Calibration measurements in laser-induced breakdown spectroscopy using nanosecond and picosecond lasers

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Received 17 March 2004; accepted 25 August 2004
Available online 30 September 2004

Abstract

The influence of laser pulse duration on laser-induced breakdown spectroscopy (LIBS) calibration curves is investigated in the present work. Two Nd:YAG lasers providing pulses of 35 ps and 5 ns, respectively, both operating at 1064 nm, have been used to create plasmas on aluminium, manganese, iron, and silicon targets and on prepared stoichiometric samples of these metals in a matrix. The time-resolved, space-averaged plasma temperatures have been deduced using Boltzmann plots, while the electron number density has been determined from the broadening of spectral lines. The effect of laser pulse duration on the plasma characteristics is discussed, and comparisons are made with previously reported data measured under similar experimental conditions. The optimum experimental conditions (i.e., time delay, gate width, laser energy) have been determined for reliable use of LIBS for quantitative analysis for both pulse durations. For each of the metals of interest, calibration curves have been constructed for concentrations ranging up to 2%.

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Keywords: LIBS; Plasma diagnostics; Time-resolved spectroscopy; Calibration curves

1. Introduction

In recent years, the application of the laser-induced breakdown spectroscopy (LIBS) technique has made significant progress toward becoming a commercial technology [1]. Because of the lack of pretreatment of the material as well as the speed of analysis, not mentioning the possibility of in situ analysis, this technique offers an attractive solution for a wide range of industrial applications. However, the existing commercial instruments are still not sufficient to guarantee reproducibility and precise quantitative results. In fact, the analytical performance of the LIBS technique depends strongly on the choice of experimental conditions that influence the laser-produced plasma characteristics [2,3].

The main parameters affecting the performance of LIBS results are as follows: laser intensity, excitation wavelength, laser pulse duration, physical and chemical characteristics of the target material and its surface conditions, and the surrounding atmosphere [4]. Although a lot of studies have been done investigating the parameters that influence the plasma characteristics, there is relatively less knowledge about the influence of laser pulse duration on LIBS calibration curves [5,6].

The main motivation of the present work is to investigate the influence of laser pulse duration on the characteristics of the plasma and on the analytical performance of LIBS. Moreover, because we are interested in the application of LIBS for the simultaneous determination of the content of different metals in solid ferronickel slags, we have included in this study samples having similar matrix to the ferronickel slag. In this respect, CaO has been used as a matrix in order to investigate its influence on the plasma characteristics and on the LIBS calibration curves. For this reason, the plasmas

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of pure metals and of the same metals incorporated in the CaO matrix have been characterized in terms of their appearance, plasma temperature, and electron number density in air, at atmospheric pressure and under picosecond and nanosecond laser excitation. Moreover, calibration curves are presented for samples containing silicon, aluminium, and iron for concentrations of these metals up to 2% for both laser pulse durations. The optimum experimental conditions for performing quantitative analysis using LIBS have also been determined and discussed.

2. Experimental setup

The experimental arrangement used is schematically depicted in Fig. 1. The laser sources employed were a Q-switched Nd:YAG laser delivering 5-ns pulses and a modelocked Nd:YAG laser delivering 35-ps pulses. Both lasers were operating at 1064 nm, at 10 Hz, and their energy was controlled by a calibrated energy meter. The shot-to-shot energy fluctuation was 5% for the nanosecond laser and 20% for the picosecond system. The principal source of uncertainty in our measurements is mainly due to laser energy instabilities. Both laser beams were focused with the same 200-mm focal length quartz lens. The lens-to-sample distance has been chosen to be slightly shorter than the focal length of the focusing lens in order to ensure that the laser focal plane was always situated behind the front surface of the sample. In this way, not only air breakdown in front of the surface was avoided, but it was ensured that most of the energy was deposited into the bulk material of the sample as well, limiting the energy dissipation in the air in front of the surface of the sample as discussed in Refs. [7,8]. For both lasers, the beam diameter at the focus in air has been measured with a CCD camera and has been found to be 36 ± 6 μm. However, because, in our measurements, the focal plane is located behind the front surface of the sample, the diameter of the laser spot on the sample surface has been measured as well. For the lowest energy used producing a plasma, a value of 100 ± 10 μm has been found.

The light emitted from the plasma was collected via a quartz fiber bundle, and it was transferred at the entrance slit of a 0.46-m imaging spectrograph equipped with appropriate entrance optics for the coupling of the fiber bundle to the entrance slit. The width of the entrance slit was fixed at 10 μm. The spectrograph was equipped with two interchangeable holographic gratings of 2400 and 1200 gr/mm, with reciprocal dispersion of 0.8 and 1.6 nm/mm, respectively. The detector used was an intensified 1024×1024 ICCD. The size of the detector chip was 13×13 mm, while the ICCD intensifier had a diameter of 18 mm, ensuring that all pixels of the array were active. Therefore, at the exit focal plane of the spectrograph, where the detector chip is located, a total spectral area of 10.4 or 20.8 nm was imaged, corresponding to a spectral coverage of 0.1 and 0.2 Å/pixel, depending on the grating used. Delay times and gate widths were chosen according to the experimental needs, and they were controlled by a 500 MHz digital oscilloscope.

For the construction of the calibrations curves, different stoichiometric samples were prepared. Pure metals in powder form purchased from Alfa Aesar were mixed with the matrix material CaO in a ball milling apparatus in order to ensure good mixing and homogeneity. Then, they were pressed into a 300 bar pellet press. In order to test the homogeneity of our samples, several LIBS measurements were performed at different locations at the surface of the pellets. All LIBS spectra presented are the average of 20 laser shots, at three different places on the sample’s surface. The standard deviation of the mean value was calculated from these measurements. All kinds of electronic noise (e.g. ICCD dark current) were measured separately and were subtracted from the measured spectra prior to the analysis.

3. Results and discussion

3.1. Plasma characterization

The main factors that influence the light emitted by the plasma are its temperature, the number density of the emitting species, and the electronic density. The number density of the emitting species (e.g. atoms, ions, etc) depends on the total mass ablated by the laser, the plasma temperature, and the degree of the excitation and/or ionization of the plasma. The vaporized amount, in turn, depends on the absorption of the incident laser radiation by the surface, the plasma shielding [9], which is related to the electron density of the plasma, and the laser fluence. Therefore, the knowledge of the plasma temperature and the density of plasma species are vital for the understanding of the dissociation--atomization, excitation, and ionization processes occurring in the plasma. For this reason, an analysis of these parameters was carried out in order to determine the optimum experimental conditions for the quantitative use of LIBS.

For a plasma in local thermodynamic equilibrium (LTE), the population density of atomic and ionic electronic states is described by a Boltzmann distribution. In this case, relative emissivities between excited states can be used to
evaluate the plasma temperature. These are the well-known Boltzmann plots. The determination of the temperature is then performed by using the following relation:

\[
\ln \frac{i_{mn}I_{nm}}{g_mA_{mn}} = \ln \left( \frac{N(T)}{U(T)} \right) - \frac{E_m}{kT}
\]

(1)

where, for a transition taking place between an upper level \( m \) to a lower level \( n \), \( I_{mn} \) is the integral intensity of the emission; \( \lambda_{mn} \), the wavelength of the transition; \( A_{mn} \), the transition probability; \( E_m \), the energy of upper level \( m \); \( g_m \), the statistical weight of level \( m \); \( k \), the Boltzmann constant; and \( T \), the excitation temperature. A plot of the expression on the left-hand side versus \( E_m \) has a slope of \(-1/kT\). Therefore, the plasma temperature can be obtained without knowing the total number density \( N(T) \) or the partition function \( U(T) \).

A necessary condition for the validity of the LTE assumption is that the electron number density exceeds a lower limit, given by the following formula:

\[
N_e (\text{cm}^{-3}) \geq 1.4 \times 10^{14} (kT)^{1/2} \Delta E^3
\]

where \( T \) (in K) is the temperature and \( \Delta E \) (in eV) is the energy difference between the upper and lower states. Under our experimental conditions, taking as an example the Si(I) transition at 390.5 nm, which has an energy difference \( \Delta E \) of 3.1 eV, and using the highest and lowest temperatures determined in this work, the lower limit for \( N_e \) was determined to be in the range of 0.26–0.4 \times 10^{18} \text{ cm}^{-3}. This value is at least two orders of magnitude lower than the space-averaged value \( N_e \) (i.e., 2.1 \times 10^{18} \text{ cm}^{-3}) deduced in this work [10–12]. Therefore, the validity of LTE can be safely assumed under our experimental conditions, permitting the determination of the plasma temperature through Boltzmann’s plots.

During the early stages of plasma formation, the emitted spectrum is dominated by an intense continuum (Bremsstrahlung radiation), on which several heavily broadened ionic lines of the elements present are superimposed. The broadening of the ionic lines is due to the high electron densities occurring at this initial period (Stark broadening). At the same time, the excited neutral atoms’ spectral lines are relatively weak; they are superimposed on the continuum and often overlap with the ionic lines. Hence, they cannot be easily isolated and measured. As a consequence, the measurement of their intensity for the construction of Boltzmann plots becomes problematic at early times (e.g., the first few hundred nanoseconds) and the use of time delay is compulsory. However, each spectral line exhibits different temporal evolution that is element and atomic energy level-specific. Therefore, it was necessary to determine an optimum time delay for all the elements of interest in order to perform measurements of all the elements simultaneously. Under our experimental conditions, a delay time of 1 \( \mu \)s and a gate width of 3 \( \mu \)s have been determined as optimum conditions. Fig. 2 illustrates as an example some LIBS spectra of pure iron and manganese, corresponding to spectral regions where isolated spectral lines, with known spectroscopic constants, can be obtained.

Using Boltzmann plots, the excitation temperatures of plasmas of pure metals and samples containing known quantity of the metal in the matrix have been determined. The spectral lines of Fe(I) and Mn(I), which have been employed, are listed in Table 1 [13]. Fig. 3 shows some Boltzmann plots corresponding to iron and manganese plasmas under nanosecond and picosecond excitation. All measurements appearing in this figure have been taken with 1-\( \mu \)s delay time and 200-ns gate width. By linear fitting, the solid lines of Fig. 3 have been obtained. Then, the temperature can be determined from the slopes of these lines. It has to be noticed at this point that, because the plasma radiation was collected through a fiber bundle, without any spatial resolution, the obtained temperatures correspond to space-averaged values of the plasma plume.

Fig. 4 shows the temporal evolution of the measured plasma temperatures corresponding to a gate width of 200 ns for various delay times ranging from 100 ns up to 2 \( \mu \)s. As can be seen, the temporal behavior is similar for both
pulse durations, decaying exponentially with time. Nevertheless, the plasma temperature under nanosecond excitation was found to be constantly higher than under picosecond excitation. In Ref. [14], Sabsabi and Cielo, studying nanosecond laser-produced plasmas of aluminium alloy targets, have found temperatures similar to the ones determined here under nanosecond excitation. Eland et al. [15], comparing the temperatures of plasmas produced by 7 ns and 1.3 ps lasers, have also found higher temperatures for the nanosecond laser-produced plasmas.

During the interaction of a nanosecond laser with a solid, the energy is transferred to the electrons of the lattice, resulting in melting and vaporization of the target, followed by an expanding vapor plume of the material. The expanding plume forms a shock wave which assists the ionization of the surrounding gas. Furthermore, the laser pulse interacts with the plasma, resulting in a more efficient reheating of the plasma by inverse Bremsstrahlung absorption [15,16].

Mao et al. [17,18], having investigated systematically the interaction of 35-ps laser pulses with metallic targets, have concluded that, at first, an air-breakdown plasma is formed, on a picosecond time scale, followed by an expanding plume of material on a nanosecond time scale and after the end of the laser pulse. Therefore, the laser–plasma interaction using nanosecond laser is fundamentally different from that under picosecond excitation. Moreover, lower plasma temperatures are expected for picosecond laser-

---

**Table 1**

<table>
<thead>
<tr>
<th>λ_{mn} (nm)</th>
<th>A_{mn} (10^8 s^{-1})</th>
<th>E_{m} (cm^{-1})</th>
<th>E_{n} (cm^{-1})</th>
<th>g_{mn}</th>
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<td>Fe(I) 399.74</td>
<td>1.50e−01</td>
<td>47008</td>
<td>21999</td>
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<tr>
<td>Fe(I) 400.52</td>
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<td>37521</td>
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<td>53093</td>
<td>28819</td>
<td>13</td>
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<tr>
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<td>36686</td>
<td>12560</td>
<td>9</td>
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<tr>
<td>Fe(I) 418.18</td>
<td>3.60e−01</td>
<td>46744</td>
<td>22838</td>
<td>7</td>
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<tr>
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<td>1.72e−01</td>
<td>44523</td>
<td>23296</td>
<td>8</td>
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<tr>
<td>Mn(I) 472.75</td>
<td>1.70e−01</td>
<td>44696</td>
<td>23549</td>
<td>6</td>
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<td>44814</td>
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<tr>
<td>Mn(I) 475.40</td>
<td>3.03e−01</td>
<td>39431</td>
<td>18402</td>
<td>8</td>
</tr>
<tr>
<td>Mn(I) 478.34</td>
<td>4.01e−01</td>
<td>39431</td>
<td>18531</td>
<td>8</td>
</tr>
<tr>
<td>Mn(I) 482.35</td>
<td>4.99e−01</td>
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<td>18705</td>
<td>8</td>
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</tbody>
</table>

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**Fig. 3.** Typical Boltzmann plots obtained from the Mn and Fe spectral lines of Table 1. The time delay and the gate width were 1 μs and 200 ns, respectively.

**Fig. 4.** Temporal evolution of plasma temperature for Mn and Fe samples under nanosecond and picosecond laser irradiation. The gate width was 200 ns and the energy fluence was 60 J/cm² for both pulse durations.
produced plasmas than for nanosecond ones, if all the other experimental parameters remain the same.

Recently, Rieger et al. [19] reported that a 50-ps laser produces higher initial electron temperatures and electron densities than a 10-ns laser does. However, it has to be noticed that in their work, a KrF laser operating at 248 nm has been used, while the intensity measurements of the spectral lines have been performed without time delay, with a gate width of 200 ns, for the low energy regime (below 10 J/cm²), that corresponds to laser fluences up to 50 J/cm², which are similar to the ones used in the present experiments. At higher laser energies (which correspond to laser fluences much higher than the ones used in this work), they have used a time delay of 100–200 ns. In addition, their temperature results are model predictions and not direct measurements. In view of the fact that all our time-resolved measurements have been performed after the first 100 ns, the plasma temperature and electron density are expected to be very different from those corresponding to the early times of plasma creation; thus, it is rather inappropriate to make any comparison.

In general, the measured profile of a spectral line emitted through a line of sight of a laser produced plasma is the result of many broadening and shift mechanisms [20] (e.g. Doppler broadening, pressure broadening by collisions with foreign species, resonance broadening, Stark broadening), which are taking place simultaneously. However, the contribution of each independent mechanism to the overall measured spectral line profile varies at each different point of the plume as a consequence of the respective variations of the number densities of the species of the plasma and the temperature. Moreover, the plume geometry can change from sample to sample and from shot to shot due to differences of the surface morphology and/or laser-induced modifications (e.g., craters, melting of the near focus material, etc) [10,21,22]. As a result, it is neither trivial nor an easy task to take all these factors into account and calculate what would be the emission escaping from the plasma, nor how it is related with plasma characteristics. This can be achieved only in some cases, like for example in the studies of laser plasmas in gases in controlled atmospheres and when the spectroscopic characteristics of the emitted spectral lines are known as well. In our case, we assume that the main contribution to the spectral line widths arises from the Stark effect [8,10–12,20]. Contributions of other mechanisms of broadening such as Doppler broadening, Van der Waals broadening, and resonance broadening can be neglected in our situation, where high electron density and high temperature plasmas are involved. Eq. (2) relates the full width at half maximum (FWHM) of a spectral line (Δλ₁/₂) with the electron number density Nₑ:

\[ \Delta \lambda_{1/2} = 2w \left( \frac{N_e}{10^{16}} \right) + 3.5A \left( \frac{N_e}{10^{16}} \right)^{1/4} \left[ 1 - 1.2N_D^{-1/3} \right] \times w \left( \frac{N_e}{10^{16}} \right) \]

The first term refers to the contribution from electron broadening, and the second term provides the ion broadening correction; w is the electron impact parameter, which can be interpolated at different temperatures, and A is the ion broadening parameter. Both w and A are weak functions of temperature [23,24]; Nₑ is the electron density (cm⁻³) and N_D is the number of particles in the Debye sphere. N_D is given by [25]:

\[ N_D = 1.72 \times 10^9 \frac{T^{3/2} (eV)}{N_e^{1/2} (cm^{-3})} \]

The contribution from quasi-static ion broadening being small in our case is neglected. Under these assumptions, Eq. (3) becomes as follows:

\[ \Delta \lambda_{1/2} = 2w \left( \frac{N_e}{10^{16}} \right) + 3.5 A \]

The instrumental broadening contribution to the observed spectral lines has been evaluated using the lines of a low pressure mercury lamp and the laser line of a He–Ne laser. It has been found to be 0.03 nm. All spectral lines employed for the electron density determination were found to exhibit a Lorentzian line shape. Hence, the Δλ₁/₂ has been obtained simply by subtracting the instrumental contribution from the measured FWHM of the line. Therefore, the electron density has been determined independently from any assumption concerning LTE.

The temporal behavior of the electron density for aluminium and silicon targets is shown in Fig. 5. In this case, the Al(II) at 281.6 nm and the Si(I) at 390.5 nm lines were selected for the determination of the electron density at different delay times for both laser pulses used. None of these lines is a resonance line, and their shape was well fitted by a Lorentzian function, indicating that self-absorption was negligible. As shown, the determined space-averaged electron densities are of the order of 10¹⁸ cm⁻³ for both samples and for both nanosecond and picosecond pulses respectively. In all cases, the determined electron densities for picosecond pulses were found slightly higher than the ones corresponding to picosecond excitation. In addition, the variation of the electron density against the time delay was found exhibiting similar exponential decay for both pulse durations used, as shown by the solid lines of Fig. 5, which correspond to least square fit of the experimental data to an exponential decay.

In Ref. [14], an electron density of ~10¹⁸ cm⁻³ has been also reported for an 8-ns laser-produced plasma of an aluminium alloy at an energy density comparable to the one used in the present experiments. Additionally, in Refs. [10,22], the electron density of a 3-ns laser-induced plasma has been determined under various experimental conditions. Again, the electron density determined in the present work is in very good agreement with the reported one for delay times and irradiances corresponding to the experimental conditions here.
However, an uncertainty remains because it is generally possible that the outer regions of the plasma plume can be at significantly lower temperature and electron density than the regions on the axis of the plume. In addition, significant absorption of the plasma radiation arising from the hotter regions can occur at the periphery, resulting in lower measured intensities of the emitted spectral lines. Nevertheless, according to Cadwell and Huwel [12], only the hottest core regions contribute significantly to the measured signals, and, thus, the measured space-averaged parameters retain their importance for the plasma characterization.

3.2. Quantitative analysis (methodology and calibration curves)

The quantitative spectral analysis relates the spectral line intensity of an element in the plasma with the concentration of that element in the sample. As discussed previously in Section 3.1, the spectrum, at early times following plasma formation, is dominated by an intense radiation continuum and strongly broadened ionic emissions. At subsequent times, emissions from neutral atoms become dominant. However, the optimum time delay depends on the selected atomic species (i.e., transition probability) and the energy of the upper level of the analytical line of the element of interest used. In the present investigation, several time delays and gate widths have been used for each of the elements of interest. As a general trend, a decrease of the slope of the calibration curves has been observed to increase the time delay for both lasers used. Finally, a time delay of 1 µs and a gate width of 3 µs have been retained for the simultaneous measurement of the species of interest, having as criterion to attain the maximum slopes of the calibration curves for all the elements of interest. In order to reduce statistical errors, the signal was averaged over 20 laser shots, at three different places on the sample’s surface, and then the mean value was used. The standard deviation is shown with an error bar. The energy density was kept at about 60 J/cm² in all cases presented here, although both lower and higher values have been considered as well.

Calibration curves have been obtained using samples of known concentrations (up to 2%) of silicon, aluminium, and iron using picosecond and nanosecond laser pulses. All samples were prepared in a CaO matrix. After the preparation of the samples, for some of them, the concentration of the metal has been also measured using atomic absorption. The results were found to be in very good agreement with the calculated concentrations. The analytical spectral lines that have been used for the calibration curves were as follows: Al(I) 309.27 nm; Fe(I) 404.58 nm; and Si(I) 288.16 nm.

Figs. 6 and 7 depict the calibration curves for Al, Fe, and Si for concentrations ranging from 0.2% to 2% for picosecond and nanosecond excitation, respectively.

As can be seen, the standard deviation of the data points of the nanosecond calibration curves was significantly lower as compared with the picosecond case, owing essentially to the more stable energy output of the nanosecond laser. In addition, the values of the regression coefficients of the linear fitting of the data were much closer to unity in the nanosecond case than in the picosecond one. The linearity of the obtained calibration curves is an evidence of rather negligible self-absorption. At this point, it is worth noticing that (i) under all the experimental conditions employed in this work, we have not observed any self-reversed line and that (ii) none of the spectral lines used for the determination of the temperature or the electron density was a resonance line. On the contrary, special attention has been given to the selection of spectral lines having the highest possible terminating energy level in order to ensure that absorption was as low as possible. Therefore, it is reasonable to assume that the plasma was optically thin at the wavelengths of the spectral lines used.

In some recent papers [26–28], it has been shown that self-absorption of the spectral lines emitted from the plasma increases with delay time and that the lines undergo...
considerable self-absorption in a temporal window of 5–6 μs. Such behavior has not been observed under the present experimental conditions.

The limit of detection $C_L$ is usually defined $^{[14,29]}$ as the concentration that produces a net line intensity equivalent to three times the standard deviation of the background, and it can be evaluated from the expression:

$$C_L = 3\sigma_B/S$$

(6)

where $\sigma_B$ is the standard deviation of the background and $S$ is the sensitivity defined as the slope of the calibration curve, that is $\Delta_{signal}/\Delta_{concentration}$. The $\sigma_B$ has been determined from spectral regions that were located close to each analytical line chosen and were free from any other spectral feature and under exactly the same experimental conditions that have been employed for the measurement of the intensities of the spectral lines.

The detection limits determined in the present work are listed in Table 2. As can be seen, these are of the order of few parts per million for all elements studied under either picosecond or nanosecond excitation. Although the picosecond calibration curves have relatively lower correlation coefficients than the nanosecond ones, these can be used satisfactorily for quantitative analysis. To the best of our knowledge, there are few experimental studies concerning the use of picosecond lasers for elemental analysis $^{[15,19]}$. Most of the research done was investigating issues related mainly to the initiation $^{[17]}$ and the dynamics $^{[18]}$ of the picosecond laser ablation. Therefore, further research on the analytical applications of picosecond excitation will be beneficial.

<table>
<thead>
<tr>
<th>Element</th>
<th>Limit of detection $C_L$ (ppm) for nanosecond laser</th>
<th>Limit of detection $C_L$ (ppm) for picosecond laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.5</td>
<td>15</td>
</tr>
<tr>
<td>Fe</td>
<td>11</td>
<td>18</td>
</tr>
<tr>
<td>Si</td>
<td>6</td>
<td>9</td>
</tr>
</tbody>
</table>

The time delay and the gate width were 1 and 3 μs, respectively.

Fig. 6. Calibration curves for Al, Fe, and Si for picosecond laser pulses. The time delay and the gate width were 1 and 3 μs, respectively.

Fig. 7. Calibration curves for Al, Fe, and Si for nanosecond laser pulses. The time delay and the gate width were 1 and 3 μs, respectively.
4. Conclusions

The LIBS technique has been applied initially on pure metals and then on samples containing the same metals in a CaO matrix. The main effort of this work has been focused on the study of the time-resolved characteristics of the plasmas produced by nanosecond and picosecond pulses in relation to the analytical performance of LIBS. Our conclusions are that both the plasma temperature and electron density are decaying similarly and that the space-averaged values determined in the nanosecond case are slightly higher than for the picosecond one. Moreover, the calibration curves obtained, for the synthetic samples, complete this comparison and indicate that the inherent sensitivity of the technique remains almost unaltered for the needs of our application, although lower limits can be achieved, e.g. by improving the efficiency of the light collection optics.

Acknowledgments

P.S. and S.C. acknowledge partial support from the University of Patras through a “KARATHEODORIS” grant. C.P., G.A., and D.P. acknowledge partial support from EU through contract no. 7210-PR-271.

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