

## LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR RAPID DETECTION OF CARBON IN SOILS

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**Abstract.** The potentials of two advanced LIBS techniques to determine total carbon content in soils have been examined. In both modes the calibrating graphs have a nonlinear trend in the actual range of carbon contents with a good  $R^2$  value (0.97). The detection limit for the carbon content is equal to 0.07 % for both techniques.

### 1. INTRODUCTION

During the last decade laser-induced breakdown spectroscopy (LIBS) applications to soil analysis is getting a growing interest, due to some of its specific features making LIBS especially promising for this purpose. Among the advantages of applying LIBS to agrochemical problems are easy preparation of samples, fast data registration and treatment, possibility of *in-situ* and remote analysis. The aim of the present work is to test the capabilities of LIBS for determination of carbon (humus) content in soils using two different modes to ablate and excite the sample material. In the first mode, double laser pulses have been applied. The second mode is based on using combined pulsed plasma (CPP), which consists of the superposition of a spark discharge and a laser ablation plume produced by a focused laser beam on the sample surface.

### 2. EXPERIMENTAL

A laser spectral analyzer (LSA) has been used to perform LIBS measurements with the double-pulse plasma (DPP) mode. LSA consists of a grating spectrometer with a focal distance of 1000 mm, an aperture of 1:20 and a grating of 1800 lines/mm. The spectrometer is equipped with a CCD array for emission spectra recording. A spectral resolution of 0.025 nm has been determined by a fiber with a 60  $\mu\text{m}$  diameter at the entrance slit with a 60  $\mu\text{m}$  width. A wavelength interval of 239–340 nm has been chosen, where carbon CI 247.86 nm atomic line has been used as the analytical one.

LSA is equipped with a Q-switched double-pulse Nd:YAG laser for sample ablation and spectra excitation. Its main parameters are as follows: 1064 nm lasing wavelength, 50 mJ pulse energy, 10 ns and 10 Hz pulse duration and repetition rate, respectively. An optimized delay between the pulses of 8  $\mu$ s has been chosen in the double-pulse excitation mode. The laser beam has been focused a bit ( $\sim$ 1.5 mm) below the surface of samples, providing a surface irradiance in the order of  $10^9$  W/cm<sup>2</sup> in the laser spot. The sample has been set on a movable (XYZ) table to allow monitoring of the laser spot by a microscope. Each spectrum has been obtained by focusing ten double shots on the sample surface.

In the CPP mode, a single pulse from a Q-switched Nd:YAG laser has been used. Its main parameters chosen for the analytical measurements are as follows: 1064 nm, 180 mJ, and 8 ns. Laser radiation has been focused on the sample surface by a lens (F=50 mm), providing laser spot irradiance of up to  $10^{10}$  W/cm<sup>2</sup>.

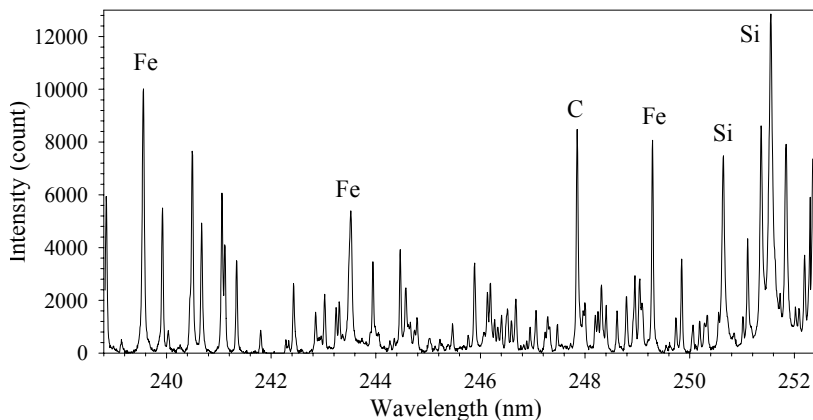
Tungsten wire electrodes with 3 mm gap have been set at a distance of 1.5 mm from the sample surface. This distance was the minimal to avoid surface self-breakdown at the operating voltage. The laser ablation plume seals-in the electric circuit containing a low inductive 1  $\mu$ F capacitor charged to 4 kV, which gives rise to a quasiperiodical (4  $\mu$ s period) damping electric discharge. In the CPP mode the energy accumulated by the capacitor has been up to 8 J. Dimensions of the resulting CPP volume are much larger than the one of the laser ablation plasma.

The CPP emitting volume has been 1:1 imaged by a lens (F=61mm) on the entrance slit of a grating (600 lines/mm) spectrometer having an aperture of 1:4.9 and a focal distance of 380 mm. An entrance slit width of 15  $\mu$ m has been set for the measurements. A CCD array of 2048 pixels has been used to record the CPP emission spectra. The atomic CI 833.52 nm spectral line has been chosen as the analytical one to avoid interferences of tungsten emission lines in the UV range. Detecting the IR spectral window to overcome some analytical problems is especially important in the case of elements that are difficult to excite such as carbon as well as chlorine, sulfur and others.

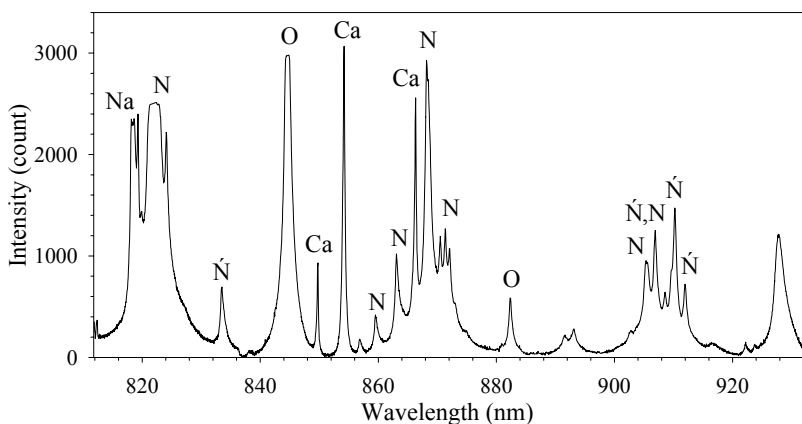
### 3. RESULTS AND DISCUSSION

Spectral ranges including analytical atomic carbon lines are shown in Figs. 1 and 2. The results indicate that in the DPP mode the enhancement factors of 7 and 30 could be obtained for CI 247.86 nm atomic line and Fe II 239.56 nm ionic line, respectively. The atomic CI 833.52 nm line intensity in CPP mode shows more than 20 times (peak to peak) enhancement in comparison to single-pulse laser excitation. For ionic Ca II 849.80 nm line the intensity enhancement factor (2) was lower.

The CPP spectra have been acquired by focusing 4 shots in each of 5 different zones of the sample surface, and the analytical line intensity has been averaged to reduce the possible influence of the sample nonhomogeneity.



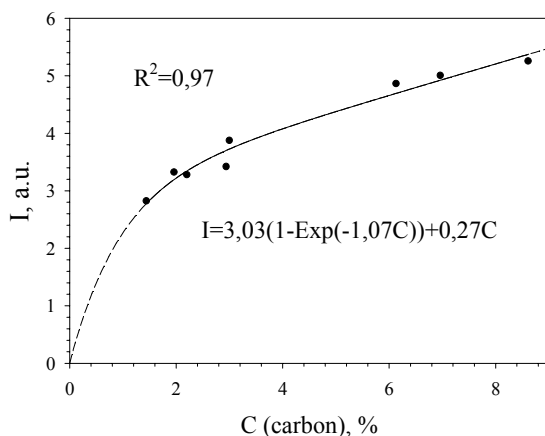
**Figure 1:** Typical spectrum of DPP.



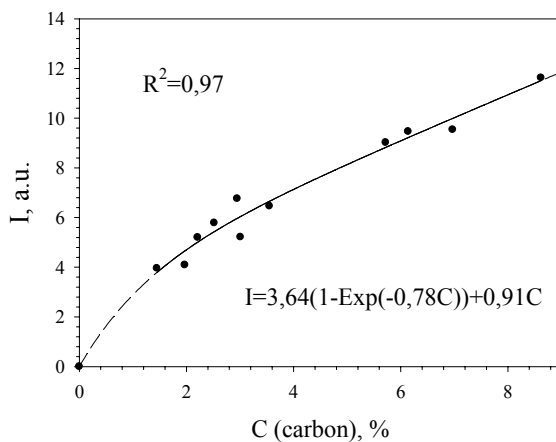
**Figure 2:** Typical spectrum of CPP.

In Fig. 3 the dependence of  $I^*=f(C)$ , for a case of DPP is presented. This graph indicates a lower sensitivity (slope of the plot) in the indicated range of concentrations in comparison with the graph for CPP (Fig. 4), that can be caused by two reasons. One of them consists in the overlapping of the carbon CI 247.86 nm line and the low-intensity iron Fe II 247.86 nm line.

Generally speaking, the main reason of the increase in the intensity of line emission in the CPP mode as compared with conventional single-pulse LIBS is explained by the extended temporal evolution of the emission and the increase in the dimensions of the plasma volume. Thus, a significant increase in analytical time (with CCD detectors) and in analytical volume is achievable. Therefore, utilization of low-cost and portable laser instrumentation and a saving mode of laser usage, as well as micro influence on the sample under study, are possible.



**Figure 3:** The calibration graph for DPP mode.



**Figure 4:** The calibration graph for CPP mode.

The CPP mode advantages consist in the larger concentration sensitivity (slope of calibration graph), smaller influence of instability of laser pulse energy on spectral lines intensity, and possibility of utilization of low laser energies. On the other hand, using CPP in the visible and UV spectral ranges is complicated, owing to the overlapping of analytical lines with numerous emission lines of the electrode material. This variant is most suitable for analytical purposes in the red visible and IR ranges especially for the determination of elements that are difficult to excite, such as carbon, chlorine and sulfur. The main advantage of DPP is the opportunity of recording spectral lines of the basic nutritious elements and toxic metals in the UV range.