

# *Técnicas Laboratoriais Avançadas I - Laser Induced Breakdown Spectroscopy*

*June 3, 2023*

## **Introduction and Basic Concepts**

Laser-induced breakdown spectroscopy (LIBS) is a technique laid on the concept of atomic emission spectroscopy after the vaporization, atomization, and excitation of a sample using a pulsed laser, creating a laser-induced plasma. A standard LIBS process involves two stages:

1. the plasma generation: an intense pulsed laser beam is focused onto a material sample, with a burst of energy transferred to the material during a short period of time - a laser pulse - heating and evaporating - i.e. ablating - a small volume of material producing a gas plume. This gas plume continues to absorb laser energy, becoming ionized and turning into a plasma;
2. the signal emission and collection: light emission starts as soon as the plasma decays and emits energy in form of radiation, which is collected using a spectrometer. As each element has its own spectral signature and associated lines, chemical elements can be identified.

### *Historical background and main features*

The origins of LIBS can be traced back to 60 years ago, with the pioneering works on laser-induced spark emission in 1962 that seeded multiple developments regarding the technical aspects involved in the subsequent years. Yet, entering the 1970s, this interest faded due to cost and reliability issues, both in accuracy and precision, which at that time were detrimental for a possible technological product when compared with established analytical techniques like atomic absorption spectrometry or inductively coupled plasma-atomic emission spectrometry. But as always in science and technology, later developments on the technological side, namely the quality and price of laser sources and sensitive imaging detectors revitalized the field in the early 1980s. This is also when the term LIBS was coined by the team at Los Alamos National Laboratory, whose pioneering work should be highlighted in particular in the detection of hazardous gases and vapors in air and beryllium in filters.

Soon, the technique found its technological applications, from monitoring environmental contamination to controlling and sorting materials in industrial systems. These days, LIBS is an established spectroscopy technique for qualitative and quantitative analysis in various domains including analysis of alloys for metallurgy and scrap sampling, soils, sediments, or water for environmental purposes, and rocks and minerals for the mining industry<sup>1</sup>. Also, allowing remote operation without significant sample preparation, it has been used to operate in harsh environments, from the deep sea to extraterrestrial environments (demonstrated in the Mars Rover)<sup>2</sup>.

Compared with other techniques, LIBS presents non-trivial features and advantages compared with other techniques:

- Ability to detect (in theory) all elements - in particular, lighter ones - from tenths of ppm to ppb;
- Ability to detect multiple elements simultaneously;
- Substituting a physical device (a pair of electrodes) with a laser to create the plasma:
  - Allows an analysis independent of the substance or the state (gas, liquid and solid-state);
  - Requires small to no previous sample preparation tasks;
  - Can be used in extreme conditions: vacuum, underwater, high temperature, and pressure;
  - Can work at high speeds, up to kHz rates;
  - Can be performed remotely (non-contact) offering opportunities for portable instruments and online analysis;
  - Limited and localized damage on the sample surface, almost non-destructive in the order of tens to hundreds of nanograms, which can be interesting for cultural heritage or artworks;
  - in-depth profiling;
- Finally, reducing its footprint it can be easily integrated with other spectroscopic techniques, e.g. Raman spectroscopy, laser-induced fluorescence (LIF) or hyperspectral imaging, thus supporting interesting sensor fusion solutions for industrial applications.

### *Ablation and plasma generation*

The first stage concerns the ablation and plasma generation and starts with the light-matter interaction: a pulsed and intense laser beam is focused onto an absorbing material. Energy absorption leads to heat generation, typically capable of producing a temperature around  $10^4\text{K}$

<sup>1</sup> Lian-Bo Guo, Deng Zhang, Lan-Xiang Sun, Shun-Chun Yao, Lei Zhang, Zhen-Zhen Wang, Qian-Qian Wang, Hong-Bin Ding, Yuan Lu, Zong-Yu Hou, et al. Development in the application of laser-induced breakdown spectroscopy in recent years: A review. *Frontiers of Physics*, 16(2):1–25, 2021

<sup>2</sup> Chen Sun, Weijie Xu, Yongqi Tan, Yuqing Zhang, Zengqi Yue, Long Zou, Sahar Shabbir, Mengting Wu, Fengye Chen, and Jin Yu. From machine learning to transfer learning in laser-induced breakdown spectroscopy analysis of rocks for mars exploration. *Scientific Reports*, 11(1):1–17, 2021

in just  $10^{-13}s$  time, thermalizing in the subsequent period of  $10^{-11}s$  and heating a layer of material close to the surface. Provided the power is large enough, the material is vaporized and the matter is ejected from the surface, a process that is referred to as *ablation*.

The most conventional model to describe the dynamics involving nanosecond pulsed lasers proceeds as following:

1. absorption of the laser radiation at the sample surface leading to the *ablation* (heating, melting, and evaporation) of the solid;
2. thermally induced fracture of the solid and ejection of matter from the surface;
3. formation (breakdown) and expansion of the near-surface plasma, together with shock and acoustic wave generation;
4. laser radiation absorption, heating of the plasma up to temperatures of  $10^4 - 10^6 K$ , inducing a plasma shielding;
5. LIBS regime as the plasma starts to decay.

#### Signal emission and collection

When you use nanosecond pulses, the ablated vapor continues to absorb energy as heat and can become ionized in about  $3 - 5ns$ . In this situation, we have the dielectric breakdown and ignition of plasma, resulting from the absorption of additional laser radiation due to the inverse Bremsstrahlung and photoionization. In this case, only part of the laser radiation reaches the surface which creates the plasma *shielding effect* that preserves up to 80% of the pulse energy in the plasma, leading to a considerable increase in its temperature (up to  $10^5 K$ ) and electron density (up to  $4 \times 10^{21} cm^{-3}$ ).

Due to the high temperature of the plasma and its electron density, in the first  $50 - 200ns$  the spectrum contains a continuous intense background caused by the Bremsstrahlung effect. Also, the presence of charged particles induces a statistical distribution of Stark shifts accompanying the recombination processes, leading to extremely Stark-broadened emission lines  $\approx 10nm$  which are unsuitable for most of the applications.

Therefore, it is crucial to use a spectrometer delay - i.e. trigger the spectrometers with a relative delay in relation to the laser pulse - to avoid these unwanted effects, thus minimizing the noise and maximizing the amount of useful information collected, which in this case correspond to the signals obtained from the emission lines of each constituent element.

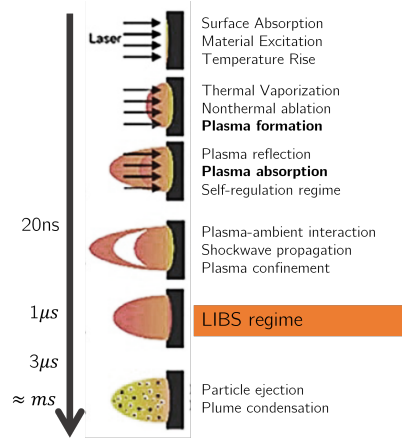


Figure 1: Plasma generation for nanosecond pulses.

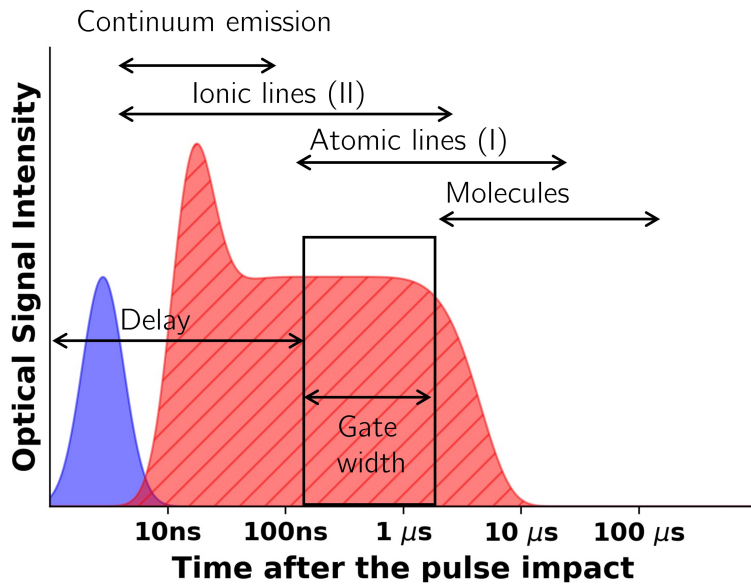


Figure 2: Spectral contributions on a LIBS experiment and timescales for distinct phenomena.

Another important aspect is to use a suitable integration window or gate. In ideal conditions (see Figure 2), one would like to have integration times / gate widths around  $1\mu s$ . Yet, such small scales require highly-sensitive spectrometers and sensors (typically Intensified CCDs - ICCDs) which tend to be prohibitively expensive for most common applications.

### *Characterizing the plasma*

The analysis of the plasma is the conceptual basis of any LIBS system. The ideal scenario would be to recover the electron density and the temperature from the data, as these are considered important parameters for a reasonable characterization of the plasma. For the purpose of this experimental activity we will characterize the plasma density using the Stark broadening for the Hydrogen alpha line of the Balmer series ( $656.28nm$ ) and the plasma temperature using the Saha-Boltzmann plot. Both methods are described in the additional notes below, but we shall stress that they only make sense in the Local thermodynamic equilibrium (LTE) conditions, as otherwise the non-equilibrium phenomena strongly limits any generalization.

### *The Experimental System*

The most popular configuration of LIBS uses a laser entering perpendicularly to the sample surface, using a single or a set of mirrors to-

There are many factors that can influence plasma generation and the amount of the material ablated, like:

- composition and types of species;
- surface roughness;
- pressure and composition of the surrounding atmosphere;
- thermal and optical properties of the substance;

gether with a single or a set of focusing lenses. Typically, the optimal focal plane is positioned around  $2 \pm 6\text{mm}$  below the surface. The plasma emission is collected by one or various lens condensers directly to the entrance of the spectrometer or onto optical fibers that are connected to the spectrometer.

The system you will use for the purpose of this experiment has the following design and structural components (see figure 3):

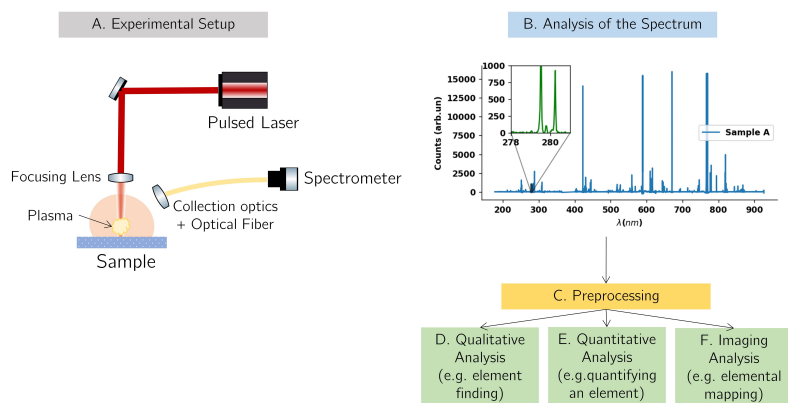


Figure 3: Visual scheme of the experimental system used for this experimental activity, and typical LIBS signal and experimental workflow.

1. Nd:YAG Laser from Quantel: an active q-switched laser operating at 1064 nm with typical energy ranging around tenths of millijoules, and pulse duration around 8ns;
2. Collection System: composed of 8 collimators connected to suitable optical fibers which direct the signal onto the spectrometers;
3. Spectrometer: a multichannel system from Avantes (8 spectrometers, with a range from around 250 nm to 890 nm, and a typical resolution of around 0.1nm);
4. Linear Stages: two linear stages from Newport that can be used to manipulate the sample in the transverse plane.

## Experimental Activity

This activity is divided into two consecutive tasks, which seek to introduce the students to both the fundamentals and standard applications of LIBS. We stress that this activity involves laser sources working at potentially harmful regimes, so we advise taking extra caution throughout all the experimental procedures, closing the door, and closing the laser shutter before opening the door. For each task, an exam-

ple Jupiter notebook with part of the analysis is provided in advance, which must be studied to better prepare the experimental activity.

### *Getting started with the fundamentals*

In the first task, we will explore the fundamentals of the LIBS process and signal.

1. Using the steel sample 1.A, start by aligning the sample before taking the first shot. Analyze the resulting spectrum, trying to identify some of the constituent emission lines plus atmospheric ones. Discuss its relative intensities;
2. Take shots varying the spectrometer gate delay parameter from  $0 - 3\mu s$ . Try to explain the differences between distinct signals and relate them to the processes involved in LIBS. For the discussion, you can plot both signals and compute the signal-to-noise ratio for a specific line of interest using

$$SNR = \frac{I_{\lambda} - I_{Background}}{3\sigma_{Background}}.$$

3. Controlling the Q-switch parameter from  $310 - 410ms$ , explain the observed differences between distinct signals and relate with the processes involved in LIBS. Explore the intensity increase for specific lines and observe if these are not saturated. Finally, explain how the active Q-switch works and relate it with the typical duration of the pulse ( $\approx 8ns$ ).
4. Characterize the plasma using the Boltzmann or the Saha-Boltzmann plot methodology (how to choose between the two methodologies?) and the Hydrogen  $\alpha$  line from the Balmer series (using the functions previously defined in the accompanying notebook) and discuss if the order of magnitude is the expected one. Take 10 shots and analyze the same quantities for each, discussing the implications of these results;
5. Use the steel sample 1.B and Rock 1.C and identify distinct emission lines, seeking for the presence of distinct elements. Compute the temperature and density of the plasma for each sample and compare it with the previous one.

### *Qualitative Analysis*

In the second task, we will see how we can use the LIBS technique to perform simple qualitative analysis, in particular, to identify distinct materials in automatic manners. Furthermore, we will explore an

additional application of the LIBS technique, scanning the transverse plane of the sample to create elemental maps.

1. Align the sample 2.A, and make a  $20 \times 20$  shots map with  $1mm$  step, scanning the region of interest;
2. Construct two maps based on lines of interest for each region and comment on the results;
3. Considering the shots as individual samples, deploy a classification strategy based on a machine learning algorithm of your choice.

# Additional Notes on plasma characterization

## *Determining the electron density*

For determining the electron density we can use methods based on optical emission spectroscopy, in particular relating to the broadening of emission lines due to the Stark effect with that obtained experimentally. Indeed, the most common method considers the effect of the collisional Stark effect and is extremely efficient for computing the electron density when the Stark effect is the dominant line-broadening mechanism, when compared against Doppler, instrumental, or pressure-broadening mechanisms. It can be proved through analytical calculations that the Stark effect leads to the following relation between the half width at half maximum (HWHM) of an emission line,  $w_{Stark}$ , and the electron density  $n_e$  as

$$w_{Stark} = [1 + 1.75A(1 - 0.75R)] w \frac{n_e}{n_e^{ref}},$$

where  $A$  is the ion broadening parameter,  $w$  the electron impact half-width,  $n_e^{ref}$  the reference electron density (usually  $10^{16}$  or  $10^{17} cm^{-3}$ ) at which the parameters  $A$  and  $w$  are calculated, and  $R$  is the ratio of the mean distance between ions and Debye radius. The equation is only valid for  $A \leq 0.5$  and  $R \leq 0.8$  and for neutral emitters (it can be extended to singly ionized ones replacing  $0.75R$  with  $1.2R$ ). These coefficients can be found in tabled references. Usually, the parameter  $A$  is much smaller than 1, meaning that the Stark broadening in LIBS is mostly electron-related. The ion term can then be dropped out and the second term becomes

$$w_{Stark} = w \frac{n_e}{n_e^{ref}}.$$

Of course, an accurate determination of electron density implies several assumptions:

- The selected line is isolated and optically thin to avoid any additional broadening due to neighbor lines or self-absorption;
- The uncertainty of the reference Stark coefficients or parameters must be as small as possible, since the main error source of the electron density determination comes from such uncertainty;
- The calculation is far more accurate for lines from the hydrogen and hydrogenic atoms, and therefore use these lines for best results;



- The technique used to extract Stark broadening from the experimental line width also plays an important role in the accuracy of the determination, already discussed in the literature reporting that the main error of electron density results from the uncertainty of fitting of the line profile and of the instrumental width. The Stark effect yields a Lorentzian broadening, whereas the Doppler and instrument broadening present Gaussian profile. As a result, the Voigt profile, which is a convolution of the Lorentz and the Gaussian profiles shall be used to extract the Stark broadening of the line from the experimental spectrum.

An alternative methodology is to extract the electron density from the spectral line shift. In this case, we shall use the Stark line shift that can be estimated from

$$d_{total} \approx \left[ \frac{d}{w} \pm 2A (1 - 0.75R) \right] w \frac{n_e}{n_e^{ref}}$$

with  $d$  the electron-impact shift parameter. The caveat of the method is that  $d$  has larger uncertainty and therefore using this method shall be avoided. Yet in cases where self-absorption is important, this method can also prove useful. To provide a quick reference, the typical electron density of plasma in LIBS analysis is around  $10^{16}$  to  $10^{18} \text{cm}^{-3}$ .

### *Determining the plasma temperature*

There are many temperatures that can be used to characterize the plasma, such as the excitation temperature  $T_{ex}$  characterizing the *Atomic State Distribution Function* among different excited energy levels, or the electron temperature  $T_e$  characterizing the electron velocity distribution function crucial for the Doppler broadening effects, and even the temperature of heavy particles  $T_H$  associated with the velocity of atoms, ions, and molecules. The assumption of the LTE simplifies these regimes assuming the same temperature for all the cases. Typical values are of the order of  $10^4 \text{K}$ .

If the LTE hypothesis is fulfilled, the plasma temperature can be calculated using the ratio of a pair of spectral lines from the same element with the same ionization state. Assuming that the populations in excited levels of a given species obey the Boltzmann distribution, the population density of the excited level  $i$  of species  $s$  is given by<sup>3</sup>:

$$n_i^s = \frac{g_i}{U^s(T)} n^s \exp\left(-\frac{E_i}{k_B T}\right)$$

where  $g_i$ ,  $E_i$  are the statistical weight and the excitation energy of the level,  $n^s$  is the total number density of the species  $s$  in the plasma,  $k_B$  is the Boltzmann constant and  $U^s(T)$  is the internal partition function

<sup>3</sup> Jozef Rakovský. Qualitative-portable to quantitative-laboratory libs. 2012; and David A Cremers and Leon J Radziemski. *Handbook of laser-induced breakdown spectroscopy*. John Wiley & Sons, 2013

of the species at temperature  $T$ , i.e.

$$U^s(T) = \sum_i g_i \exp\left(-\frac{E_i}{k_B T}\right).$$

The line intensity  $I_{ij}$ , ie. the number of transitions per unit volume per unit of time (which is related to the signal collected using the spectrometer using the maximum intensity or peak area), corresponding to the transition between  $i \rightarrow j$  is given by

$$I_{ij} = \frac{A_{ij} g_i}{U^s(T)} n^s \exp\left(-\frac{E_i}{k_B T}\right)$$

where  $A_{ij}$  is the transition probability for  $i \rightarrow j$ .

Therefore, considering two lines of the same species, say  $\lambda_{ij}$  and  $\lambda_{mn}$  we know that these are associated with different transitions but share the same plasma temperature. Therefore we can use the *Boltzmann two-line method* by applying the formula

$$T = \frac{E_i - E_m}{k_B \ln\left(\frac{I_{mn} g_i A_{ji}}{I_{ij} g_m A_{mn}}\right)},$$

but which has the caveat of significant noise and uncertainty,

$$\frac{\Delta T}{T} = \frac{k_B T}{E_i - E_m} \frac{\Delta(I_{ij}/I_{mn})}{I_{ij}/I_{mn}}.$$

To improve the accuracy of temperature determination we can use multiple transitions instead of two, creating a Boltzmann plot method using

$$\log\left(\frac{I_{ij}}{g_i A_{ij}}\right) = -\frac{E_i}{k_B T} + \log\left(\frac{n^s}{U^s(T)}\right).$$

It is easy to see that plotting the left-hand side against the transition energy leads to a linear relation with slope  $-\frac{1}{k_B T}$ , meaning that the temperature can be obtained using simple linear regression. It is also easy to conclude that you should employ as much energy levels as possible to improve the accuracy of the prediction. Yet, the extension range of  $E_i$  is usually shorter than desirable, around  $1 - 2eV$ .

A workaround to the above limitation is to combine the Saha ionization and Boltzmann distribution, considering ionized states to cover larger intervals for the effective energy difference. Indeed, significant improvements can be obtained if lines from successive ionization stages of the same element can be detected, as the extension of  $E_i$  is now enlarged by the ionization energy, much larger than the thermal excitation energy.

To enter with the ionized states one requires the additional *Saha equation* to relate the densities of the species of subsequent ionization

degrees for a considered element as

$$n_e \frac{n^z}{n^{z-1}} = \frac{2(2\pi m_e k_B T)^{3/2}}{h^3} \frac{2U^z(T)}{U^{z-1}(T)} \exp \left[ -\frac{(E_{ion}^{z-1} - \Delta E_{ion}^{z-1})}{k_B T} \right]$$

with  $z$  referring to the ionization stage ( $z = 0$  the neutral atom,  $z = 1$  the singly-charged atom and so on),  $m_e$  and  $h$  the electron mass and Planck constant respectively, and  $E_{ion}$  and  $\Delta E_{ion}$  the ionization energy and the correction to the quantity due to the interaction with the plasma. Thus, the number density  $n^z$  for the ionized species (typically for LIBS only  $z = 1$  is considered) can be deduced iteratively from the  $n^{z-1}$  and the integrated intensity of lines for all ionization states can therefore be obtained from

$$\log \left( \frac{I_{ij}^z}{g_i A_{ij}} \right)^* = -\frac{E_i^{z*}}{k_B T} + \log \left( \frac{n^0}{U^0(T)} \right),$$

with  $*$  referring to the correction for the ionized species with respect to the Boltzmann plot. Note that now you can plot both equations in the same plot taking the corrections of the ordinates

$$\log \left( \frac{I_{ij}^z}{g_i A_{ij}} \right)^* = \log \left( \frac{I_{ij}^z}{g_i A_{ij}} \right) - B^z(T, N_e)$$

with

$$B^z(T, N_e) = z \log \left( \frac{2(2\pi m_e k_B)^{3/2}}{h^3} \frac{T^{3/2}}{n_e} \right)$$

and

$$E_i^{z*} = E_i^z + \sum_{k=0}^{z-1} (E_{ion}^k - \Delta E_{ion}^k).$$

Note that the ordinate value depends on temperature, on  $\log(T^{3/2})$ , but as it is slower than  $1/T$ , the temperature can be determined using an iterative methodology. Knowing  $n_e$  (computed previously or estimated) we can employ a similar strategy as in the Boltzmann plot to obtain the plasma temperature from its slope - *Saha-Boltzmann plot methodology*.

## References

- [1] David A Cremers and Leon J Radziemski. *Handbook of laser-induced breakdown spectroscopy*. John Wiley & Sons, 2013.
- [2] Lian-Bo Guo, Deng Zhang, Lan-Xiang Sun, Shun-Chun Yao, Lei Zhang, Zhen-Zhen Wang, Qian-Qian Wang, Hong-Bin Ding, Yuan Lu, Zong-Yu Hou, et al. Development in the application of laser-induced breakdown spectroscopy in recent years: A review. *Frontiers of Physics*, 16(2):1–25, 2021.

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- [4] Chen Sun, Weijie Xu, Yongqi Tan, Yuqing Zhang, Zengqi Yue, Long Zou, Sahar Shabbir, Mengting Wu, Fengye Chen, and Jin Yu. From machine learning to transfer learning in laser-induced breakdown spectroscopy analysis of rocks for mars exploration. *Scientific Reports*, 11(1):1–17, 2021.