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# Compositional analysis of aqueous solutions by laser-induced plasma spectroscopy

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Laser-induced plasma (LIP) was generated on the surface of an aqueous solution using a single pulse of the fundamental and second harmonic from a Q-switched Nd:YAG laser. Aqueous Ca, K, Mg, Na and Sr solutions were used to observe the presence of these elements in the plasma through the emission of their atomic species. In order to obtain the spectra of the aqueous solutions, we used a charge-coupled camera (CCD) in combination with a compact spectrometer. We also determined laser-induced plasma temperatures at 1064 and 532 nm with Boltzmann plots of hydrogen lines (656.28, 486.13 and 434.05 nm).

**Keywords:** Laser-induced plasma; plasma temperature; Boltzmann plots; atomic emission spectroscopy.

En este trabajo hemos generado un plasma inducido por láser sobre la superficie de una solución acuosa usando como fuente de excitación e ionización el primero y segundo armónicos de un láser de Nd:YAG. Se han preparado soluciones acuosas de los elementos Ca, K, Mg, Na y Sr con el fin de observar en el plasma las líneas espectrales emitidas por sus especies atómicas. Para obtener los espectros de las diferentes soluciones estudiadas aquí, hemos empleado un espectrómetro compacto en combinación con una cámara CCD. También, hemos utilizado gráfica de Boltzmann en las líneas de hidrógeno para determinar la temperatura del plasma.

**Descriptores:** Plasma inducido por láser; diagnósticos de plasmas; espectroscopia de emisión atómica; gráfica de Boltzmann.

PACS: 52.25.-b; 52.25.Os; 52.38.Mf; 32.30.-r; 32.80.-t

## 1. Introduction

Laser-Induced Plasma Spectroscopy (LIPS or LIBS) is an alternative elemental study technology based on the optical emission spectra of the plasma produced by the interaction of a high-power laser with gas, solid and liquid. The increasing popularity of this technique is due to the ease of the experimental set-up and to the wide flexibility in the investigated material that does not need any pre-treatment of the sample before analysis. This peculiarity makes LIPS adaptable to automation [1] and remote sensing [2]. The LIPS technique has been generally applied for solid sample analysis for application in environmental and industrial processes, monitoring heavy metals or on-line process control [3-5]. In gases, LIPS has been used to study physical parameters [6-11] of plasma such as temperature, electron densities, temporal evolution, etc. The detection of gaseous elements such as chlorine and fluorine, mercury, and hydrocarbons has also been reported [12-15]. Although the analytical application of LIPS to aqueous solutions has been widely reported [12,16-22], the main problem in this medium is the sensitivity. Elemental detection in aqueous solution has been performed using two dispositions: on the surface of the liquid by single-pulse, or in the bulk of the solutions by single- and double-pulse techniques [12,16,17,19]. Several difficulties are encountered in performing LIPS experiments in liquids. Laser-induced plasma of a liquid, generated in bulk, have a short lifetime and this represents a drawback for sensitivity [16]. On the other hand, when laser-induced plasma is produced on the surface of the liquid, other experimental difficulties can arise. Splashing of the liquid and ripples pro-

duced by shock waves on its surface represent obstacles to the collection of radiation emitted by the plasma [15-16]. Generation of the laser-induced plasma on laminar flow, aerosols, droplets or jets can be used to solve the problem presented by laser-induced plasma on the surface of the liquid [18-19]. However, these strategies do not facilitate *in-situ* and real-time measurements, which are the most attractive advantages of LIPS. In addition, LIPS techniques for aqueous solution analysis should include fast response, on-line control of water quality, and *in situ* measurements.

In this work we have shown the possibilities offered by LIPS in the study of aqueous solutions using the first and second harmonics of a Q-switched Nd-YAG laser (1064 and 532 nm) to generate laser-induced plasma on the surface of the liquid. The emission signal of five different solutions was obtained (Ca, K, Mg, Na and Sr) and we calculated the plasma temperature through the Boltzmann plots.

## 2. Experimental

The schematic diagram of our LIPS experimental setup is represented in Fig. 1. The fundamental (1064 nm) and second harmonics (532 nm) from a Q-switched Nd:YAG laser (INDI, Spectra Physics) delivering an  $\sim 8$  ns laser pulse and a non-adjustable repetition rate of 10 Hz. The laser pulse energy was frequently measured with an energy meter (Nova, OPHIR OPTRONICS). Laser-induced plasma on the surface of the liquid was obtained by focusing the laser pulse, at right angles, through a quartz lens ( $f \sim 50$  mm). The plasma emission is collected with a quartz optical fiber (core diameter of 200  $\mu\text{m}$ , 0.6 NA, UV grade silica fused) and introduced into

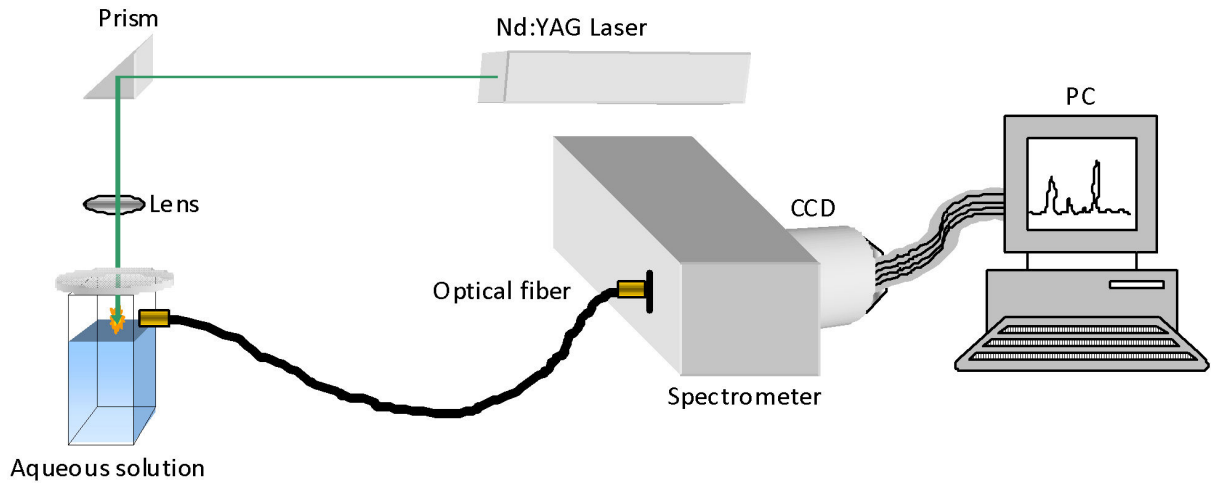


FIGURE 1. Experimental setup.

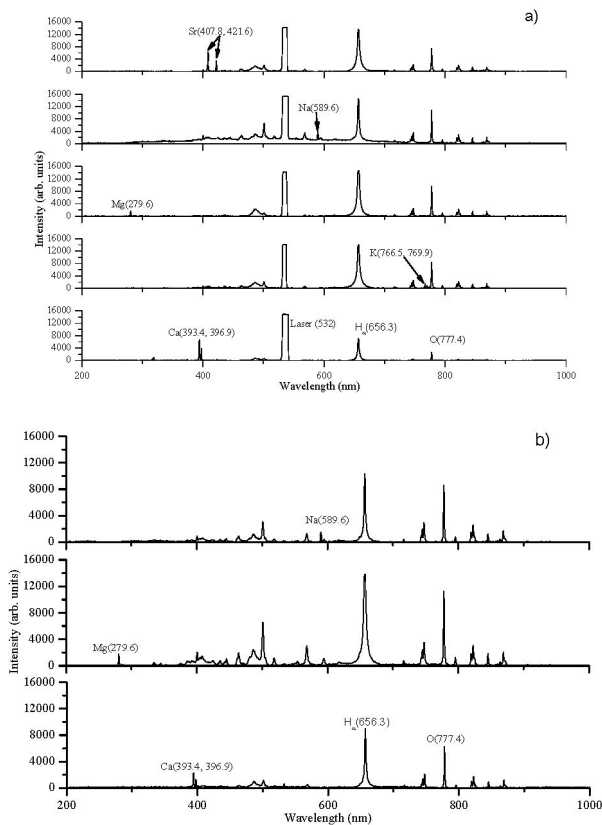


FIGURE 2. LIBS spectra of Ca, K, Mg, Na and Sr aqueous solution at (a) 532 nm and (b) 1064 nm

a symmetrical crossed Czerny-Turner spectrometer (HR4000, Ocean Optics; wavelength range from 200 to 1100 nm, optical resolution of 1.0 nm FWHM, Focal length of 101 mm and grating of 300 lines per mm) equipped with a linear, non-intensified CCD array of 3648 elements. This spectrometer uses a 300 groove/mm diffraction grating to disperse

the emission spectrum, which is projected onto the image plane of the spectrometer and recorded on the CCD detector. The laser energy density employed in the experiments was approximately 150 mJ per pulse [23].

The sample was placed into a quartz cuvette, the focused beam was tilted at an angle of 90° to the water surface with a right-angled prism as shown in Fig. 1. To avoid the splashing problem, we used the laser in the single-pulse mode. In order to shield the optical components in the vicinity from the splashing, it is necessary to use a sapphire window over the cuvette. In order to synchronize the laser shot with data acquisition, a TTL of the laser is used to start the recorder.

### 3. Results and discussion

Figures 2a and 2b show some typical single-pulse LIPS spectra at 532 and 1064 nm of aqueous solutions of

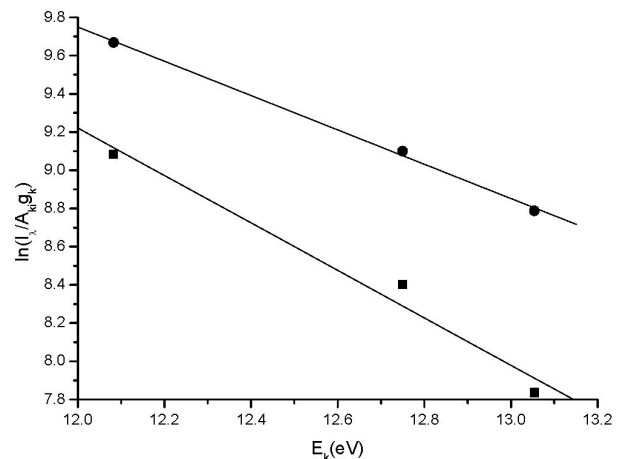


FIGURE 3. Boltzmann plot for  $\alpha$ ,  $\beta$  and  $\gamma$  hydrogen lines at (●) 532 nm and (■) 1064 nm.

CaCl<sub>2</sub> (0.05 M), KCl (0.74 M), MgSO<sub>4</sub> (0.08 M), Na<sub>2</sub>SO<sub>4</sub> (0.12 M) and SrCl<sub>2</sub> (0.35 M). The laser-induced plasma is characterized by visible emission, bubbles, shock waves and “splash”. The laser pulse energy, for both wavelengths, was approximately 150 mJ and the optical fiber was placed on the wall of the cuvette. Each spectrum was obtained for the single-pulse laser. In order to improve the reproducibility, we accumulated twenty single-pulse spectra. Each spectrum is the result of the observation of the plasma in a total lifetime, because the CCD used here does not allow the laser-induced plasma to be resolved temporally. The spectral lines of Ca (393.4, 396.9 nm), K (766.5, 769.9 nm), Mg (279.6 nm), Na (589.6 nm), Sr (407.8, 421.6 nm), H $\alpha$  (656.3 nm) and O (777.4 nm) are labeled in the spectra in Fig. 2.

In order to measure the laser-induced plasma temperature at the wavelengths used here, we have assumed the local thermodynamic equilibrium (LTE) condition [6-7]. In this condition the electrons dominate the reaction rate, so the measured intensity  $I_\lambda$  of the emission line of a single species is derived from the Boltzmann equation as:

$$I_\lambda = FC_s \frac{A_{ki}g_k}{U_s(T)} e^{-\frac{E_k}{KT}} \quad (1)$$

or,

$$\ln \frac{I_\lambda}{A_{ki}g_k} = -\frac{1}{KT} E_k + \ln \frac{C_s F}{U_s(T)} \quad (2)$$

where  $A_{ki}$  is the transition probability,  $g_k$  is the statistical weight for the upper level,  $E_k$  is the excited level energy,  $T$  is the temperature,  $K$  is the Boltzmann constant,  $U_s(T)$  is the partition function of the species,  $C_s$  is the species concentration and  $F$  is an experimental factor;  $F$  is detection-system dependent.

Plotting the left hand side of Eq. (2) versus the excited level energy  $E_k$ , the plasma temperature can be obtained from the slope of the straight line obtained. Boltzmann plots of the hydrogen lines (656.28, 486.13 and 434.05 nm) at laser wavelengths of 532 and 1064 nm are shown in Fig. 3a and 3b, respectively. The curve slope yields a plasma temperature of 12728 K at 532 nm and 9465 K at 1064 nm. Considering that the energy per pulse for both wavelengths is similar ( $\sim 150$  mJ), it is evident that at 532 nm the excess of energy after the vaporization of the sample is greater than at 1064 nm.

## 4. Conclusions

A study of laser-induced plasma spectroscopy in aqueous solutions was performed. The use of a low cost spectroscopic system coupled to a non-intensified CCD camera allowed us to obtain results comparable to those of other reports [16-20]. We have found differences between laser-induced plasma at 532 and 1064 nm. In order to study Mg and Ca, better results were obtained using the fundamental harmonic of Nd:YAG laser, while to study K, Na and Sr, the second harmonic is better. Finally, assuming LTE and similar energy per pulse, laser-induced plasma at 532 nm is hotter than at 1064 nm.

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1. S. Rosenwasser *et al.*, *Spectrochim. Acta Part B* **56** (2001) 707.
  2. S. Palanco, J.M. Baena, and J.J. Laserna, *Spectrochim. Acta Part B* **57/3** (2002) 591.
  3. F. Capitelli *et al.*, *Geoderma* **106** (2002) 46.
  4. G. Hubmer, R. Kitzberger, and K. Mörwald, *Anal. Bioanal. Chem.* **385** (2006) 219.
  5. A. Bertolini, *et al.*, *Anal. Bioanal. Chem.* **385** (2006) 240.
  6. J.A. Aguilera and C. Aragón, *Appl. Phys. A* **69** (1999) S475.
  7. A.M. El Sherbini, H. Hegazy, and Th.M. El Sherbini, *Spectrochim. Acta Part B* **61** (2006) 532.
  8. J.E. Carranza and D.W. Hahn, *J. Anal. At. Spectrom.* **17** (2002) 1534.
  9. B.C. Windom, P.K. Diwakar, and D.W. Hahn, *Spectrochim. Acta Part B* **61** (2006) 788.
  10. S.L. Lui and N.H. Cheung, *Spectrochim. Acta Part B* **58** (2003) 1613.
  11. M. Hanafi M.M. Omar, and Y.E.E-D. Gamal, *Rad. Phys. and Chem.* **57** (2000) 11.
  12. L.M. Berman and P.J. Wolf, *Appl. Spectrosc.* **52** (1998) 438.
  13. D.A. Cremers and L.J. Radziemski, *Anal. Chem.* **55** (1983) 1252.
  14. C. Lazzari *et al.*, *Laser and Particle Beams* **12** (1994) 525.
  15. J.B. Jeffries, G.A. Raiche, and L.E. Jusinski, *Appl. Phys. B* **55** (1992) 76.
  16. A. De Giacomo, M. Dell'aglio, and O. De Pascale, *Appl. Phys. A* **79** (2004) 1035.
  17. B. Charf and M.A. Harith, *Spectrochim. Acta Part B* **57** (2002) 1141.
  18. J-S. Huang, C-B. Ke, and K-C Lin, *Spectrochim. Acta Part B* **59** (2004) 321.
  19. J-S Huang and K-C Lin, *J. Anal. At. Spectrom.* **20** (2005) 53.
  20. S. Boudjemai, T. Gasmi, R. Boushaki, R. Kasbadji, and F. Medjahed, *J. Appl. Sci. Environ. Mgt.* **8**(2004) 13.
  21. S. Nakamura, Y. Ito, and K. Sone, *Anal. Chem.* **68** (1996) 2981.

22. S. Koch, W. Garen, M. Müller, and W. Neu, *Appl. Phys. A* **79** (2004) 1071.
23. F. Blanco and H. Ortiz, Tesis de Pregrado, Universidad Industrial de Santander, Bucaramanga, Colombia (2005).