Research Article

Extracting Time-Resolved Information from Time-Integrated Laser-Induced Breakdown Spectra

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Laser-induced breakdown spectroscopy (LIBS) data are characterized by a strong dependence on the acquisition time after the onset of the laser plasma. However, time-resolved broadband spectrometers are expensive and often not suitable for being used in portable LIBS instruments. In this paper we will show how the analysis of a series of LIBS spectra, taken at different delays after the laser pulse, allows the recovery of time-resolved spectral information. The comparison of such spectra is presented for the analysis of an aluminium alloy. The plasma parameters (electron temperature and number density) are evaluated, starting from the time-integrated and time-resolved spectra, respectively. The results are compared and discussed.

1. Introduction

The importance of performing time-resolved measurements in LIBS was stressed many years ago by Cadwell et al. [1], who introduced the acronym TRELBS (time-resolved LIBS) to identify this kind of analysis. The plasma parameters, in LIBS, vary in space and time; the very concept of plasma temperature and electron density makes sense only in the framework of a Local Thermal Equilibrium approximation [2], which may hold in a limited temporal window, but is surely not fulfilled in the first moments of plasma creation and expansion (the plasma expansion characteristic times being larger than the collisional equilibrium time) and in the last part of the plasma lifetime, when the plasma cools down and the electron number density drops below the limit value given by the McWhirter criterion [3]. Therefore, any kind of LIBS analysis which relies on the calculation of one of the parameters above should be, in principle, performed using a time- (and space-) resolved spectrometer.

However, time-resolved broadband spectrometers, as the one used in LIBS applications, are in general expensive and

they are often not suitable, because of their dimensions, complexity, and sensitivity to external variables such as ambient temperature, for any use outside of the laboratory. Cheap broadband spectrometers, on the other hand, are robust and reliable for the use in mobile and portable LIBS instruments, providing a more than acceptable spectral resolution, but their spectral acquisition can only be delayed with respect to the laser pulse, being the integration time typically much longer than the plasma lifetime.

One can thus wonder whether the plasma parameters that can be calculated from such time-integrated spectra, at a given delay from the laser pulse, would be actually representative of the “true” values of plasma temperature and electron number density at that moment. From an intuitive point of view, since the LIBS spectral intensity is an exponentially decreasing function of the acquisition delay time, it is reasonable to hypothesize that the main contribution to the time-integrated spectrum would come from a very limited temporal window, of the order of the decay time of the signal, thus mimicking the effect of a time-resolved measurement (see Figure 1).

TABLE 1: Acquisition delays used in this work. An additional internal delay of 260 ns must be added to the set delay for obtaining the actual delay from the second laser pulse.

	Set delay (ns)	Actual delay (ns)	$(\Delta t_i + \Delta t_{i+1})/2$ (ns)	$\Delta t_{i+1} - \Delta t_i$ (ns)
Δt_1	0	260	301	83
Δt_2	83	343	405	125
Δt_3	208	468	614	292
Δt_4	500	760	1010	500
Δt_5	1000	1260	1760	1000
Δt_6	2000	2260	3760	3000
Δt_7	5000	5260	7760	5000
Δt_8	10000	10260	—	—

FIGURE 1: Equivalent gate time in time-integrated LIBS analysis.

The purpose of this work is the analysis of the temporal dependence of time-integrated LIBS spectra, acquired at different delay times in single and double pulse configuration on an aluminium sample, with the aim of reconstructing time-resolved spectra and comparing the plasma parameters estimated from these spectra with the ones obtained using a time-integrated approach.

2. Experimental Procedure

With the purpose of obtaining time-resolved information from the time-integrated spectra, we acquired a set of LIBS spectra of a target, an aluminium sample of known composition, using the Modi Instrument [4], which is based on a double-pulse [5] Nd:YAG laser, operating at the wavelength of 1064 nm. In the present experiment, the two laser pulses were delayed of 1 μ s; each pulse had energy of 60 mJ in 10 ns. The laser pulses were focused on the target, using a 100 mm focal length lens. The LIBS signal was collected with an optical fiber and sent to a AvaSpec Dual-channel Fiber Optic Spectrometer from Avantes; the acquisition time was delayed with respect to the first laser pulse in such a way to have an effective acquisition delay from the second pulse ranging from 260 ns (internal delay of the spectrometer) up

FIGURE 2: Scheme of the acquisition delay and gate.

FIGURE 3: Time-integrated spectra.

to 10260 ns (see Figure 2 and Table 1). The integration time of the spectrometer was 2.48 ms.

100 spectra were independently acquired and then averaged, to obtain a better signal/noise ratio.

In Figure 3 are shown three time-integrated spectra, acquired at the delays of 240, 468, and 1260 ns (see Table 1).

FIGURE 4: Time-resolved spectra.

3. Time-Resolved Spectra

The intensity of the time-integrated spectra can be expressed as

$$\bar{I}(t_0) = \int_{t_0}^{\infty} I(t) dt, \quad (1)$$

where $I(t)$ represents the LIBS spectral intensity (time-depending) at a given wavelength, t_0 is the acquisition delay time with respect to the laser beam, and the upper limit of the integral is approximated to infinity (much larger than the lifetime of the plasma).

$I(t)$ can be obtained by differentiating (1) in the form

$$I(t) = \frac{d\bar{I}(t_0)}{dt_0}. \quad (2)$$

Since $\bar{I}(t_0)$ is known only at the discrete intervals reported in Table 1, the differentiation must be done numerically, according to the formula

$$I\left(\frac{\Delta t_i + \Delta t_{i+1}}{2}\right) = \frac{\bar{I}(\Delta t_{i+1}) - \bar{I}(\Delta t_i)}{\Delta t_{i+1} - \Delta t_i}. \quad (3)$$

Note that the numerical evaluation of the derivative is calculated at the time $(\Delta t_i + \Delta t_{i+1})/2$, although no actual measurement is done at that delay time.

In Figure 4 are shown three time-resolved spectra calculated at 301, 405, and 1010 ns (see Table 1).

The time-resolved LIBS spectra make the sharp decrease in spectral intensity evident with the increase of the time delay. Their analysis also reveals the presence of intense emission lines from higher ionization stages of aluminium, such as Al III, whose presence dominates the time-resolved spectra at early delays in a way that is not so evident in the original time-integrated spectra.

FIGURE 5: Al III and Al II emission, evaluated from time-resolved (a) and time-integrated (b) spectra.

Figure 5 shows the three main Al III emission lines in the region around 450 nm, in comparison with the Al II line at 466.3 nm; in the time-resolved spectra the Al III emission is stronger than the Al II one at delays shorter than 500 ns. On the other hand, in the time-integrated spectra the three Al III lines always appear less intense than the Al II emission.

Another interesting comparison between time-integrated and time-resolved spectra is the one involving the intensity of the LIBS spectra, integrated over the whole spectral range (200–900 nm) (Figure 6).

As expected, the total LIBS intensity decays exponentially with the acquisition delay. However, while in time-integrated measurements the decay constants are of the order of 600 ns, the time-resolved analysis reveals that the actual decay time is a factor of three shorter (200 ns).

FIGURE 6: Dependence of the total LIBS intensity on the acquisition delay. The dotted curves are the best fit with an exponential function. Red circles: time-integrated spectra; black squares: time-resolved spectra.

The decay time of the total LIBS emission is essentially dominated by the decay of the continuum radiation. The decay time of the emission lines is longer and varies from line to line, since the line intensity depends exponentially on the ratio between the energy of the upper level of the transition (E_k) and the plasma electron temperature ($k_B T$), where k_B is the Boltzmann constant:

$$I(t) \propto e^{-E_k/k_B T(t)}. \quad (4)$$

A further dependence on the plasma parameters is given by the Saha-Boltzmann equilibrium between neutrals and ionized species, with the ionized lines decaying faster than the neutral ones because of the decrease of plasma temperature and electron density with the delay time.

This effect is clearly visible in the time-resolved spectra, as evidenced in Figure 7.

4. Determination of the Plasma Parameters

In the hypothesis of Local Thermal Equilibrium conditions [2] the electron temperature can be estimated from the calculation of the intensity ratio of two lines emitted by the same species:

$$\log\left(\frac{g_l A_{lm} I^{ki}}{g_k A_{ki} I^{lm}}\right) = -\frac{(E_k - E_l)}{k_B T}, \quad (5)$$

where A_{ki} and A_{lm} are the transition probabilities of the two lines, g_k and g_l are the degeneracies of the upper level, and E_k and E_l are the energies of the upper levels of the transition.

In Figure 8 the time evolution of the electron temperature is reported, calculated from the ratio of the two Al II lines at 281.6 nm ($E_k = 9.5 \times 10^4 \text{ cm}^{-1}$) and 358.6 nm ($E_k = 1.23 \times 10^5 \text{ cm}^{-1}$).

FIGURE 7: Dependence of the LIBS signal on the acquisition delay. The dashed curves represent the best fit of the data with an exponential function. Red circles: Al I line at 281.6 nm; black squares: Al II line at 358.6 nm.

FIGURE 8: Comparison of plasma electron temperature evaluated from time-integrated and time-resolved spectra. The dotted line represents the best exponential fit of the data.

Figure 8 confirms the idea that the time-integrated spectra are essentially equivalent, for what is concerned with the evaluation of the plasma parameters, to the time-resolved spectra, with an “equivalent gate time” roughly corresponding to the decay constant of the LIBS lines’ intensity, which in our case is of the order 800 ns (see Figure 7).

The same conclusion can be achieved for the calculation of the electron number density (see Figure 9), which can be estimated by measuring the Stark linewidth of the Balmer alpha hydrogen line at 656.3 nm [6].

In spite of the relatively large experimental errors, the electron number density obtained from the time-resolved

FIGURE 9: Comparison of plasma electron number density, evaluated from time-integrated and time-resolved spectra. The dotted line represents the best exponential fit of the data.

spectra is in good agreement with the values derived from the time-integrated ones.

5. Conclusion

The simple method illustrated in this paper allows recovery of time-resolved spectra using time-integrated spectrometers. The technique is applicable whenever the spectral acquisition system has the capability of starting the acquisition at a programmable delay after the laser pulse. The results presented also support the idea that the time-integrated spectra give information about the plasma parameters which is substantially equivalent to the information that could be obtained using a time-resolved spectrometer, with a gate time comparable with the decay time of the LIBS spectral intensity, which is, in the typical LIBS conditions, of the order of a few hundreds of nanoseconds.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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