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Time resolving imaging spectroscopy applied to the analysis of plasmas generated by pulsed lasers

F C Alvira[1,4], L Ponce[3], M Arronte[3] and G M Bilmes[1,2]

[1] Centro de Investigaciones Ópticas (CONICET La Plata- CIC) CC 3, 1897, Gonnet, La Plata, Buenos, Aires, Argentina.
[2] Facultad de Ingeniería Universidad Nacional de La Plata, La Plata, Buenos Aires, Argentina.
[3] CICATA-IPN, Unidad Altamira, Altamira 89600, Tamps, México.

E-mail: fcalvira@ciop.unlp.edu.ar

Abstract. Start your abstract here… Time resolved imaging spectroscopy were used to study the spatial and temporal evolution of LIBS (Laser Induced Breakdown Spectroscopy) plasmas generated in Cu substrates by laser pulses of different duration. Long laser pulses (microsecond) and short laser pulses (nanosecond) as well as multipulse emission were used for excitation. Analysis was made by using an imaging spectrometer with time resolved detection. Results show that the use of long laser excitation pulses produce emission spectra with the same signal to noise ratio, but with lower resolution than those produced with shorter ones. The different species generated in LIBS experiments as neutral or single ionized have a different spatial distribution inside the plasma. We demonstrated that using spatial discrimination procedures is possible to obtain spectra with the same signal to noise ratio than those obtained with a gating detector. In this case an appreciable advantage in cost reduction is obtained by replacing the gating detector by a cheap screen.

1. Introduction

The characterization of laser generated plasmas by spectroscopic determination of their main parameters has been a topic of relevance since the advent of the laser. This interest has grown in recent years not only by the plasma physics itself. It improves the applications involving these plasmas, like Laser Induced Breakdown Spectroscopy (LIBS), and provides a better understanding of these complex and versatile spectroscopic sources.

In order to optimize the detection capabilities of LIBS it is important to know how certain parameters, as resolution and sensitivity depends on pulse duration or multi pulse excitation. Also it is relevant to determine if there is any difference between the temporal and spatial evolution of plasmas generated by long (microsecond) and short (nanosecond) laser pulses. This different pulse excitation conditions include the main regime of laser- matter interaction (thermal ablation) under wich LIBS technique is commonly employeed. It is well known that the processes that take place during laser material interaction differ significantly according with laser pulse duration[1-4]. For instance, in the case

[4] To whom any correspondence should be addressed.

of plasmas generated by long and short laser pulses there is an interaction between the generated plasma and the pulse itself (i.e. the last part of the pulse).

Another relevant question for the purpose of optimizing the detection is if there are regions, inside the plasmas generated by laser ablation, where the distribution of certain species is more abundant than others.

In this paper we used time resolved imaging spectroscopy to study the above questions and to optimize the best space-time conditions that improve the spectroscopic information obtained in LIBS.

2. Experimental Set up

Figure 1 shows the experimental set-up used. The irradiation sources were a comercial Q-switched Nd: YAG laser, with pulse duration of approximately 7 ns (FWHM) operating at 1064 nm; a home made microsecond laser with a pulse duration of 100 μs operating at 1064 nm, and a home made multipulse passive Q-switch laser that produce sequences of pulses emitted every 2 microseconds, with a duration of each individual pulse of 20 ns, and 5 mJ of energy. In this case the number of pulses emitted can be controlled from 2 to 10.

In all experiments the laser beam was focused on the sample using a 20 cm focal lens, avoiding plasma formation in the air. The energy and focusing of the laser pulse was controlled in all the experiments to have a fluence value of 10 J/cm^2 in the sample. Energy was measured using an energy meter with a pyroelectric detector (RjP-765, Laser Precision Corp.) splitting the laser pulse by means of a beam-splitter.

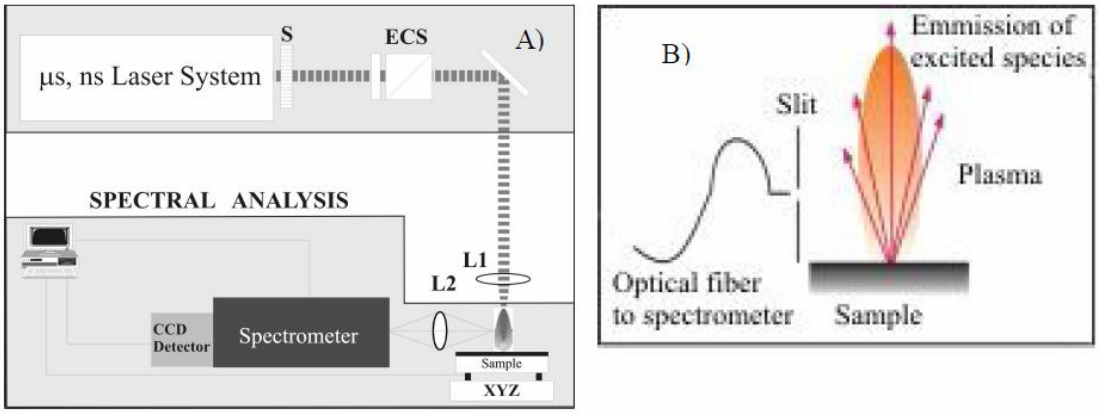

Figure 1. A) Experimental setup. S: Shutter; ECS: Energy Control System; L1 and L2: focusing lens; XYZ: motorized xyz stages. B) Sketch of the screening method used for plasma spatial selection.

3. Results and discussions

3.1. Spectral Identification and linewidths of Cu emission as a function of laser pulse duration

Figure 2 shows the emission spectra of Cu, in the region 505-525 nm, corresponding to plasmas generated by nano and microsecond lasers. Neutral and ionic Cu lines were identified as: λ= 510, 515 and 521 nm (Cu I) and λ= 509 nm (Cu II). Longer excitation pulses produce more intense emission than shorter ones. Then, to compare both spectra, the intensity of the 521 nm line was used for normalization. As it can be seen for λ = 515 nm, the line width (Δλ) obtained by exciting with microsecond pulses (0.97 nm) is wider than that registered with nanosecond ones (0.36 nm). In general (Δλ) is the sum between the natural line width, Doppler broadening and broadening by pressure or Stark[5-8]. Typically, the natural width of a line is about 10^{-3} nm and Doppler width is slightly higher, but of the same order of magnitude. In contrast, the Stark broadening or pressure broadening is an

order of magnitude greater than the previous ones[1]. Thus, in practice $\Delta\lambda$ is dominated by Stark broadening.

The observed increase in the linewidths with increasing laser pulse duration can be associated with an increase in the number of collisions between the species[9-14]. This would mean that plasmas generated by longer pulses have a higher level of electron density, which can be explained assuming that there is an interaction between the incident radiation and the generated plasma. Because the mechanism of laser ablation is similar using microsecond and nanosecond pulses, the only difference is the interaction time between the laser pulse and the generated plasma. Therefore plasmas generated with microsecond pulses have higher number of collisions and therefore greater electron density than those produced with nanosecond pulses.

The fact that laser plasma interaction is responsible for the broadening in the emission lines has been tested in an experiment carried out by irradiating the sample with a multipulse laser. In this experiment the first pulse generates the plasma, and subsequent pulses are mostly absorbed by the plasma to increase the number of collisions in it. Table 2 shows how increases the line width as a function of the number of incident pulses impinging on the sample.

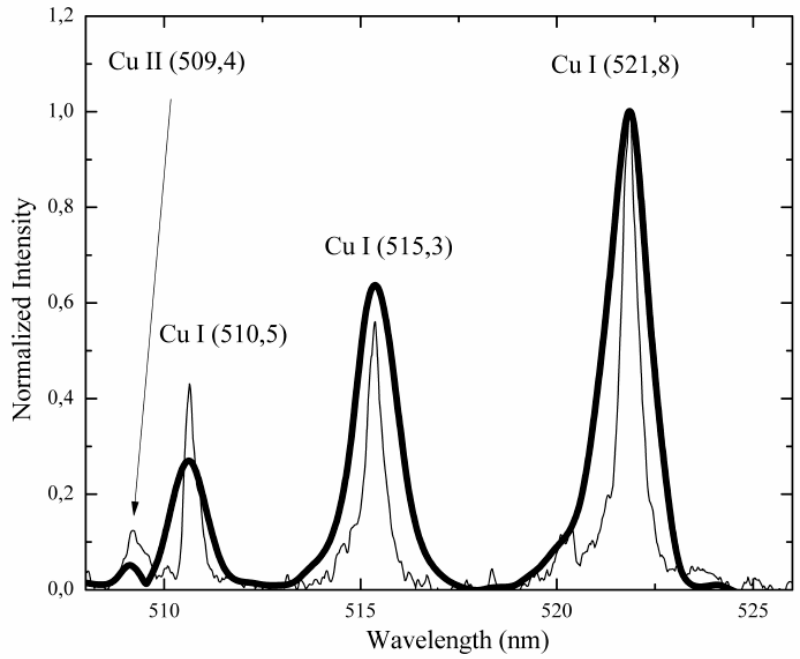

Figure 2. Cu emission spectrum generated by microsecond laser pulses (thick line) and nanosecond laser pulses (thin line). The spectra were obtained without time delay between the laser shot and detection, and in the best spatial conditions to minimize bremsstrahlung radiation.

Table 1. Linewidths $\Delta\lambda$ (nm) of the line 515 nm of Cu as a function of the number of sequential laser pulses that impinges on the sample. A multi-pulse laser with passive Q-switch was used.

Number of Laser Pulses	$\Delta\lambda$ (nm)
2	1.27
4	1.31
6	1.96
8	2.17
10	2.23

From a spectroscopic point of view and for applications in which resolution is an important parameter the above results allows to conclude that the use of long pulses or multiple pulses have the consequence of an increasing in the line widths of the emission spectra, which means less spectral resolution. Finally figure 2 shows that despite that longer excitation pulses produce more intense emission, the signal to noise ratio is equivalent with both excitation sources. So, there is not any advantage in using microsecond pulses with respect to nanosecond excitation, which provides better resolution.

3.2. Spatial distribution of species in the plasma

Figure 3 shows the spatial distribution of the normalized intensity of the emission lines of Cu in the region of 500 - 550 nm, corresponding to plasmas generated by nanosecond and microsecond pulses. Figure 3a show a typical example of a normalized intensity vs. wavelength and vs. spatial coordinate. The spatial coordinate was defined as the distance between the surface of the sample and the observation point. Figure 3b shows the intensity of each line as a function of the spatial coordinate.

In all cases the emission lines of neutral elements have a similar dynamic. This follows from observing the position from which the emission starts to appear and the location of the maximum.

The emission of the atom single ionized (λ= 529 nm) is located in a different region where most neutral species are located. It is also noted that this species is distributed from 5 to 16 mm from the sample, while the neutral species from 4 to 24 mm.

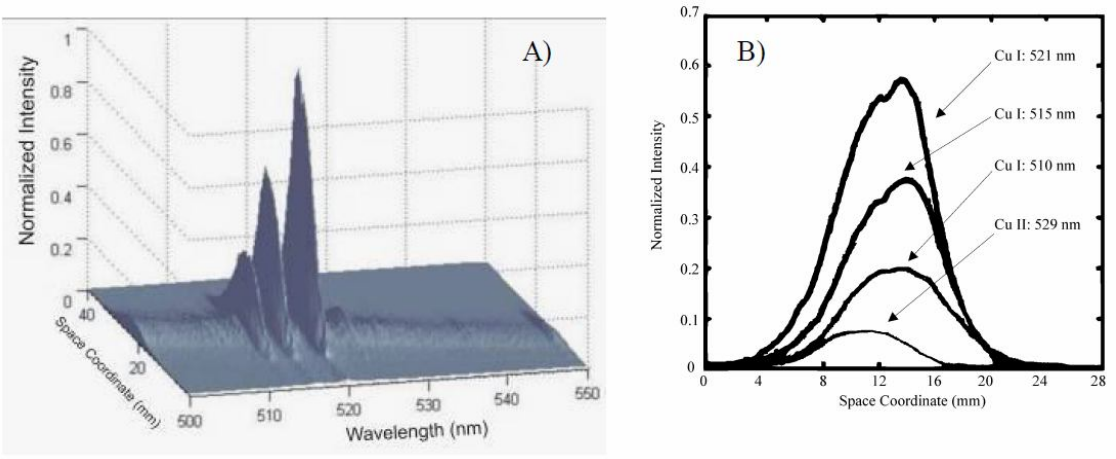

Figure 3. Spatial distribution of the normalized intensity of the emission lines of Cu in the region 500-550 nm, corresponding to plasmas generated by microsecond and nanosecond laser pulses. a) Normalized intensity vs wavelength and vs. spatial coordinate. b) Normalized intensity of the lines vs. the spatial coordinate. Time delay 2 us.

3.3. Spatial and temporal discrimination procedures to improve signal to noise LIBS spectra

Typically, recorded spectra obtained with laser produced plasmas have the emission lines of the species superimposed over a background produced by the "Bremsstrahlung" radiation[15-18]. In plasmas generated with micro and nanosecond pulses, this radiation is particularly intense during the first microsecond of the plasma lifetime, reducing the quality of the spectra and lowering the signal to noise ratio of the emitted lines[19]. To avoid this effect, temporal discrimination is typically used generating an electronic delay between the incident laser radiation and the timing of the onset detection. This delay is similar to the lifetime of the Bremsstrahlung radiation. Another approach to improve the detection of the line emission is using spatial discrimination[20]. This can be done by "screening" the spatial region near the surface sample, where Bremsstrahlung radiation is most intense[21,22]. The screening can be made by using a slit or directly blocking this part of the plasma.

Regarding to the advantages of using the temporal or spatial methods to improve signal to noise ratio we compared both procedures.

Figure 4 shows a typical spectrum obtained with temporal discrimination for micro and nanosecond pulse excitation. We show a spectrum obtained with nanosecond pulse excitation with and without time delay. As it can be seen with no delay (10 ns) emission lines of Cu are superimposed over background (thick spectrum in Figure 4) and have higher spectral width than those obtained with a proper delay time of 1.6 μs (thin spectrum in Figure 4).The differences in the registered spectral width can be explained taking into account that during the first microsecond of the plasma life, there is a large number of particles (electrons, ionized atoms and neutral atoms), colliding between them. On the other hand Figure 5 shows the effect of spatial screening on the spectrum of a Cu sample, generated by nanosecond pulse laser ablation. As it can be seen, results are equivalent to that obtained with temporal discrimination.

We can conclude that both methods can be used, with the advantage in the screening case that good quality spectra can be obtained with more simplicity and lower cost.

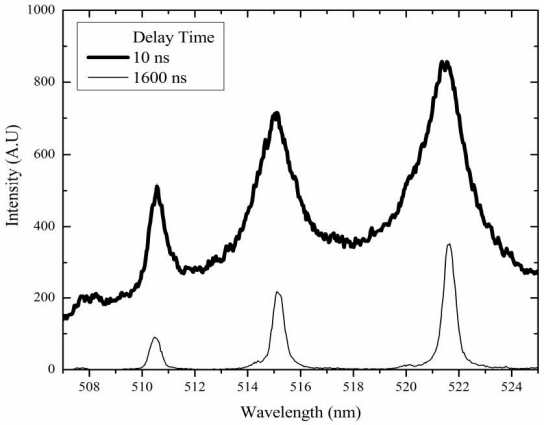

Figure 4. Cu spectra obtained with different time delays: 10 ns (thick line) and 1.6 μs (thin line). A nanosecond pulsed laser was used as excitation source.

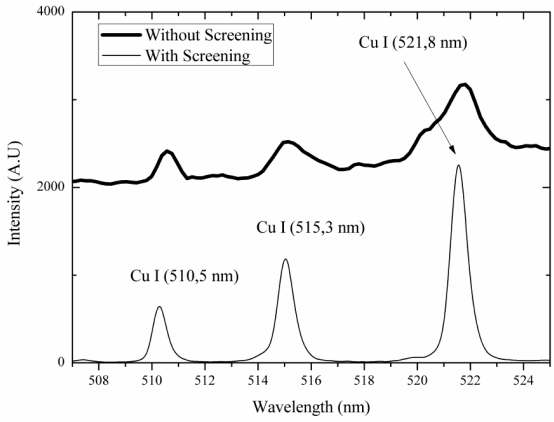

Figure 5. Cu spectra obtained without spatial discrimination (thick line) and with spatial discrimination (thin line). In the last case a 3 mm region near to the surface was screened. A nanosecond pulsed laser was used as excitation source.

3.4. Correlation between LIBS spectra obtained with spatial and temporal discrimination

An important aspect to clarify is whether there is, if any, correlation between the spatial regions where it is located the emitting species and the time interval in which its presence is larger. One way to analize this question is to compare spectra obtained at different spatial regions with those obtained at different delay times. The criteria employed to decide if two spectra are similar were that both should have the same emission lines, and the ratio between the intensities of the lines must kept constant. Figure 6 was made by using these criteria for the most usual LIBS pulse duration excitation conditions. It shows the normalized intensity of the studied three neutral Cu emission lines as a function of temporal and spatial evolution of plasmas generated by nanosecond laser pulses. The temporal evolution as expected, follows an exponential decay with a time constant of 8,0 ±1,5 μs which is in agreement with previous work[23]. In the same figure spatial evolution is shown. Both curves

are normalized to the maximum intensity value. Figure 6 shows the conditions that allows to obtain signal to noise equivalent spectra by using either temporal or spatial discrimination.

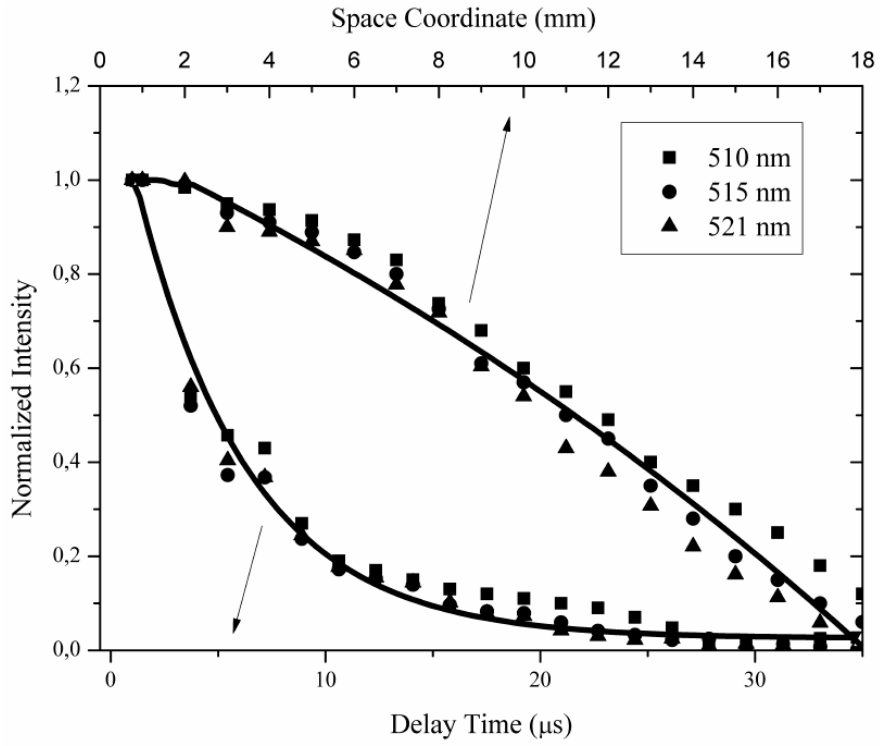

Figure 6. Normalized intensity of Cu I emission lines as a function of temporal and spatial evolution of plasmas generated by nanosecond laser pulses. Both curves are normalized to the maximum intensity value.

4. Conclusions

The use of long pulses or multiple pulses in LIBS experiments produces more intense emission spectra than those obtained with shorter ones. However signal to noise ratio is equivalent in both cases. The line widths of the spectra obtained with microsecond excitation pulses are greater than that obtained with nanosecond ones. This represents a lower spectral resolution. So, there is not any advantage in using microsecond pulses with respect to nanosecond excitation.

Spatial resolution experiments allow concluding that the different species generated by laser ablation with long and short laser pulses (i.e: neutral or single ionized) could have a different spatial distribution inside the plasma, as in the studied case of Cu.

We demonstrate that the use of spatial discrimination procedures to obtain the best signal to noise LIBS spectra, as screening the plasma, are equivalent to the use of temporal discrimination ones, as time delay detection. The analytical results obtained with both methods are the same, with the appreciable advantage in cost reduction obtained by replacing the gating detector by a cheap screen.

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