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ELEMENTAL ANALYSIS BY LASER INDUCED BREAKDOWN SPECTROSCOPY FOR AQUEOUS SOLUTIONS

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ABSTRACT: Laser Induced Breakdown Spectroscopy (L.I.B.S.) is a technique that offers the prospect of on-line and in-situ monitoring of multi-elements in water. In this way, there are two research axes: research on improving the limit of detection (LOD) by optimizing different experimental parameters and a similar emphasis of research on characterizing a commercially viable optimum sample presentation configuration. The purpose of this work is to compare between two sample configurations; jet and bulk configurations, and to demonstrate that by a proper optimization of the experimental set-up in terms of laser pulse and sample delivery characteristics, time-, spatially-, and spectrally-resolved detection system, a real time quantitative determination of trace element concentrations in water by L.I.B.S. becomes feasible.

KEYWORDS: L.I.B.S., analysis of water, limit of detection, atomic spectroscopy

1. Introduction

Laser-induced breakdown spectroscopy (LIBS), also known as laser-induced plasma spectroscopy (LIPS), is an optical diagnostic technique which can provide on-line process analysis of the concentration of various atomic and molecular species in test media.

In LIBS, a small volume of the target is intensely heated by the focused beam of a pulsed laser, and thus brought to a transient plasma state where the sample's components are essentially reduced to individual atoms. In a high-temperature plasma, atoms are ionized, or brought to excited states. Such states decay by emission of radiation, which is observed in the ultraviolet (UV), visible and near-infrared (NIR) regions of the spectrum. An atomic spectrum is obtained by means of a spectrograph, thereby allowing elemental components of the target to be identified and, using a calibration curve, quantified. LIBS measurements are generally carried out in ambient air at atmospheric pressure. For this reason, and also due to its rapidity, non-contact optical nature, and absence of sample preparation, LIBS is particularly suited for at-line or on-line measurements in industrial settings, as well as in the laboratory[1-3]. Recently, there is a growing interest and publications in LIBS applications for liquid samples[4-6]. To overcome the problems associated with plasmas generated from liquid samples, a variety of LIBS configurations have been applied in experiments on liquids, including plasma formation on the surface, in the bulk liquid[4], and on liquid jet[5-6]. In our laboratory, we used two last configurations (bulk and liquid jet). In this work, we compare the two configurations. The aqueous solution was prepared by solvating NaCl in de-ionized water and at different concentrations 10, 1, 0.5, 0.1, 0.05, 0.01 and 0.005 g/L.

2. Experimental set-up

The experimental set-up, shown in figure 1, consists on Q-switched Nd: YAG (Quantel) at 1064 nm with a repetition rate that can be varied from 1 to 20 Hz and pulse duration of 15 ns. In order to create the plasma in the water solution, the output laser energy employed for these

measurements has been varied from 20 to 250 mJ. Using a prism and a 50 mm focus lens the laser beam is directed and focalized on the liquid target. Two plano-convex lenses were used to couple the LIBS signal to the entrance of optical fiber. The diameter of the fiber core is of 100 μm. the exit end of the optical fiber is coupled to an optical spectrograph (ACTON 750) equipped with 1800 l/mm holographic grating. A 1024 × 256 element intensified charge coupled device (ICCD) (Princeton applied research) was attached to the exit of the spectrograph and used to detect the light from the laser spark. The detector was operated in gated mode using a high voltage pulse generator and was synchronized to the laser output. Data acquisition and analysis were performed using WinSpec program. In this we have compare two experimental setups for solution measurement (see Figure 1). The solutions used in the study were prepared by diluting NaCl in de-ionized water. In the first experiment, the sample solution was kept in a small beaker, and the laser beam was focalized in the bulk at a depth of 1 cm. In the second experiment, a liquid jet system was assembled to provide a stable solution jet. The liquid sample in a bottle was pumped; it produced a steady jet of 3 mm diameter. The laser beam was focused from the direction perpendicular to the liquid jet.
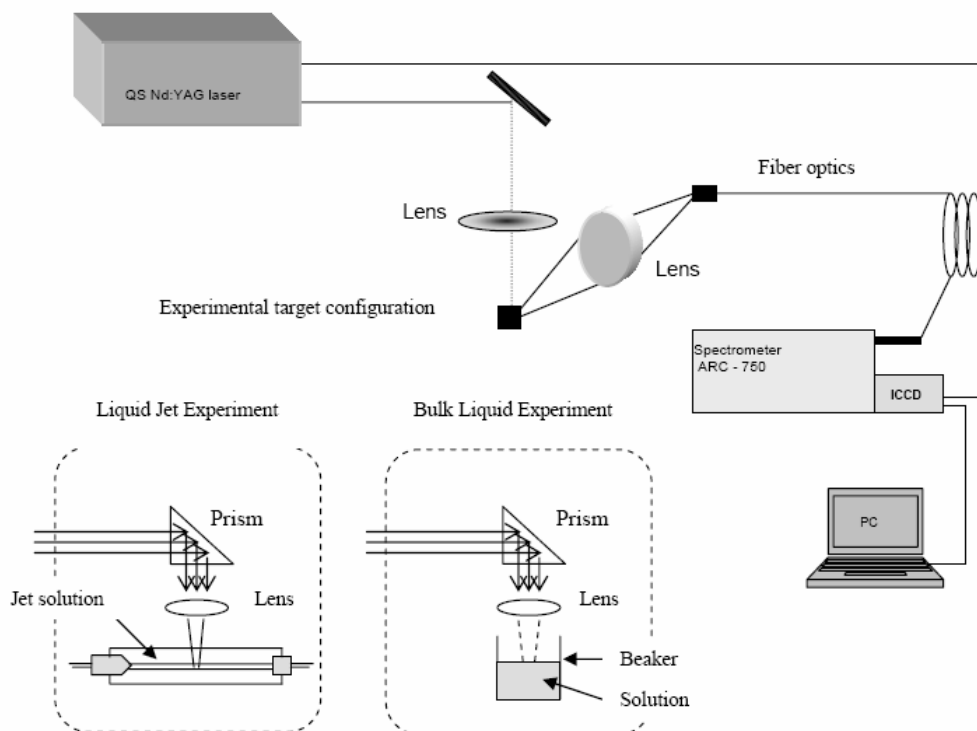

Figure 1: Experimental set-up

3. Results and discussion

Different solutions of NaCl were prepared at different concentrations.
The most experimental parameters which can affect detection limits are laser frequency, gate delay time, gate width and laser energy. These parameters were studied for measurements in both bulk liquid and liquid jet, in order to compare the two target configurations.

3. 1. Bulk liquid configuration

Firstly, we performed a series of measurements to find the optimum time delay from the laser pulse and the beginning of the LIBS spectra acquisition, as well as the optimum gate duration. The importance of optimizing these two parameters is to avoid the continuum emission and to collect the highest signal to noise ratio.

The optimum gate delay and width for Sodium lines (Na I at 589 and 589.6 nm²) were 2.5 µs and 0.5 µs respectively.

3. 1. 1. Laser frequency

In order to optimize the value of the laser frequency, we followed the evolution of the intensity of emission of the lines of the Sodium versus to the laser frequency at various NaCl concentrations. As an indication and at Figure 1, we present the 3D (three-dimensional) results obtained at a concentration of 0.1 g/L.
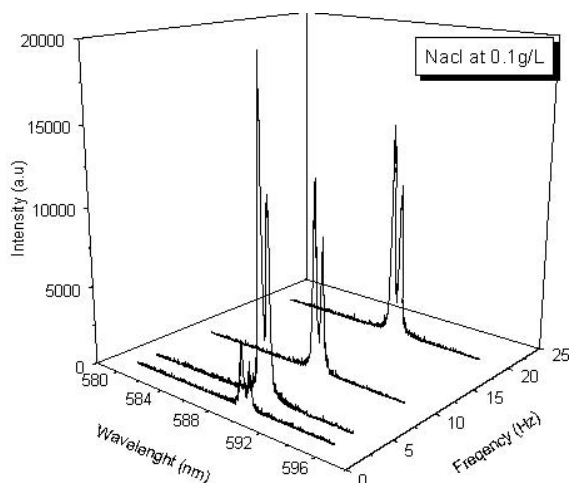
Figure 2: Evolution of the intensity of Na lines at a NaCl concentration of 0.1 g/L

From this study we have noticed that the maximum of intensity of emission of the Sodium doublet is recorded at 4 Hz that we took as optimum of laser frequency.

3. 1. 2. Laser energy

According to deposited laser energy, we followed the evolution of the intensity of emission of the sodium doublet at a laser frequency of 4 Hz and at various NaCl concentrations.
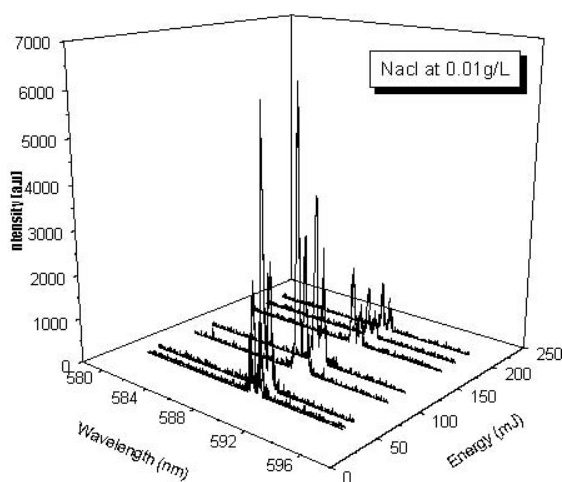
Figure 3: Three dimension evolution of the Na lines intensities according to deposited laser energy, C=0.01 g/L

From the three dimension curve; (3D evolution of the Na line intensities versus energy) we have deduced the maximum of the intensity of emission of the two lines of Sodium according to laser energy and at the different concentrations (Figure 4).
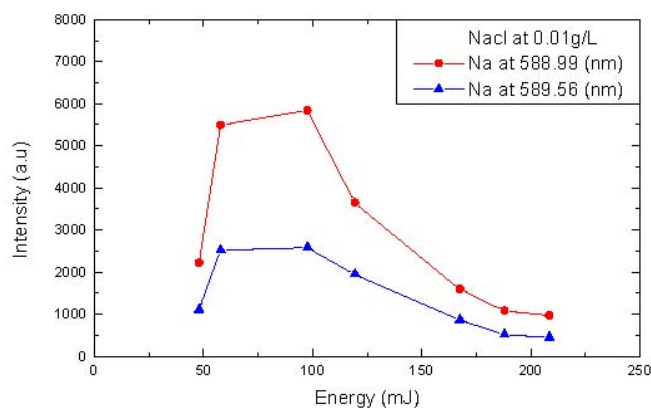

Figure 4: Evolution of the intensity of emission according to laser energy deposited, C=0.01 g/L

Through these curves we notice that the intensity of emission increases quickly according to laser energy up to an optimal value, or in a more correct way until an optimal range, and then it decreases. These optimal ranges vary according to the concentration of the solution. The intersections of these optimal ranges help us to deduce the value from the working laser energy. At this value of energy we can follow the evolution of the intensity of emission according to the concentration. We can say that this optimum in energy is a value which corresponds to the maximum of intensity of emission of the line at a small NaCl concentration.

3. 2. Jet liquid configuration

At the same experimental conditions; laser frequency and characteristics times (gate and delay width) of detection, we followed the evolution of the intensity of emission of the two lines of Sodium according to laser energy at two NaCl concentrations. At Figure 5 we present the evolution of the signal ratio on background noise of the two lines of Sodium according to laser energy at 0.5 g/L NaCl concentration.
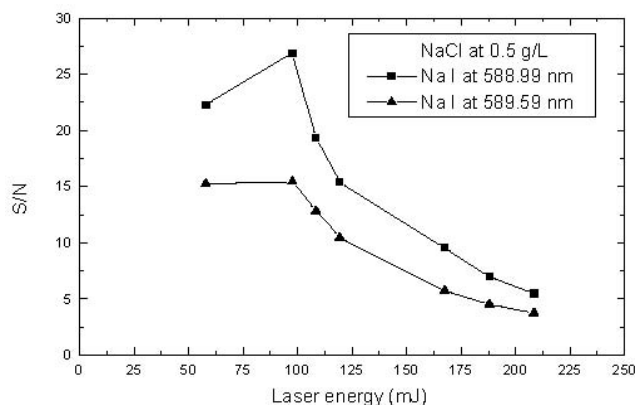

Figure 5: Evolution of the signal to noise ratio versus the deposited laser energy at NaCl concentration of C=0.5 g/L

We notice that the optimal value of laser energy is 100 mJ at 0.5 g/L NaCl concentration, and it is 60 mJ at 10 g/L. The optimum of laser energy decreases when the concentration of the solution increases. That can be explained by the increase of Sodium (Na) density.

4. Conclusion

Comparing between some emission spectra of the Sodium doublet in the two configurations bulk and jet excitation, we see that in addition to the bad resolution, the widths of the recorded lines in bulk are more important than those in the jet configuration and the excitation in jet configuration gives highest sensitivity more than in the bulk excitation. Using the bulk target configuration and Sodium chloride as solution, we encountered the problem of the bad resolution of the lines of the sodium doublet for the concentrations more than 1 g/L. We notice that the main problem in the application of LIBS in liquid media is the sensitivity comparing to the solid target. This fact is due to the water splash and consequent contamination of optical surface.

References
[1] J. D. Wu and N. H. Cheung, Applied Spectroscopy, **Vol 55**, N° 3, (2001).
[2] F. Colao, R. Fantoni, V. Lazic, A. Morone, A. Santagata and A. Girdini, Appl. Phys. **A 00**, (2004).
[3] Marwa A. Ismail, Hisham Imam, Asmaa Elhassan, Walid T. Youniss and Mohamed A. Harith, J. Anal. Spectrom, **19**, (2004).
[4] A. De Giacomo, M. Dell'Aglio and O. De Pascale, Appl. Phys. **A 79**, 1035, (2004)
[5] C. W. Ng, W. F. Ho and N. H. Cheung, Applied Spectroscopy, Vol **51**, N° 7, (1997).
[6] Sergy B. Mirov, Robert E. Pitt, Alex Dergachev, Wonwoo Lee, Dmirti V. Martyshin, Olga D. Mirov Jeremy, J. Randolph, Lawrence J. DeLucas, Christie G. Brouillette, Tasoltan T. Basiev, Yuri V. Orlovskii, Olimkhon K. Alimov, Soc of photo-Opt-Instrumentation-Engineers (SPIE). **Vol.3855**. 34 September (1999).