

Double pulse, calibration-free laser-induced breakdown spectroscopy: A new technique for in situ standard-less analysis of polluted soils

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is a promising technique for in situ environmental analysis. The potential of this technique for accurate quantitative analysis could be greatly improved using an innovative experimental setup – based on the use of two laser pulses suitably retarded – and analyzing the results with a standard-less procedure which overcomes the problems related to matrix effects. A new mobile instrument for soil analysis, developed at the Applied Laser Spectroscopy Laboratory in Pisa, is presented, and some experimental results are given.

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1. Introduction

In recent years, growing concerns on environmental issues have produced a number of regulatory actions on the quality of soils, based on the definition of acceptable upper concentration limits of potentially hazardous elements. Among the potential pollutants, heavy metals are particularly dangerous because they are not subject to bio-degradation processes and may be easily transferred to the food chain through absorption by plants or pollution of groundwaters.

Analysis of trace metals in soils is usually carried out by complex analytical techniques such as ICP, AAS, etc., which require a digestion procedure and the use of standard reference materials. Therefore, the analysis of many samples may be lengthy and expensive. This consideration makes the LIBS technique – a method that allows the determination of all the elements with a single measurement in a few seconds, without pre-treatment of the samples – particularly interesting for environmental analysis. This technique, developed in recent years, has been applied for the determination of elemental composition in a wide range of materials in the solid, liquid or gaseous phase (Rusak et al., 1997). Moreover, in LIBS measurements the samples do not need

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chemical treatments; therefore the risk of contamination of the samples is minimized.

2. Principles of the LIBS technique

Laser induced breakdown spectroscopy (LIBS), also named laser induced plasma spectroscopy (LIPS) or laser ablation spectroscopy (LAS), is a technique based on the spectral analysis of the radiation emitted by a plasma generated by focusing an intense laser pulse on the sample surface. The intense laser pulse focused on the sample surface causes evaporation, atomization and ionization of the material and produces a plasma, which expands and cools very rapidly. In typical LIBS conditions, the ablation process is stoichiometric: analysing the atomic and ionic lines emitted by the plasma provides the identification of the species present in the sample and their quantification (Adrain and Watson, 1984).

The intrinsic simplicity, robustness and quickness of LIBS make it particularly appropriate for in situ analysis even in hostile environments. In recent years, a number of applications of LIBS technique have been proposed in the field of materials science, industrial processes control, environmental protection (Ciucci et al., 1996; Vadillo et al., 1999; Martin et al., 2003) and cultural heritage conservation and study (Evans et al., 2003).

However, one of the most stringent constraints to the application of LIBS technique to environmental samples is the use of reference calibration standards which may introduce, because of the matrix effect, important errors in the quantitative analysis of the materials of interest. To overcome this problem, the Applied Laser Spectroscopy Laboratory of CNR has recently developed a methodology for the analysis of LIBS spectra, which does not depend on calibration curves or reference samples. This method, called calibration-free LIBS (CF-LIBS), could be very useful in soil analysis where the large variability of the matrix analysed makes the use of standard reference samples particularly problematic, thus producing potentially large errors in the determination of the heavy metal concentrations in the sample.

2.1. The calibration-free LIBS method

The method used for the analysis of LIBS spectra has been described in detail elsewhere (Ciucci et al., 1999); therefore the basic characteristics of this approach will be presented here. Assuming the

plasma in local thermodynamic equilibrium (LTE) in the temporal window of signal acquisition, the LIBS line integral intensity corresponding to the transition between two levels E_i and E_j can be expressed as:

$$I_{\lambda}^{ij} = FC_s A_{ij} \frac{g_i}{U_s(T)} e^{-E_i/k_B T} \quad (1)$$

where λ , C_s , A_{ij} , g_i and F are the wavelength of the transition, the number concentration of the emitting atomic species, the transition probability for the given line, the i level degeneracy and a constant to be determined after normalisation of the species concentrations, respectively. k_B is the Boltzmann constant and $U_s(T)$ is the partition function for the emitting species defined as:

$$U_s(T) = \sum_j g_j e^{-E_j/k_B T} \quad (2)$$

Taking the logarithm of Eq. (1) and substituting the following definitions:

$$\begin{aligned} y &= \ln \frac{I_{\lambda}^{ij}}{g_i A_{ij}} \\ m &= -\frac{1}{k_B T} \\ x &= E_i \\ q_s &= \ln \frac{C_s F}{U_s(T)} \end{aligned} \quad (3)$$

a linear relationship is obtained between the y and x parameters

$$y = mx + q_s \quad (4)$$

According to Eq. (4), the y values corresponding to the intensity of different lines from the same emitting species will be distributed linearly with respect to the energy of the upper transition level (x); the slope of the distribution curve is related to the plasma temperature, while the q_s parameter is proportional to the logarithm of the species concentration via the F constant factor. The F factor can be determined using the normalization relation

$$\sum_k C_k = 1 \quad (5)$$

since the sum of the relative concentrations of all the element must equal unity.

From Eqs. (5) and (3) one can obtain

$$F = \sum_k U_k(T) e^{q_k} \quad (6)$$

The application of the above described method in principle gives the concentration of all the components of the emissions, including the trace elements in concentrations up to the detection limit of the technique (typically several ppm) without the need of calibration. The minimum expected relative error in the composition determination is of the order of the percent concentration of the most abundant of the undetected elements. In typical soil samples, one would expect to have concentrations of elements, which are hardly detectable with LIBS (Cl, F, S) of the order of a few percent; therefore at the moment this figure represents the relative accuracy of CF-LIBS measurements.

However, for the specific application of CF-LIBS on soils one must consider that the laser induced plasma is indeed composed of the material ablated from the sample and elements coming from the surrounding atmosphere. Therefore, the elements present both in the sample and in the atmosphere (O, N, C in particular) cannot be easily quantified. This problem can be easily overcome using a vacuum chamber and operating in neutral (e.g., Ar) atmosphere; another possibility more suitable for in situ analysis would be fluxing the plasma region with a neutral gas. Such configuration, even if not yet experimentally tested, seems to be promising for the application of CF-LIBS on soil samples.

Although CF-LIBS might solve most of the problems related to the LIBS technique, allowing the definition of reliable procedures for LIBS quantitative analysis, it is nevertheless true that the LIBS technique still suffers a relatively poor sensitivity with respect to other analytical techniques (for instance atomic absorption (AA), inductively coupled plasma (ICP), mass spectrometry (MS)). Even considering that this drawback is, in typical environmental application, widely compensated by the possibility of performing simultaneous multi-elemental analysis with a dynamic range going from major to trace elements (ppm) in the same measurement, an improvement of the LIBS technique toward lower limits of detections for most of the elements of interest is desirable in view of practical applications.

Among the various methods proposed for improving the LIBS limits of detection, a promising technique seems to be the excitation of the plasma through a sequence of multiple laser pulses. In particular, the double pulse technique has been recently applied to the analysis of solid samples in a gaseous environment. In its simpler

version, the procedure requires two lasers emitting at the same wavelength, or a single laser emitting two pulses separated by a suitable delay. More complex experimental configurations involve the use of lasers with different wavelengths, allowing one to separate the process of laser ablation from the process of plasma excitation, or trains of several laser pulses.

2.2. Double pulse LIBS

The review of the existing literature demonstrates that, even in the simplest configuration involving two identical lasers, the double pulse technique allows one to obtain a significant increase in the LIBS sensitivity (corresponding to a marked improvement of the limits of detection) for several elements of interest. [Sattmann et al. \(1995\)](#) 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. \(1998\)](#) 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 temporal interpulse interval on an Al 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. On the other hand, they did not 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.

In order to investigate the physical reasons of such a greater ablation, the authors performed double pulse LIBS analysis on a brass target at different interpulse delay times and at different buffer gas pressures ([Cristoforetti et al., 2004](#)). The results indicate that the observed enhancement in double pulse experiments is related to the different laser-matter coupling in the first and in the second laser ablation. In fact, while the buffer gas absorbs a large part of the first laser pulse energy preventing it reaching the target, the second laser pulse operates in a rarefied ambient gas pressure, produced by the first laser pulse action, and its shielding is reduced so that all its energy can reach the target and remove a large amount of material.

3. Experimental

Some in situ environmental analyses have been performed using LIBS mobile systems based on the “classical” single pulse setup (Yamamoto et al., 1996; Theriault et al., 1998; Miles and Cortes, 1998; Castle et al., 1998; Wainner et al., 2001; Barbini et al., 2002). To the best of the authors’ knowledge, the use of double pulse LIBS for the environmental analysis has not yet been reported in the literature. Wainner et al. (2001) in fact mentioned the possible occurrence of double or multiple

pulses during their measurement, as a consequence of the use of a passively Q-switched Nd:YAG laser, but the effect was fundamentally unwanted and not controllable.

To best exploit the capabilities of the LIBS technique, the authors’ Laboratory has recently produced the first Mobile Dual-pulse Instrument (MODI) for LIBS environmental applications (see Fig. 1). The instrument integrates a dual pulse laser, which emits two collinear laser pulses with energy variable between 50 and 150 mJ per pulse at a maximum repetition rate of 10 Hz and a reciprocal delay



Fig. 1. The mobile dual-pulse instrument (MODI) for LIBS environmental applications developed at the Applied Laser Spectroscopy Laboratory of IPCF in Pisa.

which can be set from 0 to 60 μs . The LIBS measurements can be performed on soil samples (compressed in the form of small pellets with a 5-ton hand press) inside a closed experimental chamber, equipped with a motorised table for exact positioning of the sample at the focus of the laser beams. A laser pointer and an optical microscope allow the control of the region of the sample under analysis. Alternatively, for direct measurements on the ground an articulated 5-joint arm allows the focusing of the laser outside the instrument and the collection of the spectral signal. A safety switch disables the laser operation if the articulated arm head is not pressed against the ground, thus preventing accidental reflections and consequent possible eye damage.

The LIBS signal, either produced inside the experimental chamber or directly on the ground, is collected through an optical fibre and sent to a compact Echelle spectrometer coupled with an intensified CCD camera for spectral acquisition. The operations of the instrument are controlled by an integrated personal computer, which manages the sample visualization and positioning, the experimental settings of the laser (energy of the beams, delay between the pulses, repetition rate) and the spectral acquisition parameters (number of spectra averaged, acquisition delay, CCD measurement gate and gain).

The LIBS spectra, after acquisition and storage, are qualitatively and quantitatively analysed using proprietary software (LIBS++) which implements the calibration-free method. A typical environmental analysis on soil samples can take between 1 and 5 min, according to the complexity of the LIBS spectrum produced.

4. Examples

Fig. 2 shows the comparison between two LIBS spectra obtained inside the MODI experimental chamber, using single pulse and double pulse LIBS, on the same sample (PACS-1 marine sediment reference material, certified by the National Research Council of Canada for trace elements). The composition of the sample is reported in Table 1. The energy of the single pulse (160 mJ) corresponds to the sum of the energies of the two pulses (80 mJ each) which, for the acquisition of the double pulse spectrum, were delayed by 2 μs the one with respect to the other. In both cases, the spectra were acquired after 2 μs from the second pulse, with a

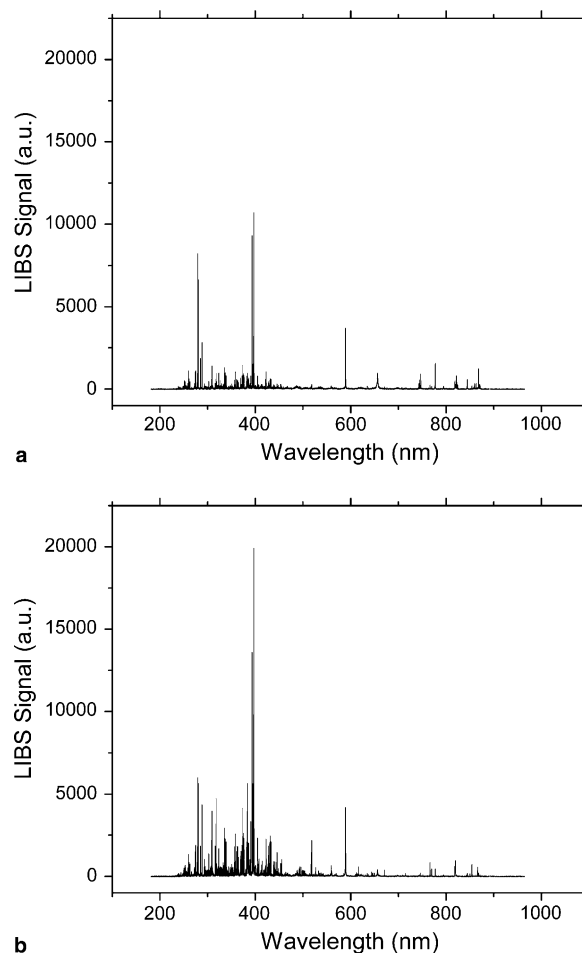


Fig. 2. LIBS spectra taken from sample PACS-1 in single pulse (a) and double pulse (b) configuration. In both cases, the total pulse energy was 160 mJ.

2 μs integration gate on the intensified CCD. Both spectra correspond to the average of three series of 30 (couples of) laser pulses acquired at three different points on the sample, in order to minimize the effect of the laser-induced crater on its surface. A repetition rate of 2 Hz was used in both cases; the acquisition of the experimental spectra was thus concluded in less than 1 min.

From the first visual comparison of single and double pulse spectra, it is clear that the double pulse spectrum gives in general a net improvement of the LIBS signal with respect to the single pulse one. However, this improvement is not the same for all the lines. Table 2 lists the intensity enhancement observed for several lines from the main components of the certified sample, along with the upper level energy value of the corresponding atomic tran-

Table 1
Certified composition of sample PACS-1

| Main components (%) | | |
|---------------------|------|--------|
| Al | 6.5 | ±0.12 |
| C | 3.69 | ±0.11 |
| Ca | 2.1 | ±0.1 |
| Cl | 2.39 | ±0.09 |
| Fe | 4.9 | ±0.1 |
| K | 1.25 | ±0.07 |
| Mg | 1.46 | ±0.05 |
| Na | 3.35 | ±0.08 |
| O | 41.5 | ±0.5 |
| P | 0.1 | ±0.007 |
| S | 1.32 | ±0.08 |
| Si | 26.0 | ±0.2 |
| Ti | 0.42 | ±0.01 |
| Trace metals (ppm) | | |
| As | 211 | ±11 |
| Cd | 2.38 | ±0.20 |
| Co | 17.5 | ±1.1 |
| Cr | 113 | ±8 |
| Cu | 452 | ±16 |
| Hg | 4.57 | ±0.16 |
| Mn | 470 | ±12 |
| Mo | 12.9 | ±0.9 |
| Ni | 44.1 | ±2.0 |
| Pb | 404 | ±20 |
| Sb | 171 | ±14 |
| Se | 1.09 | ±0.11 |
| Sn | 41.1 | ±3.1 |
| Sr | 277 | ±11 |
| V | 127 | ±5 |
| Zn | 824 | ±22 |

sition. Differently from results obtained on metallic alloys (not shown here), where the signal improvement given by the double pulse LIBS approach appears proportional to the energy of the upper level of the transition, in all the environmental samples analysed until now such a relationship is not evident. On the contrary, as illustrated in the example of the sediment PACS-1, lines from low energy excited levels are generally more enhanced. This result is an indication that the plasma temperature in double pulse configuration is slightly lower than in single pulse configuration, and therefore the intensity enhancement in this case is mainly related to an increase of the laser ablated mass, rather than to an increase of the plasma temperature, that would have produced an increase of the population of the high upper state energy levels (and, consequently, a larger enhancement of the corresponding emission lines), with respect to the lower levels (see Fig. 3). As an independent check, the plasma temperature has been evaluated by linear regression of the Boltzmann plot including 19 neutral Fe lines

Table 2

Signal enhancement observed for double pulse compared to the single pulse of the same total energy (ratio of the integral intensities, averaged on three series of 30 laser pulses)

| Element and ionization | Wavelength (nm) | E_i (cm ⁻¹) | Enhancement |
|------------------------|-----------------|---------------------------|--------------|
| Fe II | 261.187 | 38,660 | 1.3 |
| Al I | 265.248 | 37,689 | ^a |
| Mg I | 277.669 | 57,874 | 9.4 |
| Mg II | 279.078 | 71,491 | 1.9 |
| Ca II | 315.887 | 56,839 | 5.9 |
| Ti II | 336.121 | 29,968 | 2.4 |
| Fe I | 349.057 | 29,056 | ^a |
| Al I | 394.4 | 25,348 | 4.4 |
| Ti I | 398.976 | 25,227 | 3.5 |
| Fe I | 404.581 | 36,686 | 3.2 |
| Pb I | 405.78 | 35,287 | ^a |
| Sr II | 407.771 | 24,517 | 7.3 |
| Fe I | 426.047 | 42,816 | ^a |
| Ca I | 428.301 | 38,552 | 7.7 |
| Ba II | 455.403 | 21,952 | 7.5 |
| Ba II | 493.409 | 20,262 | 8.4 |
| Ti I | 506.466 | 20,126 | ^a |
| Mg I | 518.361 | 41,197 | 5.4 |
| Fe I | 561.564 | 44,677 | ^a |
| Li I | 670.776 | 14,904 | 2.7 |
| Ba I | 728.03 | 22,947 | ^a |
| K I | 766.491 | 13,043 | 3.5 |
| Ca II | 854.202 | 25,414 | 3.5 |

The sample is the certified soil PACS-1.

^a Signal not measurable with single pulse.

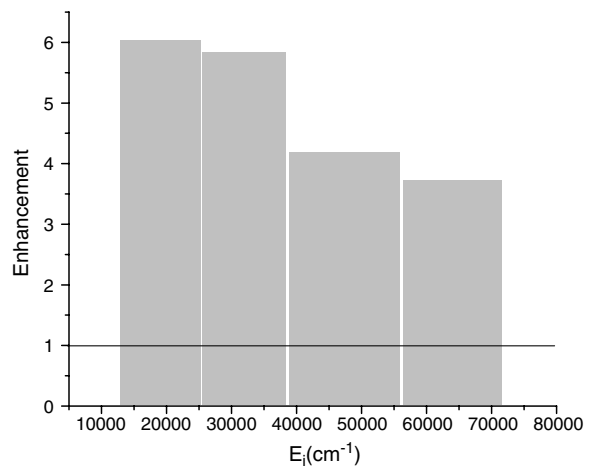


Fig. 3. Average LIBS signal enhancement in double pulse LIBS with respect to single pulse, as a function of the upper level energy E_i .

from the spectral region between 355 and 390 nm (no overlap to the lines listed in Table 2); the spectral parameters required for the calculation have been extracted from the NIST Atomic Spectra

Table 3
Comparison of chemical elements detected in single and double pulse configuration

| Element | Single pulse | Double pulse |
|---------|--------------|--------------|
| Cr | No | Yes |
| Cu | Yes | Yes |
| Mn | Yes | Yes |
| Ni | No | Yes |
| Pb | No | Yes |
| Sr | Yes | Yes |
| V | Yes | Yes |
| Zn | Yes | Yes |

The sample is the certified soil PACS-1.

Database. The temperature value obtained for single pulse (6300 K) is indeed slightly higher than the one obtained in double pulse configuration (6100 K). However, the uncertainty on temperature determination, of the order of 5%, does not really allow differentiation between these values.

The enhancement of the LIBS signal in double pulse configuration allows the detection of elements not visible in the single pulse LIBS spectrum. A list of trace elements detectable in single and double pulse configurations is shown in Table 3.

However, the analysis of the double pulse enhancement obtained using other soil and sediment samples suggests that the signal improvement also depends on sample granulometry, with fine grained soils showing lower enhancement with respect to more compact samples. This effect is probably related to the presence of fine particle aerosols preventing the second pulse to properly reach the sample.

5. Conclusions

In this paper, the first application of the double pulse LIBS technique on soils and sediments has been demonstrated, using a mobile instrument specifically made for in situ analysis. Improvements on LIBS signal of the order of 5–10 times, depending on the upper level energy of the transition, are typically obtained on easily compactable samples, while a smaller improvement, or even a reduction of the LIBS signal, are observed on fine grained samples.

The enhancement of the LIBS signal obtained using the double pulse technique corresponds to an improvement of the LIBS limit of detection for that particular transition and, in general, for the corresponding emitting element. This effect is partic-

ularly interesting for quantitative analysis using standard-less procedures (CF-LIBS).

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