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Laser induced breakdown spectroscopy; advances in resolution and portability

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Sumario. La espectroscopia de plasma inducido por láser (LIBS) puede ser considerada como una de las técnicas más dinámicas y prometedoras en el campo de la espectroscopia analítica. LIBS se ha convertido en una poderosa alternativa en aplicaciones desde la exploración geológica hasta la inspección industrial, incluido el monitoreo medioambiental, el análisis biomédico, el estudio de obras patrimoniales, la seguridad y defensa, entre otros. Los avances en la instrumentación LIBS han permitido mejorar progresivamente los servicios y calidad de análisis, sobre la base de un mejor conocimiento de los principios de la tecnología. Recientemente, los sistemas de doble pulso han facilitado una mejor dosificación de la energía, la mejora de la relación señal-ruido y el estudio de las diferentes etapas del proceso. Los nuevos avances como sistemas multi-pulsos entre otros, aun por explorar, deben ofrecer nueva información para avanzar en este conocimiento. Por último, lo que hace a esta tecnología ser realmente atractiva, es la aptitud para ser empleada en condiciones de campo, o para la detección de la composición elemental a largas distancias. En esta presentación se discuten los diseños de una instrumentación portátil, compacta y de bajo costo, que puede mejorar sustancialmente las posibilidades de LIBS.

Abstract. Laser Induced Breakdown Spectroscopy (LIBS), can be considered as one of the most dynamic and promising technique in the field of analytical spectroscopy. LIBS has turned into a powerful alternative for a wide front of applications, from the geological exploration to the industrial inspection, including the environmental monitoring, the biomedical analysis, the study of patrimonial works, the safety and defense. The advances in LIBS instrumentation have allowed improving gradually the analysis services and quality, on the basis of a better knowledge of the technology principles. Recently, systems of double pulse have facilitated a better dosing of energy, the improvement of the signal-noise relation and the study of the different process stages. Femtosecond lasers offers the possibility of study in detail the ablation and atomic emission processes. New advances like multi-pulse or multi-wavelentgh systems -in fact stilling without exploring, must offer new information to advance in this knowledge. Finally, which it does to this technology really attractive, is the aptitude to be employed in field conditions, or for the detection of the elementary composition at long distances. In this presentation there are discussed the designs of portable instrumentation, compact and low cost, which can improve substantially the LIBS possibilities.

Keywords. Laser ablation 79.20.Eb, laser spectroscopy 42.62.Fi, breakdown 51.50.+v, 52.80.-s, 77.22.Jp

1 Introduction

The Laser Induced Breakdown Spectroscopy (LIBS), is a technique that has been firmly established for the rapid determination of the elemental composition[1]. It relies on material ablation by using a short duration laser pulse with high density energy enough to produce plasma. By analyzing the light emitted by the plasma, it is possible to determine the elemental composition of practically any material. This technique has significant advantages over other conventional analytical techniques[2-4]. For example, requires no sample preparation, may be performed in solid, liquid or gas phase in samples with any shape or dimension. Moreover, it allows an in-depth study in order to characterize the composition of multicomponent material[5, 6]. It is especially suitable for field work by offering the possibility of real-time analysis with high portability. Thanks the above mentioned advantages, the LIBS technique has experienced strong growth, which is reflected in a large and growing number of publications.

LIBS is not a new technique: firsts laser-induced breakdown studies go back to the early 1960s and important application studies date from the 1980s with the work of Radziemski[7]. A comprehensive review of LIBS development and applications through the mid-1990s was produced by Rusak et al.[3].

The technique has many attributes that make it an attractive tool for chemical analysis, particularly as regards its potential as a field-portable sensor for geochemical analysis. LIBS is relatively simple and straightforward, so skilled analysts are not required. Little to no sample preparation is required, which eliminates the possibility of adulteration of the sample through improper handling or storage or cross-contamination during sample preparation. LIBS provides a real-time response and simultaneous multi-element detection and analysis. The laser plasma is formed over a very limited spatial area, so that only a very small amount of sample (picograms to nanograms) is engaged in each laser micro-plasma event. All components of the instrument can be made small and rugged for field use and LIBS sensors can be operated either as a point sensor or in a standoff detection mode. The detection limits of LIBS are in the low hundreds to tens of ppm range for most common elements, so field-portable LIBS should be capable of field surveying and screening for the geochemical exploration and environmental remediation applications envisaged.

The existing equipment on the market used predominantly solid-state lasers based on Nd:YAG crystals. This is because this type of lasers, in addition to the advantages of robustness and compactness; allow obtaining very short pulses with high power density. To ensure the appropriate parameters, it works in the so-called Q: Switch regime. In this mode of operation, is introduced into the laser cavity an optical shutter based on a crystal whose transmittance is electrically switched, allowing the production of single-pulse of several nanoseconds in duration and very high intensity. In the last years several works have reported an improvement of plasma intensity, and therefore the limits and quality of detection, using systems that generate two consecutive pulses, delivered from one or two synchronized lasers[8]. Recently, it was reported a system with dual crystal modulator by using two LiF crystals[9]. While this system improved the signal-noise relation and the intensity of the plasma emission, has the disadvantage associated with the gradual degradation of these crystals[10].

In our study we propose a new low cost LIBS system, which uses passively Q:Switched Nd:YAG laser by using as optical switch Cr:YAG crystal. This design allows obtaining high intensity laser plasma using a very compact and low cost device, where the switching element is extremely simple and durable.

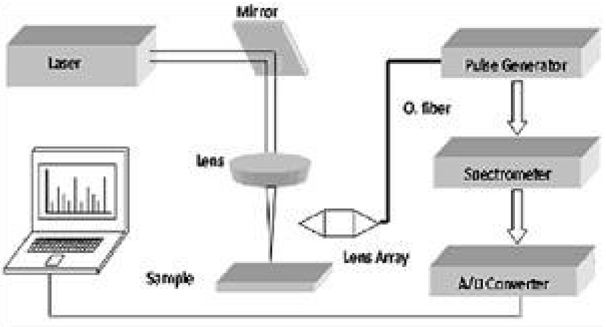

Figure 1. Schematic of experimental setup

2 A low cost and portable LIBS device description

Figure 1 shows an outline of the experimental setup. A Nd:YAG laser emitting at 1064 nm, produces pulses with energy adjustable up to 0.9 J. The active element is a 6 x 60 mm Nd:YAG rod, pumped by a xenon lamp. It uses a Q:Switch consisting of a Cr:YAG crystal with 6 mm in diameter and 3 mm in thick. The light emitted by laser is focused through a 5 mm focal length lens. The distance between the lens and the surface of the sample was 8.5 cm to achieve an area of 0.19 cm^2. For the experimental conditions used, this means a yield of 4.7 J/cm^2. The sample is placed on metallic base ensuring that the sample surface is located at the focal point.

An optical system coupled with the entry of optical quartz fiber, whose entry can be moved respect to the sample surface. By this way it is possible to capture the emission from a specific region of the plasma.

The spectrometer used in our configuration was an USB4000 Ocean Optics, with 350 nm to 900 nm spectral range and 0.2 nm resolution. The spectra were processed in computer by using Spectra Suite software.

2.1 Nd:YAG laser with passive Q:Switch

In the laser head of our device the pump radiation is produced by xenon pulse lamp. The light from this lamp is concentrated on the active medium of Nd:YAG through an special reflector made from monolithic quartz with external metallic coating. The quartz block is doped with atomic Ce at 1 % doping level. This feature avoids the optical damage of the active medium due the ultraviolet light emitted by xenon lamp. On the other hand, the conversion of UV to visible radiation contributes to enhance the absorption of pump light in laser crystal and, in consequence, the laser efficiency.

For obtaining a compact device, the resonator mirrors of 99,8% and 50 % reflectance respectively, were placed at 1.5 cm form the rod ends. The rod dimensions are 5 x 50 mm. As a Q:Switch element a YAG:Cr crystal with dimensions 6 mm in diameter and 3 mm thick was used. The initial transmittance of Q:Switch was 21 % for 1064 nm wavelength.

For this configuration, the laser can produce a train of pulses with duration for each pulse of about 20 ns, separated by 10 µs interval, with a total duration of the pulse train about 700 µs. In figure 2 the acquired signal of laser pulse for passive Q:Switched laser is showed.

All system elements are mounted on a stereomicroscope in order to obtain better facility for positioning and observation of samples as well as to follow the results of irradiation. The dimensions and weight of LIBS device is 40 x 20 x 15 cm and 5 kg respectively. Figure 3 shows a photograph of device, called MicroLIBS.

3 Results and discussion

The use of LIBS as an analytical tool depends on three underlying assumptions: (i) that material ablation is stoichiometric so that the composition of the plasma generated is fully representative of the sample composition; (ii) that an optically thin plasma is generated so that emission from the central high-temperature portion of the plasma plume is not reabsorbed in the colder plasma boundary region; and (iii) the plasma is in local thermodynamic equilibrium. These conditions have been verified by Chan & Russo[11] and Corsi *et al.*[12] and it is understood how to realize these conditions analytically.

The use of LIBS for elemental detection is simple and readily accomplished via peak matching against a spectral library constructed in advance for a specific application. For this type of application, which can be accomplished through statistical analysis of LIBS spectra[13], it is only relative peak intensities and overall spectral shape that is important, not absolute peak intensities. Quantitative LIBS analysis of specific elements in natural materials is significantly more difficult because of the broad issue known as "matrix effects". This is an observed dependence of the intensity of the LIBS emission response to the nature of the material analysed[14], which manifests as variations in laser-target coupling and resultant plasma intensity variations. These two facets of the sample, which are generally lumped together as "matrix effects"[12], will determine LIBS signal reproducibility, namely sample composition and sample surface character.

3.1 Multi-pulse excitation

An important approach for enhance the detection limits and the signal-noise relation was developed in Laboratory of Laser Technology (LTL) at IMRE-Havana University, and consist in the use of multi-pulse scheme in order to perform the plasma formation-excitation process. In order to establish a comparison, it was used an electro-optically Q:Switched Nd:YAG laser with similar parameters with the passively Q:Switched laboratory-made device. In the first case, the laser pulse energy of 0.14 J was focused on an area of 1 mm diameter, thus obtaining a fluency of 4.6 J/cm^2, similar to that used in the passively Q:Switched laser.

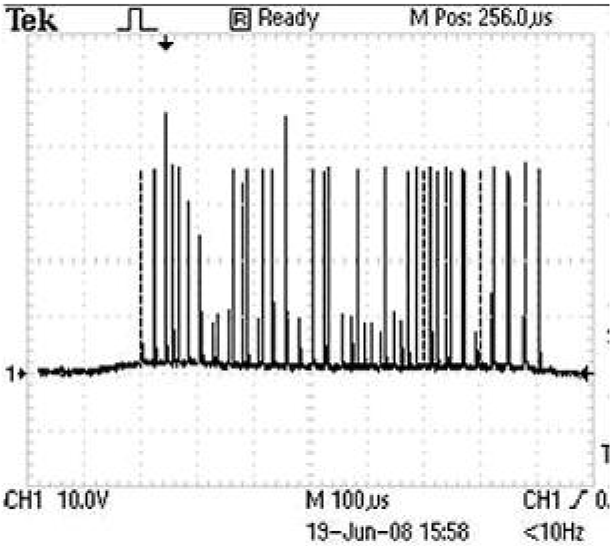

Figure 2. Schematic of pulse train obtained with passive Q:Switch.

Figure 3. Photograph of MicroLIBS system

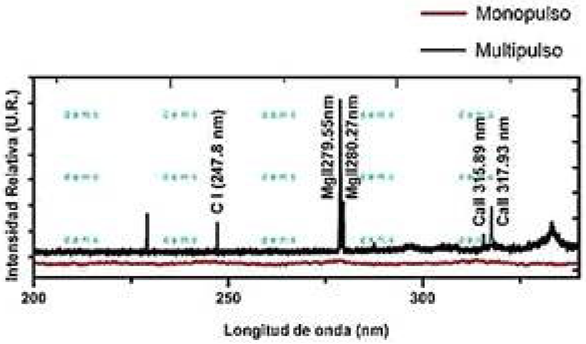

Figure 4. LIBS spectra captured by using multipulse (above) and single-pulse (below) configurations.

The only experimental difference: Pulse duration of 20 ns in single pulse configuration and 700 μs total duration for the multi-pulse configuration. In figure 4 are observed an example of spectra captured for both lasers. The spectra chosen to illustrate the comparison were collected form Prickly Pears spines. As can be seen, are clearly identified several peaks associated with the CaII, MgII and CI. These peaks, like the rest of the spectrum, have higher intensity and better signal-noise relation for a train of pulses configuration.

These results can be explained through a several steps process[10]. Initially, the absorption occurs in the first laser pulse at the sample surface, with the consequent overheating above the melting point. This causes the explosive material ablation, his rupture and rapid heating of the surrounding atmosphere, and a strong electronic emission. The steam flow expands and produces a shock wave, which in its motion dragging behind an area of low pressure. The initial pressure is restored after about 100 μs, as estimated experimentally[15].

By influencing subsequent pulses, separated from each other by a few tens of microseconds, the conditions for these interactions are the same as the first except for the presence of the above mentioned area of low pressure and a broadcast electronics (noise), much lower, because at that time the flow of electrons has disappeared. Moreover, the highest line intensity for multipulse regime can be explained by the additional excitation pulses produced in the steam of initially ejected material. Thus, the use of pulse trains by using passive Q:Switch, produce higher emission intensities and betters signal noise rate.

3.2 Free-running excitation

Typically, the LIBS technique is performed using Q:Switched lasers with high power pulses (megawatt range), produced with time durations in nanosecond range. As far as we know, no LIBS experiments were performed by using free-running regime until the recent reports of LIBS in Prickly Pear[16], because the low energy density for this mode of laser operation. However, in the mentioned report, due to the strong absorption in areoles, an intense plasma emission takes place even for microsecond range in pulse duration with kilowatts/cm^2 range of laser fluency. As we demonstrated, this allows to use in our experiments not only a Q:Switched laser but also a free running low cost Nd:YAG laser regime. The experiments in free-running regime have a great practical interest because at this regime is possible to obtain a higher productivity in spines elimination. On the other hand, the laser operating at this regime is less expensive and the operation cost is lower.

At present, the LTL research group is working of high energy and long pulse LIBS excitation, performed at millisecond pulse time duration. The special interest of this exotic conditions in plasma generation, is explained by two reasons: The possibility of simulation of some natural events like interstellar jets or atmospheric thunders from one side, and, the on-line monitoring of several industrial applications in millisecond range as hole perforation or pulse welding from the other side.

In principle, as lower pulse duration them better resolution can be obtained, if we taking in to account the fact that typically with shorter pulse duration avoid higher power densities and better plasma ionization level. I also important the fact that the plasma life is extended no more than several microseconds, and, in consequence, if the pulse duration is longer, them the interaction with subsequent excitation must be taken in consideration in the LIBS spectra interpretation. As an example of line-width behaviour for different pulse duration, LIBS spectra captured on metal sample are showed in figure 5.

3.3 Field applications

An exciting example of our LIBS device is the on-line elemental determination for laser de-thorning process. In this new application a Nd:YAG laser is used for selective ablation of thorns of cactus called opuntia. In figure 6, is showed a deep-profile LIBS measurement of thorn-cortex systems illustrating the behavior of Na(I) 589.5 nm line and C-H band.

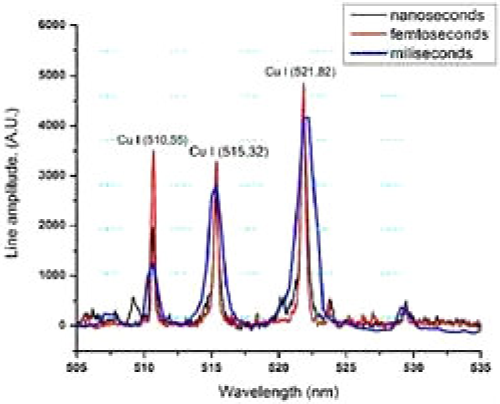

Figure 5. LIBS spectra obtained from Cu sample.

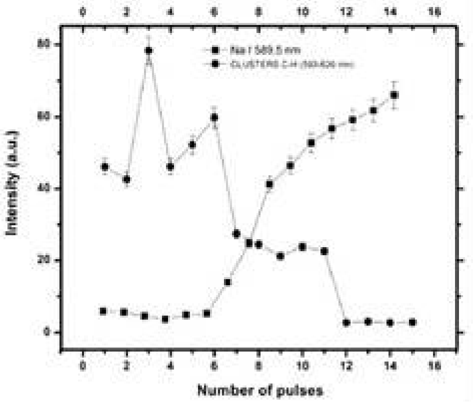

Figure 6. Intensity profile curves Na I (589.5 nm) y emission band of the C-H clusters

These curves shows that LIBS technique contribute to control the spine elimination process: For C-H line the relative intensity reach the maximal value after two or three pulses and decrease gradually until the full thorn elimination reaching in this moment a fixed value that correspond to lower percent of C-H concentration in cortex. In opposite direction, the Na line intensity grows gradually reaching a higher level simultaneously with C-H decrease. The high concentration of Na in cortex is reached after spine elimination precisely when the inner part of cactus is to be ablated.

On the other hand, it is another important difference between the two curves showed in figure 5. While the Na pike dependence versus number of pulses growth continuously, the C-H dependence shows periodical changes. It's remarkable that similar variations were detected in previous work[16] by photo-acoustic technique when the signal intensity versus number of pulses was measured. In principle, these changes can be attributed to periodical character of combustion process in laser dethorning, consisting in several stages combustion-ablation: While the first pulse prepare the surface making it darker by combustion , the second pulse irradiate a surface with strong absorption and ablate it at very high rate.

4 Conclusions

Recent technological advances are leading to the development of fully field-portable LIBS systems as show MicroLIBS, the compact, portable and low cost LIBS device developed by IMRE-Havana University. The use of Cr:YAG crystal as Q:Switch element allows simplifying the design and reducing costs as compared to electro-optical Q:Switch and also to guarantee more duration that LiF elements. The application of pulse trains as an excitation source helps to achieve a higher intensity of plasma emission and a substantial improvement in the signal-to-noise ratio compared with single-pulse systems.

The advances in modification of laser parameters open new applications no limited to elemental determination but also covering the laser material processing on-line monitoring or the simulation of specific plasma events in wide range of energies or pulse durations.

Finally, the LIBS technique is shown to be a suitable method for new industrial processes as was demonstrated for the case of opuntia de-thorning technology. Additionally, the approach of complex band emission pattern recognition can be used for determining of contamination problems in such vegetable food.

Acknowledgments

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