

Identification of metal elements by time-resolved LIBS technique in sediments lake the “Cisne”

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Abstract. Laser induced breakdown spectroscopy (LIBS), is a kind of spectral method of atomic emission that uses pulses of radiation high energy laser as excitation source. One of the advantages of technical LIBS lies in the possibility of analyse the substances in any State of aggregation, already is solid, liquid or gaseous, even in colloids as aerosols, gels and others. Another advantage over other conventional techniques is the simultaneous analysis of elements present in a sample of multielement. This work is made in the use of this technique for the identification of metal pollutants in the Swan Lake sediment samples, collected by drilling cores. Plasmas were generated by focusing the radiation of Nd: YAG laser with an energy per pulse 13mJ and 4ns duration, wavelength of 532nm. The spectra of radiation from the plasmas of sediment were recorded with an Echelle spectrograph type coupled to an ICCD camera. The delay times were between 0.5 μ s and 7 μ s, while the gate width was of 2 μ s. To ensure the homogeneity of the plasmas, the sediment sample was placed in a positioning system of linear and rotary adjustment of smooth step synchronized with the trigger of the laser pulse. The registration of the spectra of the sediment to different times of delay, allowed to identify the lines prominent of the different elements present in the sample. The analysis of the Spectra allowed the identification of some elements in the sample as if, Ca, Na, Mg, and Al through the measurement of wavelengths of the prominent peaks.

1. Introduction

Laser Produced Plasma by Spectroscopy (LPPS), also known as LIBS (Laser Induced Breakdown Spectroscopy) [1,2], is a method of Atomic Spectroscopy that has become a very effective technique for the analysis of sediments from lagoon origin [3]. Works like Harmon R, et. al. [4]; B Salle [5] used this technique to detect metals in sediments that only requires a small amount of the sample to spectrally analyse its components and in many cases do not need advance preparation. With the appropriate instrumentation, the recording and the analysis of the spectra can be spatial or temporarily according to the detection to be studied [1].

In LIBS technique, a plasma is generated by the interaction of the laser pulses with the material, what allows the detection of spectral lines of elements present in the excited sample. The spectra obtained reveal the basic characteristics of the composition of the sample. Measuring the wavelength of each peak intensity of the spectra it is compared with the spectral database of National Institute Standard and Technology (NIST) [6].

The implementation of the LIBS technique resolved in time to analyse the toxic components of the soil, this reduces the time of analysis of the samples and the results associated facilitate the design of strategies to combat environmental pollution in targeted sites. In this paper this technique is used for



the identification of polluting metallic elements in samples lagoon sediments, which were collected in the lake the “Cisne” by core drilling is done.

2. Sample preparation and experimental description

The proper choice of instruments is essential for a good sampling and laboratory analysis. In the case of metal contaminated soils, elements for sampling must be plastic, Teflon or stainless steel; for this work nucleators pvc were used [7].

The samples were collected on the lakeshore by introducing into the sediment the corer, so that a portion thereof to a depth of 25cm was mined, then the pellets were homogenized in a plastic tray for storage in airtight bags until Analysis.

Once in the laboratory, samples were dried in an oven at a temperature of 110°C for three hours to extract the moisture content. With the dry sediment, uniform pellets of 10mm in diameter and 8mm thick with a press were developed.

Plasmas sediment samples were generated in air atmosphere and argon atmosphere, focusing the radiation from a Nd: YAG (Tempest 10, New Wave Research) operating at a wavelength of 532nm, with an average energy per pulse 13mJ and duration of 4ns. The firing frequency was 2Hz. The sample was mounted in high precision motor stepper stage as possible plasmas in the same plane and under the same conditions engine, because in each point of interaction of the laser pulse with the material is causing erosion and leaving a small crater. Figure 1 shows a basic diagram of the experimental set LIBS time resolved technique. The radiation emitted by the plasma was collected with an optical fibre. The collimated light was focused to the entrance slit of an Echelle spectrograph (Mechell 5000, Andor Technology) equipped with a ICCD camera (iSTAR 334T, Andor Technology), giving a broadband coverage from 200nm to 900nm with resolution of 0.1nm. The acquisition and recording of the spectra was set in Solis T operating software, the parameters of delay time was set between 0.5 μ s and 7 μ s, with steps of 0.5 μ s each record with 20 accumulations, and temperature cooling to -10°C [8].

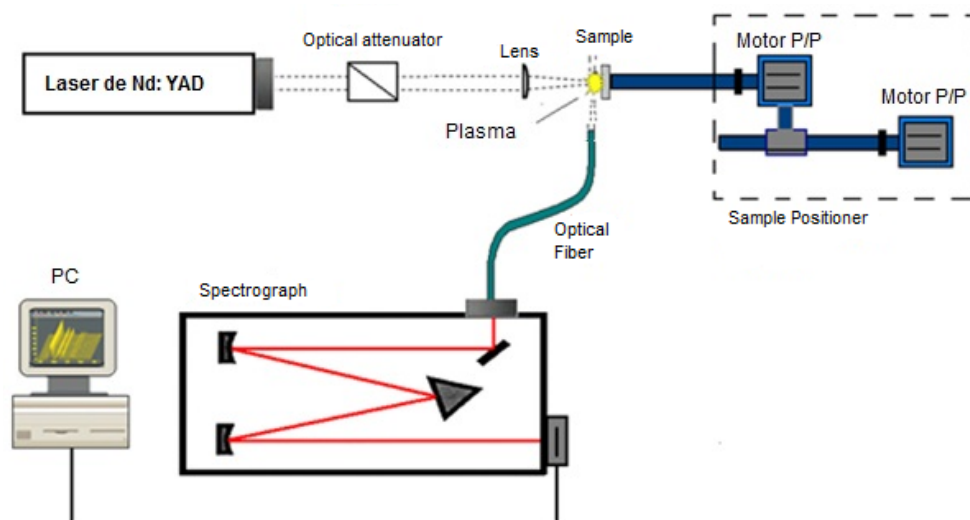


Figure 1. Experimental setup of the LIBS technique resolved in time.

3. Discussion of results

For the analysis of the spectra of laser plasmas, sediment samples variation of the various parameters of acquisition of the spectra were taken into account delay time to select the most appropriate spectra; the type of atmosphere, humidity conditions of the sample which affects the spectra obtained. The spectra are affected by humidity and a significant drop in the relative intensity of the spectral lines compared to the spectra of the dry sample for both atmospheres as shown in Figure 2. To a higher

humidity, plasma is cooled by the water vapour in full accordance with reference [9]. It is also observed that the relative intensity of the lines and appears more intense spectrum under argon in air atmosphere for both dry and wet samples.

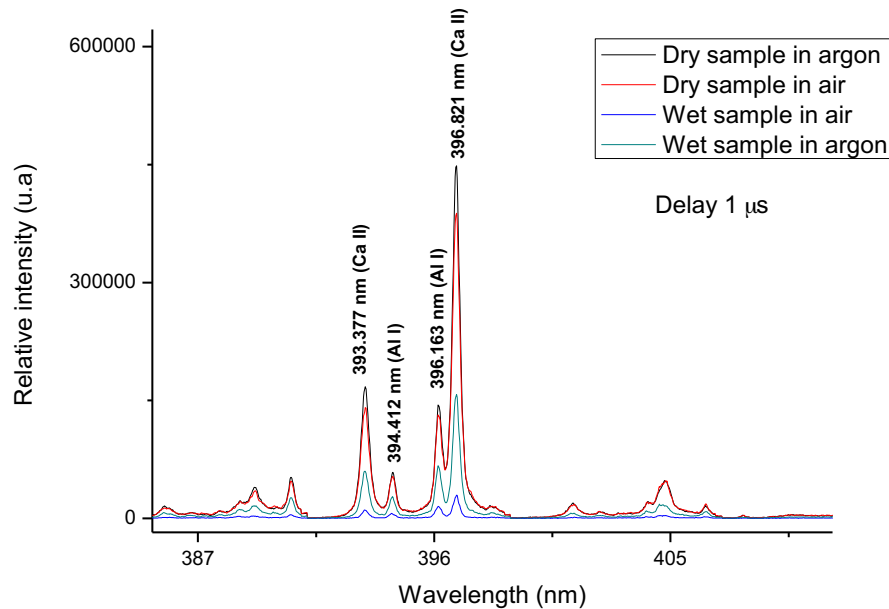


Figure 2. Overlapping spectra of laser plasma sediment wet and dry in air and argon atmosphere with delay time $t_d=1\mu s$.

For delay time of $1\mu s$, the spectra was display with a continued strong and ionic lines broadened Ca II and Mg II as shown in Figures 2 and 3. For longer delays to $1\mu s$ persistent atomic lines of neutral atoms Ca I, Si I, Al I, Mg I, K I, Na I.

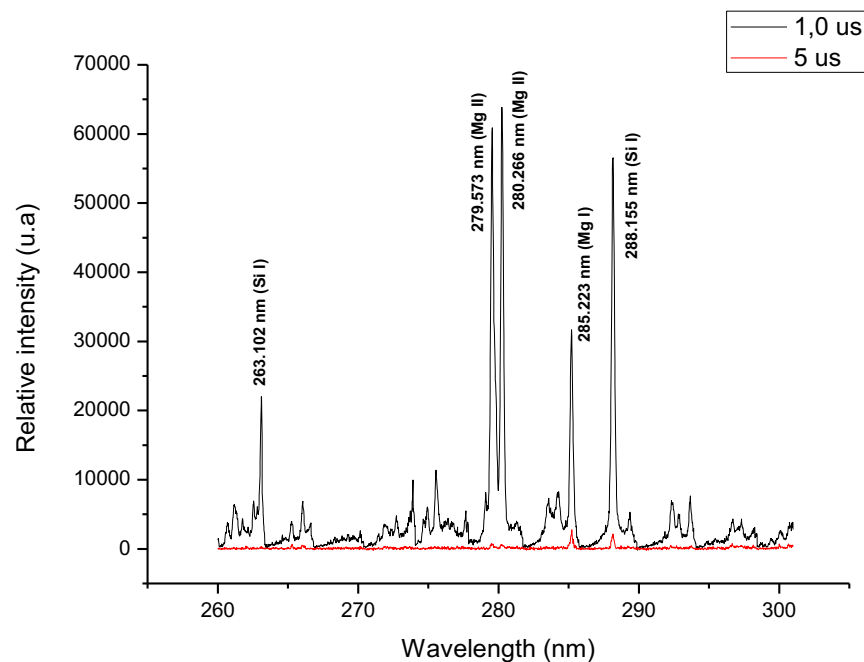


Figure. 3 Spectra overlapping laser plasma sediment in the region between 260nm-300nm for delay times $t_d=1\mu s$ (black) and $t_d=5\mu s$ (red).

Figure 4 shows the behaviour of LIBS spectra for different delay time in the region between 300 and 450nm. The analysis of temporal records allows better discrimination and allocation of atomic and ionic lines simultaneously presented in the multielement spectra.

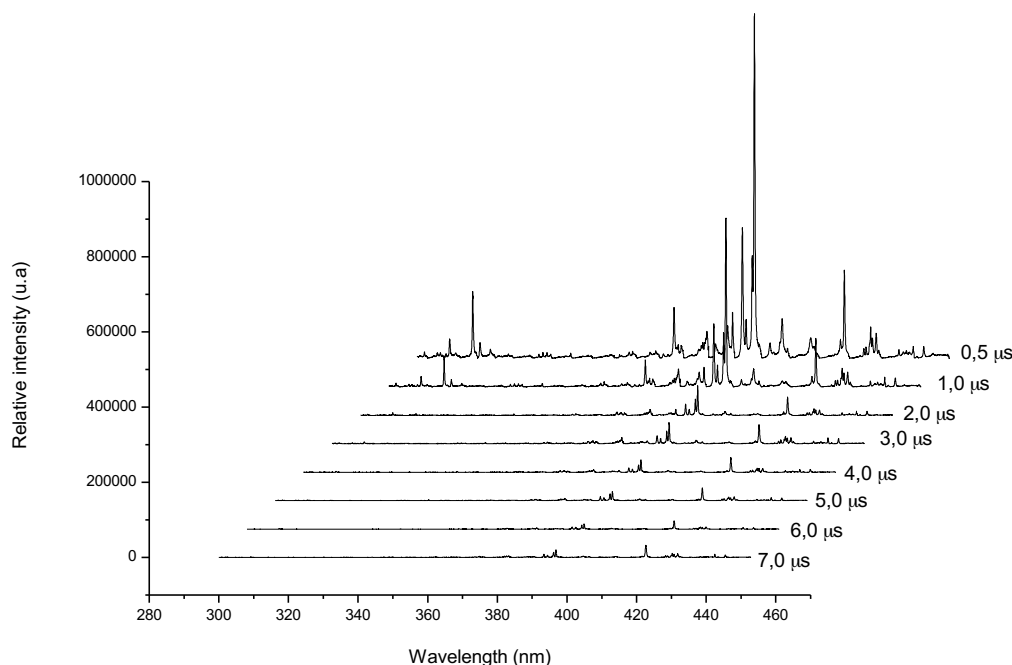


Figure 4. Plasma-laser spectra sediment taken with different delay times t_d .

Table 1 shows some of the observed and measured in the LIBS spectra sediments lake the “Cisne” located in the north of Barranquilla, Colombia.

Table 1. Spectral lines of the species presented in the plasma-laser sediment.

Element	Wavelength (nm)	Element	Wavelength (nm)
Si I	243.515	Ca I	422.705
Si I	251.647	Ca I	442.454
Si I	251.902	Ca I	445.456
Si I	252.369	Ca I	558.873
Si I	252.843	Ca I	559.492
Si I	263.102	Na I	588.968
Mg II	279.573	Na I	589.572
Mg II	280.266	Ca I	610.298
Mg I	285.223	Ca I	612.209
Si I	288.155	Ca I	616.206
Al I	309.238	Ca I	616.975
Ca II	315.906	Ca I	643.902
Ca II	373.621	Ca I	646.247
Si I	390.554	Ca I	649.365
Ca II	393.377	Ca I	671.796
Al I	394.412	Ca I	714.803
Al I	396.163	Ca I	720.283
Ca II	396.821	K I	766.475
K I	404.730	K I	769.873

4. Conclusions

The LIBS technique was applied for analysis of time resolved spectra of the sediment lake the “Cisne”, which allowed us to detect some elements present in the samples collected. The main elements were detected Ca, Si, Al, Mg, K and Na. Other lines present in the spectra are being validated for confirmation.

References

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