

Laser induced breakdown spectroscopy: Fundamentals, applications and challenges

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) is a technique that provides an accurate in situ quantitative chemical analysis and, thanks to the developments in new spectral processing algorithms in the last decade, has achieved a promising performance as a quantitative chemical analyser at the atomic level. These possibilities along with the fact that little or no sample preparation is necessary have expanded the application fields of LIBS. In this paper, we review the state of the art of this technique, its fundamentals, algorithms for quantitative analysis or sample classification, future challenges, and new application fields where LIBS can solve real problems.

INTRODUCTION

Laser induced breakdown spectroscopy is a type of atomic emission spectroscopy. In this technique highly energetic laser pulse mainly use to provoke optical sample excitation. So highly energetic laser pulse use as the excitation source. The interaction between focused laser pulses and the sample creates plasma composed of ionized matter. The formation of the plasma only begins when the focused laser achieves a certain threshold for optical breakdown which generally depends on the environment and the target material. Plasma light emissions can provide “spectral signatures” of chemical composition of many different kinds of materials in solid, liquid or gas state. so we can say laser induced breakdown spectroscopy is a rapid chemical analysis technology that uses a short laser pulse to create a micro plasma on the sample surface. This analytical technique offers many compelling advantages compared to other elemental analysis techniques.^[1]

These include:

- Extremely fast measurement time, usually a few seconds for a single spot analysis.
- Broad elemental coverage, including lighter elements such as H, Be, Li, C, N, O, Na, and Mg.

- Versatile sampling protocols that include fast raster of the sample surface and depth profiling.
- Thin sample analysis without the worry of the substrate interference.^[2]

LIBS can provide an easy, fast and in situ chemical analysis with a reasonable precision, detection limits and cost. Additionally, as there is no need for sample preparation, it could be considered as a “put & play” technique suitable for a wide range of application. Now a days LIBS is considered as an attractive and effective technique when a fast and whole chemical analysis at the atomic level is required. The advantage of this method is high flexibility and high measuring speeds. Due to these features, laser measuring methods and applications have encountered a dynamic development during last few years.^[3]

PRINCIPLE

The principle of laser induced breakdown spectroscopy is shown schematically in figure.^[4]

A pulsed laser beam is focused on the surface of a substance to be analysed. radiation energy is locally coupled into the material and material starts to evaporate. Within this material vapour and the surrounding gas atmosphere a plasma is generated, leading to the excitation of the material constituents and their spontaneous emission of radiation. The plasma decays and emits element specific radiation. this emission is resolved spectrally and is detected by a spectrometer. For solid substances a hole is formed finally. The evaporated material is removed partially from the interaction zone driven by the intrinsic dynamics of the plasma expansion and by an externally impressed gas flow. The process denoted in phase as evaporation is a simplified description and refers to solid inorganic substance.in general there is no pure sublimation from the solid phase to the gaseous phase. Besides the evaporation and dissociation processes also particles are ablated e.g. small particulates or droplets, which are ejected due to the impact of the pressure exerted by the plasma and the accompanying shockwaves on a melt layer. For organic substances the initial material is disintegrated, fragmented and dissociated.^[4]

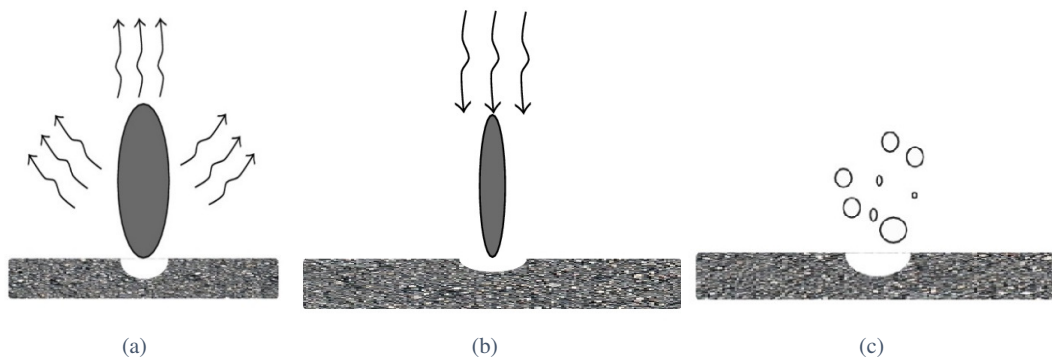


Figure 1 Plasma life stages:(a) plasma ignition (b) plasma expansion and cooling and (c) particle ejection and condensation^[4]

So how does LIBS work?

The main physical process that forms the essence of LIBS technology is the formation of high temperature plasma, induced by a short laser pulse. when the short pulse laser beam is

focused onto the sample surface, a small volume of the sample mass is ablated. In a process known as laser ablation, this ablated mass further interacts with a trailing portion of the laser pulse to form a highly energetic plasma that contains free electrons, excited atoms and ions.^[5]

When the laser pulse terminates, the plasma starts to cool. During the plasma cooling process, the electrons of the atoms and ions at the excited electronic states fall down into natural ground states, causing the plasma to emit light with discrete spectral peaks. The emitted light from plasma is collected and coupled with an ICCD spectrograph detector module for LIBS spectral analysis. Each element in the periodic table is associated with unique LIBS spectral peaks. By identifying different peaks for the analysed samples, its chemical composition can be rapidly determined. Often, information on LIBS peak intensities can be used to quantify the concentration of trace and major elements in the sample.^[5]

With the advancement of powerful chemometric software for LIBS data analysis, and with steady progress in understanding laser ablation fundamentals.^[5]

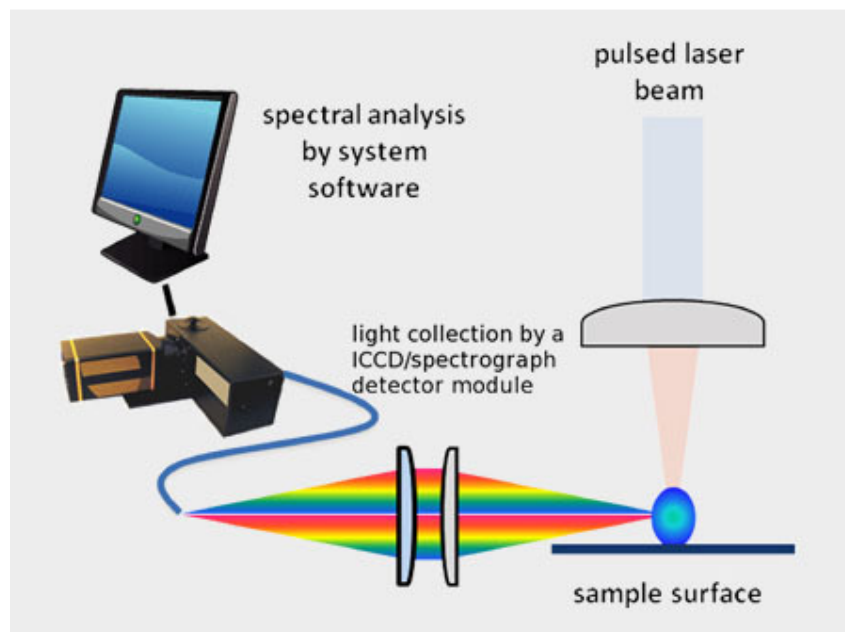


Figure 2 Emitted light collection by a set of optical lens and optical fibre^[5]

FUNDAMENTALS OF PLASMA AND ITS SPECTRA

Understanding the plasma physics of LIBS is essential to provide an optimized setting for LIBS measurements. A large number of environmental factors affect the plasma life time and features, changing the spectral emission and the performance of this technique for chemical analysis at the atomic level.^[6]

Laser ablation and plasma physics of LIBS

Laser-matter interactions are governed by quantum mechanics laws describing how photons are absorbed or emitted by atoms. If an electron absorbs a photon, the electron reaches a higher energy quantum mechanical state. Electrons tend to the lower possible energy levels and in the decay process the electron tends to the lower possible energy levels and in the decay process the electron emits a photon. These emissions are the spectral emission lines found in

LIBS spectra and its features and their associated energy levels are well known for each atom.^[6]

If the energy applied to the atom is high enough electrons can be detached by the atom inducing free electrons and positive ions (cations). Initially, the detached electron is the most external one because it has the lowest ionization potential, but with higher energy supply it is possible to detached more electrons overcoming the second ionization potential, the third, and so on. These ions can emit photons in the recombination process (cations absorbs a free electron in a process called free-bound transition) or in the deexcitation process. These emissions can be continuum due to the different energies of the ions and the different energy transitions, however cations deexcitation has discrete (or quantized) set of energy levels with characteristic emission lines for each kind of element, allowing its identification together with the atomic emission lines.^[6]

The plasma, induced by the interaction pulsed laser-sample, emits light which consists of discrete lines, bands, and an overlying continuum. These discrete lines, which characterize the material, have three main features; *wavelength, intensity, and shape*. These parameters depend on both the structure of the emitting atoms and their environment. Each kind of atom has some different energy levels which determine the wavelength of the line. Besides the identification of the elements in the sample, the calculation of the amount of each element in the sample from the line intensities is possible taking in account different necessary conditions fixed by local thermodynamic equilibrium or problems related with matrix effects which can reduce the accuracy of quantitative analysis. On the other hand, the intensity and shape of the lines depend strongly on the environment of the emitting atom.^[6]

Basically, there are three stages in the plasma life time. The first one is the ignition process. This process includes bond breaking and plasma shielding during the laser pulse, depending on laser type, irradiance, and pulse duration.^[6]

If the selected laser is a femtosecond one, nonthermal processes will dominate the ionization. The pulse is too short to induce thermal effects; hence other effects should ionize the atoms, depending of the kind of sample. The pulse has a huge amount of energy and effects like multiphoton absorption and ionization, tunneling, and avalanche ionization excite the sample. With this amount of energy, the electron-hole created will induce emission of X-rays, hot electrons, and photoemission. This will create highly charged ions through a process called Coulomb explosion. The absence of thermal effects creates a crater with highly defined edges without melted or deposited materials.^[6]

The next step in plasma life is critical for optimization of LIBS spectral acquisition because the plasma causes atomic emission during the cooling process. After ignition, the plasma will continue expanding and cooling. At the same time, the electron temperature and density will change. This process depends on ablated mass, spot size, energy coupled to the sample, and environmental conditions (state of the sample, pressure, etc.).^[6]

Plasma Emission Spectra

The emission lines from the atomic species can be hidden by continuum radiation that is caused by two processes. The first one is due to radiative recombination. Both continuum and line photons can be produced in such a recombination event as the electron passes from the free state into the upper bound levels of the ion and then cascades down to form a ground state ion. The other effect involved in continuum radiation is called Bremsstrahlung. This effect is related to free-free transitions corresponding to the loss of kinetic energy by an electron in the field of an ion. The electron loses energy in the deceleration process when it

travels into the field of the ion, emitting photons in different wavelengths, depending of its initial energy and the loss of this energy. Continuum emission can hide atomic emission peaks; thus this effect should be avoided.^[7]

Environment

The plasma size, propagation speed, energy, and emission properties are related to the ambient gas into which the plasma expands. The ambient gas can help or prevents the plasma shielding. For example, the gas can shield the sample from the laser beam if a gas breakdown occurs before sample vaporization. These undesirable effects are less important for gases and aerosols, but they can be important for solid samples.

Gas pressure will influence plasma expansion. Low pressures increase energy losses and uniformity of the plasma energy distribution. In addition, different gases have different behaviours at different pressures.^[7]

LIBS APPLICATION

LIBS is useful in a wide range of fields, namely, those which can benefit from a quick chemical analysis at the atomic level, without sample preparation, or even in the field.^[7]

1 LIBS in Archeology and Cultural Heritage

Samples with archaeological or cultural value are sometimes difficult to analyse. These samples cannot usually be moved or destroyed for analysis, and some chemical techniques to prepare the sample or a controlled environment in a laboratory are needed. In the first place, portable LIBS devices can be used, solving the problem when the sample cannot be moved. In the second place, LIBS does not need contact to analyse the sample, avoiding damage in valuable samples. Although LIBS ablates an amount of the sample, the crater is nearly microscopic and practically invisible to the eye. In addition, this microscopic ablated surface improves the spatial resolution, providing accurate spatial analysis and even a depth profile analysis of the sample. The sample does not need to be prepared; hence the analysis is clean and fast. Besides, LIBS probes based on optical fibres allow the analysis of samples with difficult access. Despite these facts, LIBS is a micro destructive technique and the researcher should pay attention to experimental parameters in order to avoid critical damage in valuable samples. Many cultural heritage artefacts can be analysed with the right LIBS set-up. LIBS is feasible with virtually all types of materials, for instance ceramics, marble, bones, or metals, usually applying quantitative analysis. The most common analysis attempts to determine the elemental composition of the sample in order to help to date it, but it works with bones for analysis of paleo diet. LIBS has been used with delicate samples such as Roman coins or other metallic alloys like bronze, even under water. In the field of painting, it can determine the elements that compose the pigments. This analysis of pigments can help to date and authenticate frescos or paintings. Moreover, LIBS can be used, combined with other techniques, in order to sum the potential of them, such as Raman or X-ray fluorescence (XRF).^[8]

2 LIBS in Biomedical Applications

Biomedicine and LIBS are fields that have not been working together for long. For that reason, this field may provide a large number of new developments in a few years. LIBS can analyse chemical compositions of biological samples such as human bones, tissues, and fluids. LIBS can help to detect excess or deficiency of minerals in tissue, teeth, nails, or bones, as well as toxic elements. In the same way, cancer detection is possible with LIBS and it can provide a surgical device which can detect and destroy tumour cells at the same time. In

addition, classification of pathogenic bacteria or virus is possible too. The analysis of samples from plants is difficult, because they need a difficult preparation of the sample based on acid digestion processes in order to obtain accurate analysis of micronutrients. LIBS can provide a fast analysis tool with easy sample preparation, for instance in micronutrient analysis of leaves.^[9]

3 LIBS in Industry

LIBS has been targeting many industrial processes for many years, because it is a fast analytical tool well suited to controlling some manufacturing process. Moreover, LIBS can work at a large range of distances, allowing analysis of samples in hazardous and harsh environments. For example, remote detection of explosives has been assessed with LIBS, even at trace levels. In the nuclear energy industry, the effects of radiation on living beings and devices are widely known. LIBS can work far away from nuclear waste or reactors, using stand-off configuration or with fibre optic probes, avoiding dangerous radiation levels. In the metallurgical industry, smelters, and final products can reach high temperatures, and LIBS can analyse the alloy compositions in production line or detect impurities in other production sectors, such as the automotive industries. LIBS can also be useful to detect toxic products like heavy metals in industrial wastes. These waste products should be recycled or stored, and knowing the elements in them can provide key data to reduce the environmental impact of the process. In the renewable energy field, analysis and detection of impurities in solar cells can be a useful tool to improve the manufacturing processes or to achieve high efficiency solar panels. There are recent research works in this field although there is a huge amount of work to do. ISRN Spectroscopy.^[10]

4 LIBS and Geological Samples

Towards Extra-terrestrial Limits. Analysis of some kinds of minerals is possible using LIBS, in particular, of soils and geological samples in situ. Sample features can strongly affect the experimental conditions and reduce the accuracy, but quantitative analysis is still possible. LIBS analysis can detect traces of toxic material in soils, rocks, or water without sample preparation and in the natural environment of the sample. LIBS can work in a wide range of environmental conditions and with different atmospheres, from air to vacuum. This feature, coupled with the capability to analyse soil samples and the possibility to build a portable set-up, enables the possibility to work in the space. Recently, a spacecraft has been launched to Mars to provide spectral analysis of Mars, geological samples. This spacecraft contains, among other things, a hybrid LIBS-Raman spectrometer.^[11]

LIBS CHALLENGES

Probably, the main challenge that LIBS needs to address is its recognition as a standard in chemical quantitative analysis. Calibration-free algorithms offer a good approximation to this goal, but the results are not perfect yet. There are different research lines with the goal of a standard quantitative analysis, attempting to improve the calibration-free algorithm or add new capabilities to it. There are recent works based on spectral normalization to improve the final result or to detect the elements in the sample automatically. This goal may be the most important and could place LIBS definitively among the most widely used spectrochemical techniques.^[12]

In order to widen its use in real applications, new advanced and cost-effective instrumentation is required. Currently, a cumbersome and expensive set-up is needed to achieve accurate analysis, and work is in progress to reduce the size and complexity of LIBS set-ups. A recent (“hyphenated”) approach combines LIBS with other spectrochemical techniques in order to

unite the features of them. The Mars Science Laboratory (MSL) is a good example of this because it is a hybrid LIBS-Raman system.^[12]

Advances in new techniques and approaches for LIBS analysis, such as optical catapulting and molecular LIBS are being explored. Optical catapulting LIBS (OC-LIBS) uses a pulsed laser below the plasma threshold energy on the sample surface to create a solid aerosol which is analysed with LIBS. Molecular LIBS, on the other hand, analyses the emission of molecules resulting from sample ablation or from the recombination between target elements and ambient air. LIBS can improve its performance with this ability and so enable the analysis of organic samples.^[12]

CONCLUSIONS

LIBS is a useful spectrochemical technique that can provide chemical analysis in situ without sample preparation, in a quasinondestructive way, which can be used in a wide range of environments. Nevertheless, advances in key optical components, pre-processing, and post processing algorithms in LIBS are essential to go beyond the spectral signatures. Therefore, additional research effort is required to meet the aforementioned challenges and to obtain useful, cost-effective, portable LIBS instrumentation.

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REFERENCES

- 1 DAVID A. CREMERS AND LEON J RADZIEMSKI, Handbook of Laser Induced Breakdown Spectroscopy, pp:23-96.
- 2 https://en.wikipedia.org/wiki/Laser-induced_breakdown_spectroscopy#cite_ref-isbn0-470-09299-8_1-0
- 3 JAGDISH P SINGH, SURYA N. THAKUR, Laser Induced Breakdown Spectroscopy, Second edition, pp: 3-101
- 4 SERGIO MUSAZZI, UMBERTO PERINI, Laser Induced Breakdown Spectroscopy theory and applications, pp: 169-550.
- 5 <https://appliedspectra.com/technology/libis.html>
- 6 REINHARD NOLL, Laser Induced Breakdown Spectroscopy fundamentals and applications, pp:7-15.
- 7 F. ANABITARTE, A. COBO AND J.M. LOPEZ –HINGUERA, Laser-Induced Breakdown Spectroscopy: Fundamental, Applications and Challenges, International Scholarly Research Notices, 2012:1-12.
- 8 L. FORNARINI, F. COLAO, R. FANTONI, V. LAZIC, and V. SPIZZICCHINO, “Calibration analysis of bronze samples by nanosecond laser induced breakdown

- spectroscopy: a theoretical and experimental approach,” *Spectrochimica Acta Part B*, vol. 60, no. 7-8, pp. 1186–1201, 2005.
- 9 M. A. KASEM, R. E. Russo, and M. A. HARITH, “Influence of biological degradation and environmental effects on the interpretation of archeological bone samples with laser-induced breakdown spectroscopy,” *Journal of Analytical Atomic Spectrometry*, vol. 26, no. 9, pp. 1733–1739, 2011.
 - 10 V. LAZIC, A. PALUCCI, S. JOVICEVIC, M. CARAPANESE, C. Poggi, and E. BUONO, “Detection of explosives at trace levels by Laser Induced Breakdown Spectroscopy (LIBS),” in *Chemical, Biological, Radiological, Nuclear, and Explosives (CBRNE) Sensing XI*, vol. 7665 of *Proceedings of SPIE*, April 2010.
 - 11 J. M. ANZANO, M. A. VILLORIA, A. RUIZ-Medina, and R. J. LASHERAS, “Laser-induced breakdown spectroscopy for quantitative spectrochemical analysis of geological materials: effects of the matrix and simultaneous determination,” *Analytical Chemical Act*, vol. 575, no. 2, pp. 230–235, 2006.
 - 12 S. Rai and A. K. Rai, “Characterization of organic materials by LIBS for exploration of correlation between molecular and elemental LIBS signals,” *AIP Advances*, vol. 1, no. 4, Article ID 042103, 11 pages, 2011.