identification of the chemical elements, one of its main advantages consisting in its real-time response. The detection limits for LIBS vary from one element to the next, depending on the objects' type, the irradiation conditions (wavelength, pulse area, energy), the detection conditions (gain, delay, gate width), the experimental conditions experiments etc., but mainly the volume of material necessary for obtaining a good spectrum for the identification of the chemical elements' emission lines is less than 0.1 mm³. It is necessary to take into consideration the materials' heterogeneity factor, mainly the sum of impurities present in the investigated surface, which

could affect the accuracy of the analyses. The present paper presents a comparative study on experimental results collected applying LIBS on three certified reference material samples with different copper concentration. The main interest of the study is the tuning of the LIBS set-up for onsite operation, as well as elaboration of documentation for future calibration protocols. The quality of the spectra and the accuracy of the results are evaluated and discussed for different irradiation and detection parameters.

2. Principle of the experiment and the setup

The LIBS analyses can be obtained either using single pulse (sp) or double pulse (dp) method. The second method provides us higher analytical capabilities based on the increased intensity of the collected signal, therefore a smaller volume of material consumed (microns' order) [3]. Also, in underwater investigations the double pulse method is extremely useful, as the first laser pulse induced a rapid heating of the liquid that is followed by an explosive expansion and formation of a gas bubble and the second laser pulse (send with an ns delay) excites the plasma inside the bubble, having as result a relatively intense and narrow spectral emission [4,5]. Both methods (sp and dp) are currently validated and successfully applied in laboratory conditions, therefore the LIBS system is at this time transposed into a transportable set-up for on field investigations.

The double pulse LIBS setup can be obtained using the collinear configuration or the orthogonal configurations: pre-ablation pulse or reheating of the plasma.

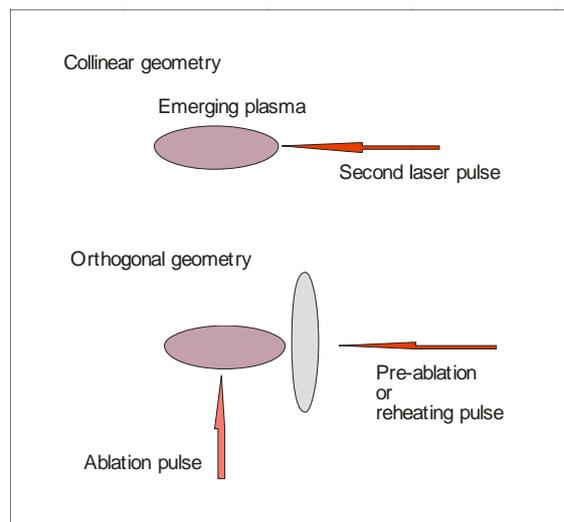


Fig. 1. The configurations for double pulse LIBS investigations: collinear geometry; orthogonal geometry.

The LIBS set-up used in the investigations consisted in two Nd:YAG lasers, Q-switched, one emitting at 355nm and the other at 1064 nm, with energies of 20 mJ, respectively 350 mJ. The two lasers were synchronized using a delay generator and the delay between the two laser pulses was set at 3 μ s. The detection was accomplished using an Echelle type spectrometer with ICCD and the acquisition of the spectra was made by dedicated software from Andor.

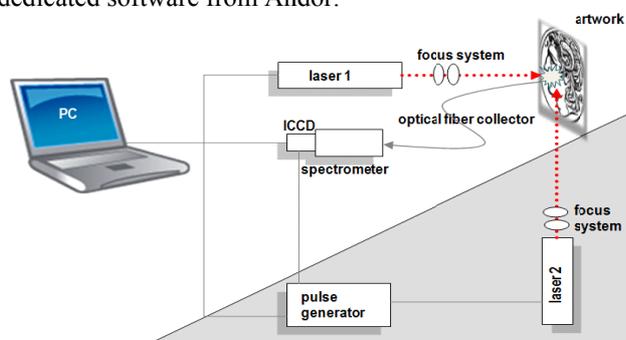


Fig. 2. LIBS double pulse onsite set-up.

The major parameters drawn in the time-resolved detection are the gate delay or delay time and the gate width. τ_d is the time since the laser pulse is triggered until the start of recording, and τ_w is the time period over which the spectrum is recorded.

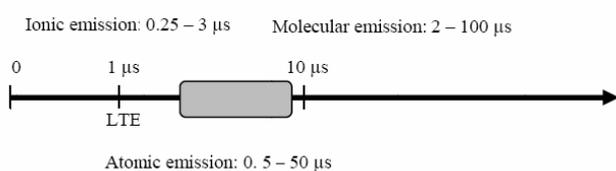


Fig.3. Plasma time-line.

The LIBS spectrum evolves rapidly in time due to the fact that the laser plasma is a pulsed source. At the beginning the plasma light is dominated by a continuum *white light* that is caused by Bremsstrahlung, as free electrons and ions recombine in the coupling plasma. If the plasma light is integrated over the entire emission time of the plasma, this continuum light can seriously interfere with the detection of weaker emissions from minor and trace elements in the plasma. Usually, LIBS measurements are usually carried out using time-resolved detection so that the detector will be turned on after this *white light* had significant impact on the intensity, but the atomic line emissions are still present. Another significant parameter is the gain that can help us overcome the read noise limit. Therefore, it was evaluated the impact on the quality and accuracy of the acquired spectra using a delay of 2 μ s and 3 μ s, with gatewidths of 8 μ s and 10 μ s and gain values of 220 and 240.

The spectral signal was obtained from application of sp and dp LIBS - with the previous mentioned delays, gate widths and gains - on three standard samples with different copper concentrations, that have known and homogenous composition. These samples have been selected for their representativeness in current metallic artwork conservation, having in view the large exploitation of bronze in both art and archaeology.

a. *Certified reference material 212XNA4A* - chill cast, copper concentration of 20.34%



Fig. 4. CRM 212XNA4A photo.

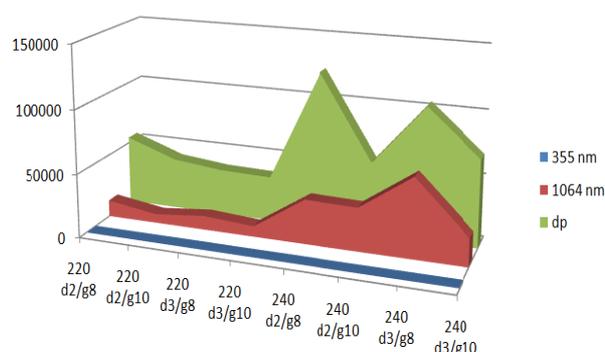


Fig. 5. Evaluation of sp and dp LIBS – copper main line: 324.7 nm.

In Fig. 5 there is presented the intensity of one of the major copper lines: 324.7 nm, for single pulse 355 nm, single pulse 1064 nm and dp 355 nm and 1064 nm. For each sp/dp regime the delay and gate width were also fluctuated, in the following manner:

- delay 2 μ s/gate width 8 μ s;
- delay 2 μ s/gate width 10 μ s;
- delay 3 μ s/gate width 8 μ s;
- delay 3 μ s/gate width 10 μ s;

The spectra were acquired using 220 gain and 240 gain. Taking a look at fig.4, it can be clearly observed that the dp is providing an almost double height intensity lines than the sp 1064 nm. The sp 355 nm signal is very low, although the spectra can provide us the emission line information.

212xx - 220 gain

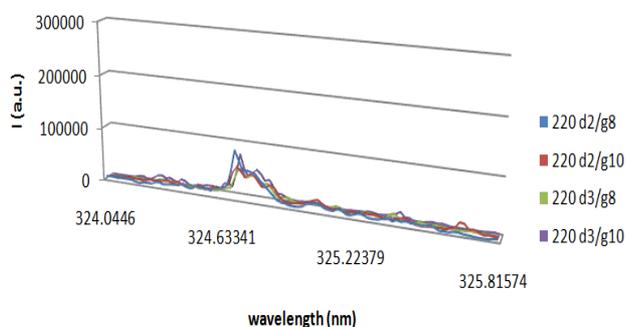


Fig. 6. LIBS dp spectra for 220 gain

212x- 240 gain

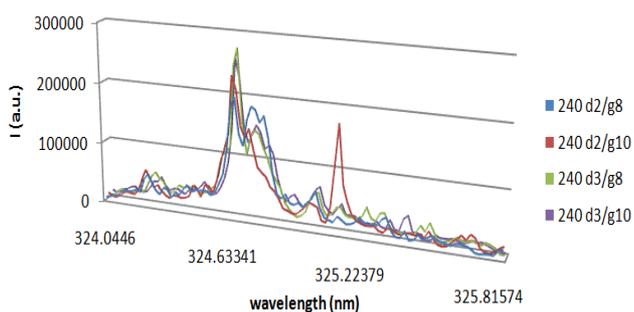


Fig. 7. LIBS dp spectra for 240 gain

As it can be observed from Fig.6 and Fig.7, 240 gain provide a much higher intensity lines, due to the better signal/noise ratio – as it was expected.

In the case of CRM 212XNA4A sample, with a copper concentration of 20.34%, the best result corresponds to dp LIBS, detection regime of: delay = 2 μ s, gate width = 10 μ s and 240 gain.

b. Certified reference material: 32XLB15 - chill cast, copper concentration of 72.52%



Fig. 8. CRM: 32XLB15 photo.

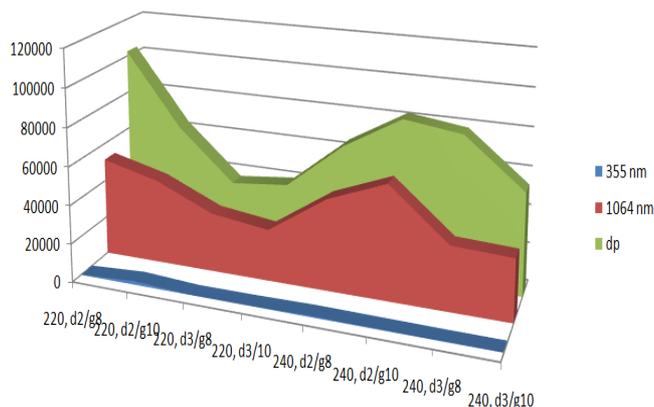


Fig. 9. Evaluation of sp and dp LIBS – copper main line: 324.7 nm.

In Fig. 9 it is presented the evaluation of the intensity of 324.7 nm copper line for single pulse 355 nm, single pulse 1064 nm and dp 355 nm and 1064 nm, gain 220 and 240, delay and gate width of:

- delay 2 μ s/gate width 8 μ s;
- delay 2 μ s/gate width 10 μ s;
- delay 3 μ s/gate width 8 μ s;
- delay 3 μ s/gate width 10 μ s;

Taking a look at Fig.9, it can be clearly observed that the dp is providing much higher intensity lines than the sp 1064 nm. The sp 355 nm signal is very low, although the spectra can provide us the emission line information.

32x - 220 gain

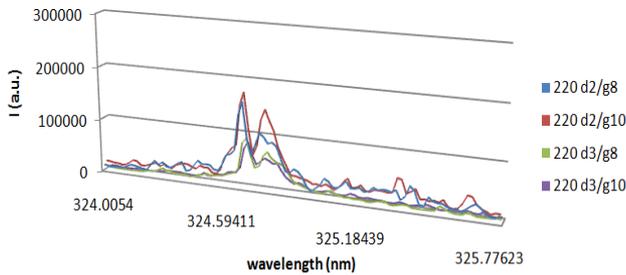


Fig. 10. LIBS dp spectra for 220 gain

32x - 240 gain

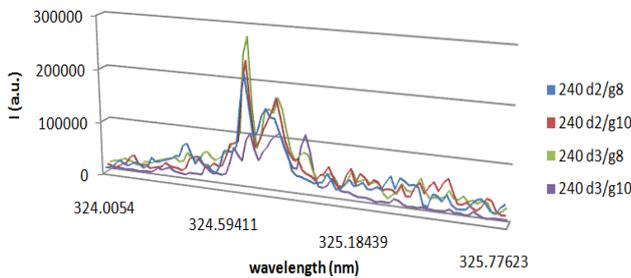


Fig. 11. LIBS dp spectra for 240 gain

As it can be observed from Fig.10 and Fig.11, 240 gain provide a much higher intensity lines, due to the better signal/noise ratio – as it was expected.

In the case of CRM 32XLB15A sample, with a copper concentration of 20.34%, the best result corresponds to dp LIBS , detection regime of: delay = 3 μs, gate width = 8 μs and 240 gain

c. Certified reference material: 36XCN22A - chill cast, Cu= 91.80%



Fig.12. CRM 36XCN22A photo.

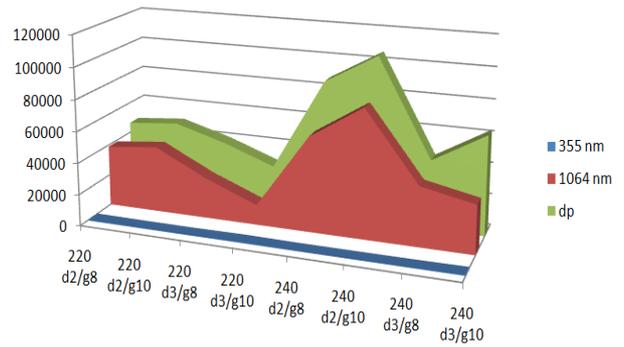


Fig. 13. Evaluation of sp and dp LIBS – copper main line: 324.7 nm

The evaluation of the intensity of 324.7 nm copper line is presented in Fig. 13. Similar to the other 2 samples it was subjected to LIBS with single pulse - 355 nm, single pulse - 1064 nm and dp 355 nm & 1064 nm. The delay and gate width were selected as follows:

- delay 2μs/gate width 8μs;
- delay 2μs/gate width 10μs;
- delay 3μs/gate width 8μs;
- delay 3μs/gate width 10μs;

Taking a look at fig.13, it can be clearly observed that the dp is providing much higher intensity lines than the sp, both in 220 gain and 240 gain cases. The sp 355 nm signal is very low, although the spectra can provide us the emission line information

36x - 220 gain

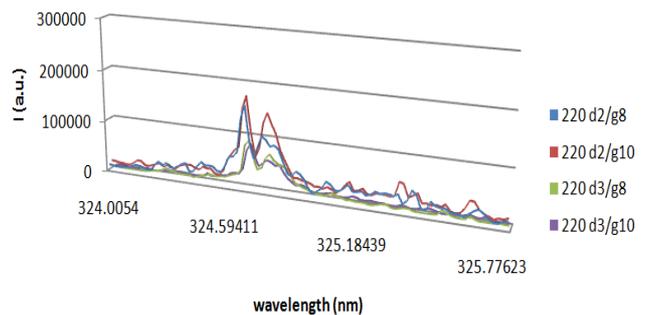


Fig. 14. LIBS dp spectra for 220 gain

36x - 240 gain

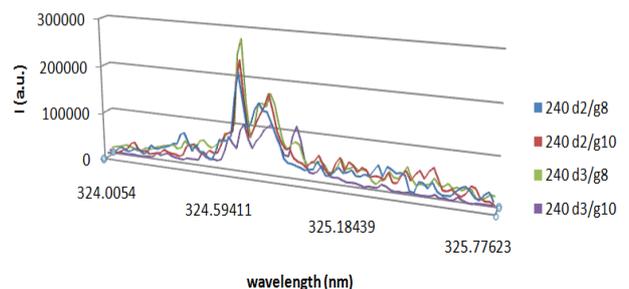


Fig. 15. LIBS dp spectra for 240 gain.

In the case of CRM 36XCN22A sample, with a copper concentration of 91.80%, the best result corresponds to dp LIBS, detection regime of: delay = 2 μ s, gate width = 10 μ s and 240 gain.

3. Conclusions

This study, preliminary to the spectroscopic optimization, evaluates the quality of the spectra for the on site transportable setup for sp and dp LIBS analysis. The parameters taken into consideration were the delay, the gate width and the gain – from the detection system and the sp (355 nm or 1064 nm) and dp LIBS methods. The quality of spectra does not change much between the delays and gate widths fluctuation, so future studies will consider greater unit differences. The spectra acquired helped to the elaboration of documentation for future calibration protocols.

Although it is clear that dp LIBS has the most qualitative outcomes, we must also take into consideration the fact that the detection limits vary from one element to the next, depending on the material type and the experimental conditions, undertaking a reduced spectroscopic reproducibility. The best spectral information it is observed when we accumulate a series of spectra, but we must take into consideration the fact that these analyses are made on cultural heritage objects, and every micrometric bit of the object has an inestimable value. Therefore we have to make the best from less.

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