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Effects of Pulse Duration in Laser-induced Breakdown Spectroscopy

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is a technique that leverages atomic emission towards element identification and quantification. While the potential of the technology is vast, it still struggles with obstacles such as the variability of the technique. In recent years, several methods have exploited modifications to the standard implementation to work around this problem, mostly focused on the laser side to increase the signal-to-noise ratio of the emission. In this paper, we explore the effect of pulse duration on the detected signal intensity using a tunable LIBS system that consists of a versatile fiber laser, capable of emitting square-shaped pulses with a duration ranging from 10 to 100 ns. Our results show that, by tuning the duration of the pulse, it is possible to increase the signal-to-noise ratio of relevant elemental emission lines, an effect that we relate with the computed plasma temperature and associated density for the ion species. Despite the limitations of the work due to the low-resolution and small range of the spectrometer used, the preliminary results pave an interesting path towards the design of controllable LIBS systems that can be tailored to increase the signal-to-noise ratio and thus be useful for the deployment of more sensitive instruments both for qualitative and quantitative purposes.

Author Keywords. Laser-induced Breakdown Spectroscopy, Fiber Laser, Pulse Duration, Square Pulses.

Type: Research Article

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a process laid on the concept of atomic emission spectroscopy after the vaporization, atomization and excitation of a material using a laser, creating a laser-induced plasma. These days, LIBS has established as a promising technology in many domains, from geology (Fabre 2020) to agriculture and food science (Nicolodelli et al. 2019), by leveraging two major advantages: the real time detection of multiple elements, including the lighter ones (not available with X-Ray Fluorescence), and the remote micro-destructive analysis of non-prepared samples. Still, while it proves useful for both qualitative and quantitative purposes, the poor performances on the latter remain the

caveat of the technique, with the variability of the method being one of the most relevant factors.

The variability is a multifactorial problem that is mostly associated with the variable plasma volume and inhomogeneity generated between distinct shots, and stoichiometric issues. While most of the literature reports to the normalization of the detected signal (Guezenoc, Gallet-Budynek, and Bousquet 2019), increasing the signal-to-noise ratio (SNR) is also an important matter as average techniques can become detrimental when this ratio is particularly low. Multiple studies have focused on the process of laser ablation and plasma excitation to increase the SNR, with the most common being the use of double-pulse systems (Babushok et al. 2006). More recently, the effects of the laser pulse duration also became a topic of discussion, with long nanosecond duration pulses allowing for improvements of SNR and limit of detection, in particular in challenging operation conditions (e.g., underwater analysis) (Elnasharty 2016; Li et al. 2021). In this work, we explore the possibility of enhancing the SNR by varying the pulse duration, making use of a controllable LIBS system with an optical fiber laser.

2. Experimental System

A standard LIBS experimental setup was used in this work (Figure 1). An ytterbium-doped fiber laser (MWTechnologies, model PFL-1064-FL-10kW, M^2=1.4) emits 1064.8 nm pulses with a diameter of 0.51 mm. The laser is capable of operating in single pulse or with a repetition rate up to 250 kHz. Pulses can be from 5 to 305 ns long with the possibility of controlling their shape with 5 ns resolution.

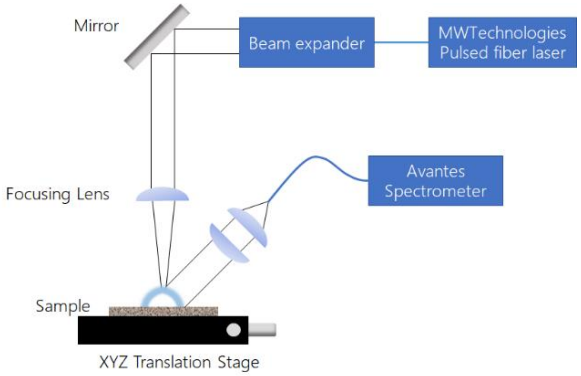

Figure 1: Schematic of the experimental setup with the optical fiber laser

For this experiment, pulses with 10, 20, 50, 75, and 100 ns of pulse width (Figure 2) were designed in-house as square-shaped and with energy around 90 µJ each. These pulses are expanded with an x12 beam expander and then focused onto the surface of the sample using a 100 mm plano-convex lens. The resulting spectra are collected with a 2 lenses optical system into a 200 µm optical fiber and redirected to the spectrometer (Avantes, model AvaSpec-ULS2048CL-EVO, 482-615 nm, resolution < 0.1 nm).

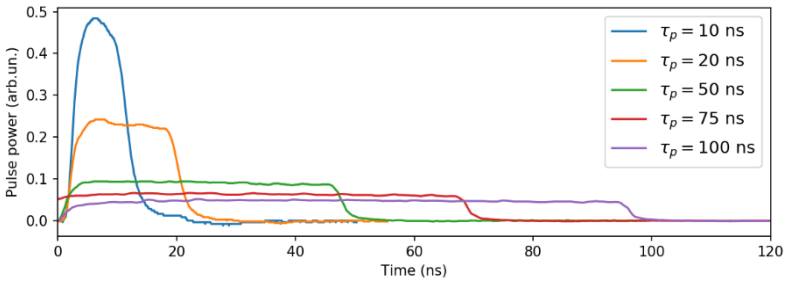

Figure 2: Tailored laser pulses

The analyzed sample was a copper sputtering target (ref. C8-9000-D70) (Figure 3) with 99.999% purity. For each pulse width, 10 single shots were made onto the sample, with a 1 mm distance apart. The spectra were collected with an integration time of 30 µs, which contained the plasma lifetime (non-gated). For the data analysis, we averaged the set of 10 spectra and removed the background and baseline using an asymmetric least squares method.

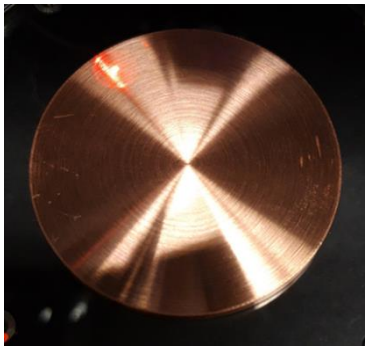

Figure 3: Copper sputtering target with 99.999% purity

3. Results

Some averaged spectra are presented in Figure 4, revealing an increase in intensity with the pulse duration. In Figure 5 Top, it is possible to observe the variation of the integrated intensity of the emission line of Cu I at 578.2 nm, revealing an increase by a factor above x1.5 for longer duration pulses when compared against the shortest ones. To explain the results, we recover the Boltzmann theory, valid under the local thermodynamic limit, that gives that the intensity of a given line, associated with the transition between an upper energy level E_i and the lower energy level E_j is given by:

$$I_{ij} = \frac{C}{\lambda}\frac{N_1(T_p)A_{ij}g_i}{U_1(T_p)}\exp\left(-\frac{E_i}{k_B T_p}\right) \quad (1)$$

where C is an experimental constant, λ the emission wavelength, A_{ij} the amplitude for the transition, g_i the degeneracy, E_i the energy of the upper level, k_B the Boltzmann constant and T_p the plasma temperature. By taking the logarithmic of the Equation (1), an estimate of the plasma temperature can be achieved through the slope of the Boltzmann plot (Figure 6). Furthermore, $N_1(T_p)$ and $U_1(T_p)$ stand for the atom density in the given ionization state (we consider just the first ionized state only) and the partition function, respectively. In particular, $N_1(T_p)$ can be calculated recursively using the Saha ionization equation given by:

$$\frac{N_{i+1}N_e}{N_i} = \frac{2}{{\lambda_B}^3}\frac{g_{i+1}}{g_i}\exp\left(-\frac{E_{i+1}-E_i}{k_B T_p}\right) \quad (2)$$

with λ_B being the de Broglie wavelength, while the partition function $U_1(T_p)$ is given by:

$$U_1 = \sum_i e^{-\frac{E_i}{k_B T_p}} \quad (3)$$

By looking at Equation (1), it is straightforward to conclude that for a given line, the integrated intensity can only increase in two distinct scenarios: the plasma temperature increases; or the ratio $R(T_p) = N_1(T_p)/U_1(T_p)$ increases. Yet, it is important to notice that this ratio depends on the density of the ionized species and partition function and that both quantities vary with the plasma temperature, thus involving a complex interplay that shall be taken into consideration in our analysis. Indeed, the results depicted in Figure 5 Bottom suggest that while the plasma temperature decreases, the ratio R (computed using the Saha equation and partition function definition) increases (around x1.5 times), which suggest that the second

scenario may be the dominant mechanism responsible for the enhancement of the SNR for longer pulses.

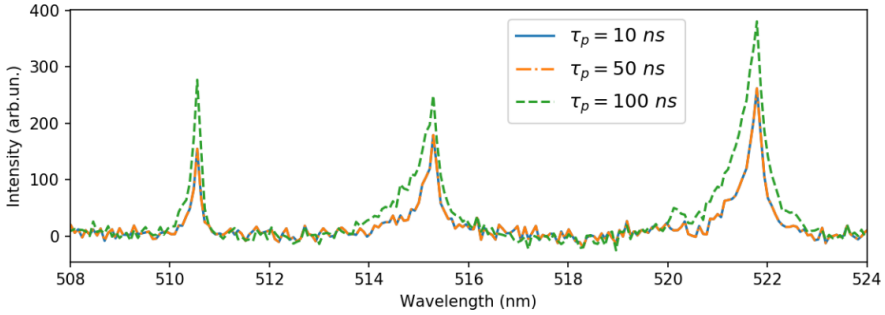

Figure 4: Averaged results of the spectra (10 shots) collected for the distinct pulse durations used

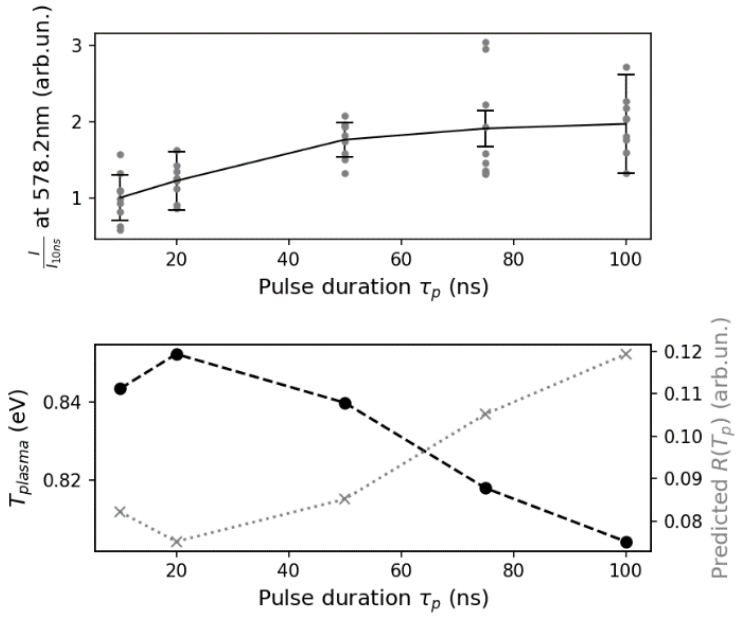

Figure 5: Results obtained for varying pulse durations. Top: Variation of the integrated intensity of the emission line of Cu I at 578.2 nm, normalized to that obtained for the pulse of 10 ns of duration. Bottom: Plasma temperature computed using the Boltzmann plot method and predicted associated R as defined in the main text

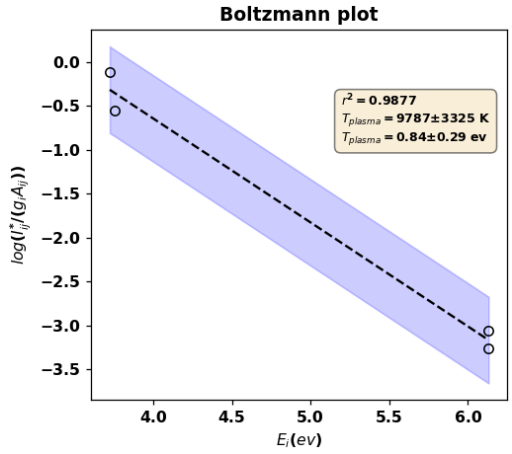

Figure 6: Typical result of a Boltzmann plot, here obtained for the 50 ns pulse duration

4. Conclusions

In this work, we explore the influence of the variable time duration of square pulses on the detected intensity of the element peaks of the LIBS spectra. Our findings show that long nanosecond pulses can enhance SNR detected for a given emission line when compared against shorter ones having the same energy. These results show that controlling a LIBS system at the pulse duration level can be an interesting approach towards deploying more sensitive instruments, both for qualitative and quantitative purposes. Nevertheless, we note that an analysis based on the Saha-Boltzmann equation system suggests that this behavior may be associated with a complex interplay between plasma temperature, the density of the first ionized state, and the corresponding partition function, which suggest that the results shall be confirmed using different samples and materials. Further work would allow checking if it is possible to optimize one pulse shape to every sample or if each sample would require a different pulse optimization.

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Acknowledgments

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