Three-dimensional analysis of laser induced plasmas in single and double pulse configuration


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Abstract

In this work we studied the morphology of plasmas induced by single and double laser pulses, with the purpose to improve the understanding of the formation and evolution of the plume in the two cases and the reasons of the increase of sensitivity and detection limits in the double pulse configuration. Single and double pulse laser-induced breakdown spectroscopy experiments were carried out on a brass sample in air. Spectrally, temporally and spatially resolved measurements have been performed on the plume and a deconvolution algorithm has been applied on the line-of-sight integrated spectra in order to separate the spectral information coming from different regions of the plasma. While in single pulse configuration only the major elements in the matrix were observed, in double pulse case also the minor elements emission lines were measurable. The values of line emission intensity, plasma temperature and electron density have been evaluated at different positions in the plume in both the configurations. Appreciable differences in plume dimensions (three times wider in double pulse configuration), and electron density values (two times higher in single pulse case), have been found while the maximum temperature in the plasma core was similar in the two configurations. Beside the spectroscopic measurements, we used the shadowgraphic technique to observe the evolution of the plume in single and double pulse configuration. In double pulse configuration, the expansion of the plume induced by the second pulse is sensibly faster than the one induced by the first pulse and, in double pulse case, the plume tends to fill the region encompassed by the shock wave formed by the first pulse; on the other hand no shock wave produced by the second pulse was visible. The results obtained by the two different approaches were compared and an explanation of the physical processes occurring is proposed.

Keywords: Laser induced breakdown spectroscopy; Shock-wave; Double pulse; Deconvolution; Spatial mapping

1. Introduction

The analysis of the radiation emitted by a laser-induced plasma has been used since the 1960s for elemental diagnostic purpose, giving origin to the laser induced breakdown spectroscopy (LIBS) technique [1]. The requirement of a mere optical contact of the probe (the laser beam) with the target has favored a number of applications of LIBS for the analysis of solid materials, conductors and non-conductors, as well as liquid and gaseous samples [2–4]. In recent years, following the availability of new technologically advanced instrumentation, the LIBS technique has been proposed as a valuable analytical tool in a number of different fields, ranging from monitoring of industrial processes [5,6], material analysis [7,8], environmental protection [9–13] and cultural heritage conservation and study [14–17]. The intrinsic simplicity, robustness and quickness of the LIBS method make it the election technique for in-situ analysis even in hostile environment [18–20]. However, even considering that most of the problems related to the LIBS technique have been now overcome, especially for what concerns the definition of reliable procedures for LIBS quantitative analysis [21,22], it is nevertheless true that the LIBS technique still suffers of a relatively poor sensitivity with respect to other analytical techniques. Although this drawback is, in typical LIBS
application, widely compensated by the possibility of performing multi-elemental simultaneous analysis with a dynamic range going from major to trace elements (ppm) in the same measurement, a number of researchers have devoted their work to the improvement of the LIBS technique in view of achieving lower limits of detections for most of the elements of interest [23,24].

Among the various methods proposed for improving the figures of merit of LIBS in terms of limits of detection, a promising technique seems to be the excitation of the plasma through a sequence of multiple laser pulses. In particular, double pulses have proved to be very efficient in increasing the LIBS sensitivity in the analysis of liquids [25] or solids immersed in liquid [26,27].

The double pulse technique has been recently applied also to the analysis of solids in a gaseous environment [28–34]. In its simpler version, the procedure requires two lasers pulses with the same wavelength [30,31], or a single laser emitting two separated pulses with a suitable delay [29,33]. More complex experimental configurations involve the use of lasers emitting at different wavelengths [32,34], which allows separating the process of laser ablation from the process of plasma excitation, or trains of several laser pulses [28].

Both perpendicular and collinear beams’ arrangements have been experimented. In condition of reduced pressure, Uebbing et al. [35] proposed the use of two Nd:YAG lasers in a reheating scheme in order to enhance the signal intensity: a first pulse directed perpendicularly to the sample made the ablation and created the plasma, a second pulse parallel to the sample reheated the plasma after a delay of tens of microseconds. The authors reported an improvement in the calibration curves built by internal standardization, due to the use of double pulses.

In a series of papers, Angel et al. [30,31,36,37] described the use of two Nd:YAG lasers in perpendicular configuration exploited in the reverse temporal order with respect to the work of Uebbing. The first pulse was directed parallel to the sample, and focused in order to create a plasma plume in air approximately 1–2 mm above the sample surface. Some microseconds after this pre-ablation spark, the second beam was fired perpendicularly to the sample, in correspondence to the focal region of the first beam. The first air spark was properly designed in order not to cause sample ionization or ablation: line emission from the sample was observed only after the second ablating pulse. For different kinds of samples this arrangement led to a large increase of the line intensity (up to 40-fold, depending on the matrix), compared to those obtained in both the arrangements with single pulse and double reheating pulse. It was demonstrated that the increased intensity is systematically associated with enhanced ablation.

Other authors reported experiments performed in collinear arrangement. Sattmann et al. [28] observed increased intensity and enhanced ablation when using multiple pulses from the same Nd:YAG laser, compared to the single pulse with the same energy of the two combined laser pulses. St-Onge et al. [29] also used a Nd:YAG laser in double pulse mode and studied the temporal evolution of line intensity, plasma temperature and electronic density as a function of the interpulse interval on an aluminium alloy sample. They found a significant enhancement of the line intensity, and noticed that the signal-to-continuum ratio is especially improved in the double pulse mode. However, they didn’t observe significant increases in the plasma temperature and electronic density values. The signal enhancement is, therefore attributed not to a more efficient excitation of the pre-existing plasma, but instead to a stronger ablation which increases the number of particles in the plasma and the volume of the plasma itself. The work of Colao et al. [33], who studied the characteristics of the plasma created on an aluminium sample by a Nd:YAG in double pulse collinear mode is in substantial agreement with the above-mentioned results. They confirmed the observation of an increase in the line intensity, an improvement of the signal-to-continuum ratio and an increase in the decay constants, compared to the case of single pulse of energy equal to the sum of the two pulses.

The review of the existing literature demonstrates that, even in the simplest configuration involving two identical lasers, the double pulse technique allows obtaining a significant increase in the LIBS sensitivity (corresponding to a marked improvement of the limits of detection) for several elements of interest. However, the reasons of this improvement are yet not clear, thus motivating further study of the basic properties of laser ablation and laser-induced plasma in those experimental configurations.

The aim of the present experiment is the three-dimensional characterization of the plasma plume obtained in LIBS measurements in single and double pulse mode. Spectrally, temporally and spatially resolved measurements have been performed on the plume, by sampling along a two-dimensional grid all the emitting regions of the plasma. Moreover, assuming a cylindrical symmetry of the plume, a deconvolution algorithm of the recorded plasma image has been performed in order to extract the spectral information coming from different regions of the plasma along the plume radius and at different distances from the target. At the end, values of line emission intensity, plasma temperature and electron density have been evaluated in order to achieve a better understanding of the physical processes arising in double pulse LIBS, which are responsible of the improvement of the LIBS signal with respect to a single-pulse configuration. Finally, we used the shadowgraphic technique to observe the evolution of the plume in single and
double pulse configuration and compared the results obtained by imaging and spectroscopical approach.

2. Experimental

In order to compare the processes of laser ablation and plasma formation obtained with single and two sequential laser pulses, we used two different techniques. First we acquired the spatially and temporally resolved spectra from the plume for performing the deconvolution of the signal and then we compared the obtained results with the temporally resolved images of the plasma acquired using the shadowgraphic technique.

The sample used is a ~60% Cu, ~40% Zn brass alloy target containing Fe, Mn, Pb, Sn, Ni and Al as minor components.
The experimental setup used for spectroscopic analysis is sketched in Fig. 1a. The laser sources were two Nd:YAG lasers, each one emitting a laser pulse with energy approximately 200 mJ in 8 ns FWHM at the wavelength of 1.06 μm. The delay time between the pulses, fixed to 2 μs, has been chosen among the intervals reported by other researchers [34,37] as the most effective in increasing the signal. Such a delay was monitored during the actual experiment by sending a small fraction of the laser beams to a fast photodiode coupled to a digital oscilloscope. The signal of the photodiode allowed also to monitor the stability of the emission of the two lasers. The two laser beams were aligned on the same axis (hereafter named Z), perpendicular to the sample surface, and then focussed on the brass alloy target using a 10 cm focal length lens. The focus of the lens was set a couple of millimeters under the target surface in order to improve the reproducibility of the micro-plasma. As for the collection optics, a lens doublet with the optical axis parallel to the target surface was used to generate a 4× magnified image of the plume; the direction of the doublet optical axis will be hereafter identified as the axis X. Then, a 1 mm diameter fused silica optical fiber, held on a computer-controlled Y–Z micrometric translation stage, was used for collecting the signal perpendicularly to the axis of the plume. The space-resolved optical signal was then sent to an Echelle type spectrometer (Mechelle 7500 by Multichannel Instruments, Sweden) coupled with an intensified CCD camera (PCO). The Echelle spectrometer allows a broad band collection of the optical spectrum in the range between 200 and 900 nm; however, the collection optics introduce a wavelength cut-off at approximately 350 nm so that the effective range of the system is between 350 and 900 nm.

In order to collect the spatially resolved spectra required to perform the deconvolution on the whole plume shape, the optical fiber was moved across the magnified plume image along a two-dimensional grid covering all the emitting regions. The scanning step in both directions was chosen in order to match the optical fiber size; the corresponding sampling resolution in both directions was chosen in order to match the optical covering all the emitting regions. The scanning step in magnified plume image along a two-dimensional grid lying on the Y–Z plane, the line-of-sight integrated intensity from each single cell (as sketched in Fig. 2) can be expressed by the general expression:

$$I_{\exp}(i,m) = \int_{z_m}^{z_{m+1}} dz \int_{Y_i}^{Y_{i+1}} dy \int_{-\infty}^{+\infty} \frac{1}{R^2 - y^2} \times e(x,y,z) \exp[-\tau(x,y,z)] dx$$

where $e$ is the emissivity, $R$ is the radius of the plume,
\(y_i, y_{i+1}, z_m, z_{m+1}\) are, respectively, the \(y\) and \(z\) coordinates of the scanning cell boundaries and \(\tau\) is the optical depth, i.e. the absorption coefficient integrated along the optical path.

Usually, a numerical procedure called Abel inversion allows to deconvolve the partial contributions to the recorded signal originating from the different regions of the source. The plasma plume model and the algorithm used here are a variation of the Abel algorithm proposed by Aguilera [38]. The main requirements in order to apply such a deconvolution procedure on the plasma plume emission are the cylindrical symmetry of the plume and the assumption that the plasma is optically thin for the radiation analyzed.

If these hypotheses are verified, expression Eq. (1) becomes:

\[
I_{\text{exp}}(i,m) = 2 \int_{z_m}^{z_{m+1}} \int_{y_i}^{y_{i+1}} \int_{\sqrt{r^2 - y^2}}^{\infty} d\gamma \, e(r,\gamma) r \, dr
\]

(2)

In order to simplify further this expression we modelise the plasma slice of width \(\Delta z\) as an ‘onion’ structure composed of \(n\) shells of constant thickness \(\Delta r\), which has been chosen equal to the scanning step \(\Delta y\), so that the radius of shell \(i\) is \(y_i = \Delta r \cdot i\). For a fixed value of the distance from the target \(z_m\), each shell \(i\) is characterized by a constant emissivity \(\varepsilon_{i,m}\).

In this case, the integrated expression Eq. (2) becomes:

\[
I_{\text{exp}}(i,m) = 2\Delta z \sum_{j=i+1}^{n} \int_{y_j}^{y_{j+1}} \int_{\sqrt{r^2 - y^2}}^{\infty} d\gamma \, e_{i,m}(r,\gamma) r \, dr
\]

(3)

where the two terms represent the contributions of the inner shell (region A in Fig. 2) crossed by the line of sight and of the external shells (region B in Fig. 2), respectively. \(\Delta z\) is a proportionality coefficient which will be hereafter included in the geometrical factors resulting from the integrals. In fact, after simple calculations we can write:

\[
I_{\text{exp}}(i,m) = 2\varepsilon_{i,m} F(i) + \sum_{j=i+1}^{n} \varepsilon_{j,m} G(j,i)
\]

(4)

where \(F(i)\) and \(G(j, i)\) are geometrical factors. From expression Eq. (4) we find \(\varepsilon_{i,m} = \frac{I_{\text{exp}}(i,m) - 2I_{\text{ext}}(i,m)}{2F(i)}\).

Bearing in mind that \(I_{\text{exp}}(i, m)\) is the result of the measurement on the single cell and that \(F(i)\) is easily calculable from the integral, we can use an iterative algorithm starting from the external shell. In particular, from the relation \(\varepsilon_{n,m} = \frac{I_{\text{exp}}(n,m)}{2F(n)}\) we can derive \(I_{\text{ext}}(n-1, m)\), and then \(\varepsilon_{n-1, m}\) and so on for all the shells.

In the specific case of our measurements, utilizing the above algorithm we calculated the emissivity in all the spectral range covered by our experimental apparatus (namely, in the interval 350–900 nm) at different distances from the target surface, in single and double pulse setups.

4. Results and discussion

In order to achieve a better understanding of the physical processes arising in double pulse LIBS, which are responsible of the improvement of the signal with respect to a single-pulse configuration, we determined the plasma parameters of interest from the spectra corresponding to the plasma shells, as obtained by the deconvolution algorithm. These spatially resolved spectra are characterized by low intensity levels, especially those corresponding to the external regions of the plasma. As a consequence, we were forced to use the information carried by strong lines, though not resonant, of major elements of the target (Zn and Cu) for which the fulfilment of the thin plasma hypothesis can be questionable. This issue has been therefore carefully analyzed case by case, with the aid of a home-made software which simulates the emission and the optical depth in each point of a plume modelised like the one previously described.

4.1. Single pulse spectroscopic analysis

In the line of sight-integrated spectra obtained with single pulse LIBS technique, strong Cu I and Zn I lines and neutral lines from ambient elements, N and O, are evident while the minor elements (Pb, Sn, Fe, Al, Ni, Mn) in the sample are not detectable. Applying the deconvolution algorithm to these spectra we obtain, for the inner shells in the center of the plume (0.5–0.75 mm from the target), negative emissivity values for the Cu I and Zn I strong lines, as shown for example in Fig. 3a for the case of the neutral zinc line at 472.2 nm.

This result is a clear sign that the deconvolution algorithm fails because self absorption in the line of sight-integrated spectra is an important and non-negligible phenomenon at those wavelengths. The self absorption effect prevents a substantial part of the radiation coming from shells located in the rear side of the plasma to reach the detector. Therefore, we can’t use those lines in order to estimate the temperature and electron density of different shells. However, looking at the deconvoluted lines corresponding to air elements, as
Fig. 3. Deconvoluted emissivities for all the plasma shells, calculated from spectra taken in single pulse configuration at a distance of 0.5 mm from the target; (a) Zn I at 472.2 nm, (b) N I at 746.8 nm.

shown in Fig. 3b for the line of NI at 746.8 nm, we always obtain positive emissivity values. We assumed then that the NI line at 746.8 nm and the OI triplet at 777.3 nm are optically thin. This hypothesis is corroborated by the fact that the lower levels of the above mentioned transitions have high energies, respectively, 10.3 and 9.1 eV, and then, in the LTE assumption, are poorly populated; self absorption of those lines is thus negligible. Therefore, we can obtain the electron density and temperature values using such lines, as follows.

Assuming that the population of the excited levels follows the Boltzmann distribution, we can express the ratio of intensity of NI 746.8 nm line and total intensity of OI triplet at ~777.3 nm as

\[
\frac{I_{\text{OI}}}{I_{\text{NI}}} = \left( \frac{n_{\text{OI}}}{Z_{\text{OI}}(T)} \frac{\sigma_{\text{OI}}A_{\text{OI}}}{g_{\text{OI}}k} \exp\left( -E_{\text{OI}}/kT \right) \right) / \left( \frac{n_{\text{NI}}}{Z_{\text{NI}}(T)} g_{\text{NI}} A_{\text{NI}} \exp\left( -E_{\text{NI}}/kT \right) \right)
\]

(5)

where \( Z(T) \) represents the partition function, \( n \) is the absolute density, \( E_k \) and \( g_k \) are the energy and the
degeneracy of the upper level of the transition, \( A_{k_i} \) is the transition probability, \( g_{\text{tot}} \) is the sum of the degeneracy values of the triplet and the labels NI and OI indicate the relative species.

The expression can be simplified if we consider that in typical measurements of laser induced plasmas in air the values of electron densities are in the range \( 10^{16} < n_e (\text{cm}^{-3}) < 10^{18} \) and the temperatures are in the range \( 0.7 < T (\text{eV}) < 1.2 \). In these conditions and assuming LTE all the nitrogen and oxygen molecules can be considered almost completely dissociated \( \left( 10^{-4} < n_{\text{O}_2}/n_N < 0.1, \ 10^{-6} < n_{\text{O}_2}/n_O < 10^{-4} \right) \) [39] and the atoms neutral \( \left( n_{\text{NI}}/n_{\text{N}_2} \sim 10^{-6} \right) \), so the ratio \( n_{\text{O}_2}/n_{\text{NI}} \) is equal to the ambient value of \( n_{\text{O}_2}/n_N \approx 0.25 \). Moreover, in the typical range of temperatures of LIBS, \( Z_{\text{NI}}(T)/Z_{\text{NI}}(T) \approx 2 \). So, knowing all the other parameters we can estimate the temperature of each shell of the plume from expression Eq. (5); the result is shown in Fig. 4b. The uncertainties, of the order of 20%, have been calculated by propagating the relative uncertainties of the ratios \( n_{\text{O}_2}/n_{\text{NI}}, \ Z_{\text{NI}}(T)/Z_{\text{NI}}(T), \ A_{k_i}/A_{k_i}, \ I_{\text{NI}}/I_{\text{N}_2} \), each of the order of 10%.

However, we derived the electron density value by means of the Stark broadening of the NI lines according to the approximated formula \( W_{\text{tot}} = w(T) \cdot \left( \frac{n_e}{10^{16}} \right) \), where \( W_{\text{tot}} \) is the experimental line half-width and \( w(T) \) is the Stark parameters tabulated by Griem [40], and taken at the calculated temperature.

The results are shown in Fig. 4a. The estimated errors of approximately 20% come from the uncertainty in the Stark parameter \( w \) and the experimental error in the determination of the Stark broadening of the lines.

4.2. Double pulse spectroscopic analysis

The line of sight-integrated spectra obtained in double pulse configuration exhibit a large variety of lines from major (Cu, Zn) to minor (Pb, Sn, Al, Fe, Mn, Ni) elements from the target, with an improvement in the signal up to a factor of 30 and in the signal to noise ratio up to a factor of 10 with respect to the single pulse configuration. The opposite behavior is observed for the air elements lines, which show similar or lower intensities than in single pulse spectra; this prevents the use of NI and OI lines, as we made in the previous case, for calculating plasma’s properties. This feature was expected in view of the predictions of the point strong explosion theory. This theory, formulated by Sedov [41,42], focuses on the effect of a large amount of energy liberated in a small volume of a homogeneous atmosphere during a short time interval; the release of the laser pulse energy during a breakdown or ablation process is a typical situation that can be described by the Sedov model [43,44,47]. According to this theory, during the expansion of the shock wave produced by the sudden release of laser energy most of the mass of the ambient gas that was originally homogeneously distributed inside the region encompassed by the shock wave is then compressed in a thin layer near its front surface. As a consequence, at the beginning of the shock wave expansion the ambient gas density in the bubble core lowers progressively (see Ref. [42]) because of the radial expansion, until it starts to grow again when the shock wave has lost most of its energy, the ambient gas.
counter-pressure becomes effective and the perturbed gas re-approaches again the original unperturbed conditions. In our experimental conditions the shock wave relaxation occurs on a time scale of approximately 10 μs. However, in our double pulse experiments, the second pulse was fired 2 μs after the first one, and the corresponding spectrum acquisition started after 2 more μs, that is still during the initial expansion stage of the shock wave generated by the first pulse. Therefore, the ambient gas density detected after the second pulse is still reduced compared to the single pulse case, while the new ablation induced by the second pulse enriches the plume of new material from the target. These effects thus results in a reduction of the number of emitting atoms from atmosphere and, consequently, in a reduction of the intensity of Nitrogen and Oxygen emission line with respect to the single pulse configuration. Unfortunately, this also results in the impossibility of using N and O lines for determining plasma temperature and electron density.

However, applying the deconvolution algorithm to the experimental spectra we obtain non-negative emissivity values for all the lines and lower emissivities in the core than in middle shells for the emission lines of all elements of the sample, as shown in Fig. 5a. The similar trend of deconvoluted emissivity along the plume profile for strong and weak lines suggests that, in this case, self absorption is negligible also for strong Zn I and Cu I
lines. This allows us to calculate the plasma temperature from the Boltzmann plot of Cu I lines and the plasma electron density from the Stark broadening of Zn I 468.0 nm line, using the Stark parameters as in Ref. [45]. The uncertainties on the temperature, coming from uncertainties on emission lines fitting, transition probability values and linear regression in the Boltzmann plane, are of the order of 10%. However, the uncertainty affecting the electron density is higher, approximately 30%, mainly because of the uncertainty on the Stark parameter \( w \).

The calculated spatial maps of temperature and electron density are shown in Fig. 6 and will be discussed in the next section.

In order to verify the hypothesis of thin plasma for the double pulse configuration we used a home made software, which modelises an inhomogeneous plasma as a shell structure and simulates its emission properties, requiring as input parameters the temperature, absolute density of the species considered and electron density profiles along the plume, the line shape, and the spectral data characteristics of the transition considered. For the temperature and the electron density we used the values experimentally calculated while for estimating the absolute density profile we assumed the local neutrality of the plasma and that the plume composition is the same of the target, since the air elements are scarcely present. From the first hypothesis we could identify the electron density with the total ionic density and then from the second one and from the temperature we could calculate the absolute density specie by specie. Inserting these input parameters, the software calculated the optical depth \( \tau(x, y, z) \) in each point in the plume. An example of the calculated values of \( \tau \) along the plume diameter (i.e. along the main axis \( X \) inside the plume, with \( y = 0 \)) and at a distance from the target fixed to 2.5 mm is shown in Fig. 5b, where the dotted line represents the optical depth of Zn I 468.0 nm line, for a photon traveling from left to right (the detector is on the right side). As expected, a photon emitted from the rear side of the plume with respect to the detector has a greater chance to be absorbed (higher optical depth) than a photon emitted in the front side. However, the values obtained for the optical depth of all the lines used in temperature and electron density calculation are much less than one, which constitutes an a posteriori verification of our assumption of optical thin plasma.

Fig. 5b depicts also the normalized profiles of upper level population of Zn I 468.0 nm transition and its emissivity at a distance of 2.5 mm from the target, as obtained by the simulation. It is interesting to notice that the measured temperature profile (see Fig. 6b), used as input data for the simulation, produces a depression of population of Zn I in the core of the plume, where most of Zn is ionized, and a maximum in external layers, where Zn is mostly neutral. This also causes a reduction of the Zn I emissivity in the core of the plume. This behavior is in fact particularly clear observing the experimental emissivity of neutral Zn, as shown in Fig. 5a (also referring to a height of 2.5 mm from the target), but this trend is also evident for all the other elements present in the sample. Such depression in the emissivity was not found, however, at low and high distances from the target (not shown here), in agreement to the lower temperature values found at the plume boundaries (see Fig. 6). Though it was not possible to check experimentally the spatial distribution of ionic
zinc, due to the spectral cut-off of the optics in the experimental setup, a confirmation of the proposed interpretation is given by the paper by Aguilera et al. [38], who found a similar population distribution in a Fe-plasma induced in air. Looking back to the nitrogen emissivity profiles in single pulse configuration, we can notice in Fig. 3b that the line from N I has higher emission in the core because of the nitrogen high ionisation energy.

4.3. Shadowgraphic imaging and interpretation of the results

A first step toward the comprehension of the enhancement effect in double-pulse LIBS comes from the shadowgraphic analysis of the plasma evolution. A sequence of frames, describing the evolution of the plasma produced by a single laser pulse, is shown in Fig. 7a.

The exposure time of the single frame is 100 ns. The sequence, acquired by eight consecutive expositions spaced by 500 ns, evidences the generation of the plasma at the surface of the sample and its evolution and decay, associated to the contemporaneous generation of a shock wave, which propagates in the surrounding atmosphere. The shadowgrams of the plasma obtained in double pulse mode (Fig. 7b) reveal that the second laser pulse, coming 2 μs after the first pulse, initiates a new plasma at the sample surface (frame 4), which very rapidly propagates, moving away from the target and almost fills the region encompassed by the shock wave front formed by the first pulse, resulting in a plume wider than in single pulse configuration.

This effect is in agreement with the results of the spectroscopic analysis of the plumes: comparing Figs. 4 and 6 it is evident that the emitting region obtained in double pulse configuration is larger (approx. 3 times) than that obtained with a single pulse. This finding is, moreover, in agreement with the emission images acquired by Stratis et al. [37]. It is interesting to note that the positions reached by the shock wave expanding front in the sequence of Fig. 7b are substantially coincident with the ones obtained for the single pulse (Fig. 7a). Moreover, the shock wave possibly formed by the second pulse is not visible at all in the present experiment (see Fig. 7b), while it has been clearly seen when the delay between the pulses was higher (e.g. 10 μs). This suggests that the second pulse is not able to generate a second shock wave or in any case that the jump in absolute density at the shock wave front is low and not detectable by our shadowgraphy instrumentation. This evidence is again in agreement with the hypothesis of the rarefied ambient present in the bubble produced by the first pulse, as described by the strong point explosion theory, which predicts a sharp decrease of the ambient gas density behind the front of the shock wave toward the centre. The gas density ρ₁ at the shock wave front can be expressed by $\rho_1 = \rho_0 \left( \frac{\gamma + 1}{\gamma - 1} \right)$ where $\rho_0$ is the density in the unperturbed gas and $\gamma$ is the adiabatic exponent [42]. Such formula evidences also that an explosion in a rarefied atmosphere yields jumps in density and pressure lower than in atmospheric pressure, which is a possible reason to explain the failure in detecting the second shock wave by the shadowgraphy technique. At long times after the explosion the ambient gas density in the center of the bubble tends to increase again until it comes back to the unperturbed density value so that at a delay between the two pulses of approximately 10 μs the second shock wave is again detectable.

In the present conditions, however, the propagation of the plasma produced by the second laser pulse occurs in a rarefied medium, resulting in higher velocity because of the reduced collisions with the buffer gas molecules ($V \propto \rho_0^{-1/5}$ [42]). The interpretation of the
shadowgrams is then in agreement with the occurrence of low signals from air elements, as oxygen and nitrogen, observed in double pulse spectra. The confinement of air elements mostly in the outer layer of the plume, pushed back by the shock wave, and the prominence of the elements removed from the target in the core of the plume, have been confirmed also by some simulation codes [46] and spectroscopic measurements [38,47]. The situation is thus similar to that of laser ablation experiments in low-pressure environment, where the hydrodynamic expansion of the plasma is fast, not contrasted by the counter-pressure of the buffer gas.

Another interesting information on the single and double pulse plumes can be derived from the comparison of the temperature-electron density maps obtained by the deconvolution algorithm. Looking at the temperature maps, we see that the maximum value in single and double pulse configuration is roughly the same but in double pulse plasma the spatial distribution of temperature is much more complex evidencing a larger hot region than in the single pulse case.

The temperature distribution map can be compared to the shock wave image taken at the same acquisition time. As can be easily calculated from Fig. 7b, 4 μs after the first laser pulse the shock wave radius reached approximately 4 mm, just larger than the emitting plume size shown in Fig. 6. This suggests the occurrence of a regime during which the second plume is confined by the front of the shock wave created by the first pulse. In fact, the second plasma initially expands at high velocity because of the low density in the center of the bubble formed by the first shock wave, but successively, when it catches up the shock wave front, it encounters an increasing density, which slows down the evolution.

In order to make the picture of the phenomenon more convincing, it remains to explain why the temperature values observed in double pulse configuration are considerably higher in comparison to similar experiments done in rarefied mediums [48,51]. We think that it can be due to two main reasons: firstly the second plasma expands in a medium rarefied but with a residual temperature of approximately 6000–7000 K, then considerably higher than the ambient temperature, secondly the confinement effect could lead to a slower decay of temperature, as found by Colao et al. [33].

However the electron density maps evidence that the values in double pulse plasma are a factor 2 lower than in single pulse case, in agreement with the results reported by St-Onge et al. [29] and by Colao et al. [33], although they were obtained in different experimental conditions. The lower values of electron density are also explainable in view of the lower background gas density and are in qualitative agreement with the behavior of electron density in rarefied mediums [48,51], where the ionization of the buffer gas by the shock wave is less effective.

On the basis of the plasma evolution features here described we can identify some possible mechanisms leading to an improved signal obtained in double pulse configuration with respect to the single pulse one.

First of all, a contribution to the double pulse intensity enhancement is given by the stronger mass ablation from the sample, as found by direct crater size measurement by Stratis et al. [37]. Though we didn’t measure directly the mass ablated, it is well known [49–51] that laser ablation induced in rarefied mediums leads to an increase of mass ablated. The main cause of greater ablation for low buffer gas pressures, as demonstrated by Iida [51], is probably the lower shielding effect of the laser beam. Bearing in mind that our excitation source is a nanosecond infrared laser, it is likely that when the target is placed in atmospheric environment the larger part of laser energy can’t reach its surface and is absorbed in front of it. However, the laser shielding process becomes less effective with the decrease of the buffer gas density. The double pulse technique, therefore takes advantages of the benefits of low density buffer gases without the experimental complication of working with vacuum chambers.

Another reason for the signal increase in double pulse configuration is probably the wider region of the plume at high temperature, as suggested by St-Onge et al. [29]. The dependence of emissivity of neutral lines from temperature is not so trivial because on one hand a higher temperature is associated with higher excitation, which yields higher emission, but on the other hand it produces a higher ionization, lowering the neutral absolute density. It is clear from Fig. 5b that the region of the plasma responsible for the most part of radiation observed is constituted by intermediate shells with temperature in the range 8500–10 000 K. Anyway, the wider plume results also in a wider region with the suitable temperature for emission, and then with a larger number of atoms excited.

Finally, the lower values of electron density and the large extent of high temperature in the double pulse plasma can play an important role in the fact that self absorption is less important, as observed in our case.

5. Conclusions

For the first time the morphology of the plasma induced by single pulse and double pulse LIBS has been investigated through spectroscopic and shadowgraphic analysis.

The shadowgraphic investigation consisted of the acquisition of a sequence of frames, covering an interval of some microseconds, showing the expansion and evolution of the laser induced plasma and shock wave. The strongest evidence obtained by comparing the shadowgrams corresponding to the two configurations is that, in our experimental conditions, the expansion law
of the shock wave created by the first pulse was found to be the same in both cases. On the contrary, the expansion of the plasma initiated by the second pulse at the sample surface is more rapid than the first one. No evidence of a second shock wave has been observed.

The spectroscopic analysis consisted in the acquisition of the spatially resolved emission from the plasma plume, followed by the application of a deconvolution algorithm in order to separate the emissivity contributions from the different concentric shells. This analysis demonstrated that at a fixed delay time, the region of the plasma with higher temperature and higher electronic density is much wider in the case of double pulse. The maximum value of the temperature, however, is similar to the case of the single pulse. The electronic density values are lower by a factor 2 than in the case of the single pulse.

Taking into account these results, a better understanding of the plume evolution and of the physical processes that lead to higher signals in the double pulse configuration can be achieved. The expansion in a rarefied medium allows the plume to extend over a wider region in a shorter time, until the shock wave front generated by the first pulse is reached. Then, the confining effect given by the same front is effective to keep the temperature to high levels for a longer time.

Furthermore, the qualitative analysis of the spectra in double pulse configuration confirmed the high potentiality of this technique to lower LOD values of minor elements in LIBS analysis. While in single pulse configuration we were able to detect only the lines from major elements in the sample (Cu, Zn), in double pulse configuration we succeeded in detecting lines from all the other minor elements (Pb, Sn, Al, Fe, Mn, Ni).

References


