

# Environmental Monitoring of Total Carbon and Nitrogen in Soils using Laser-Induced Breakdown Spectroscopy

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**Abstract:** We have successfully demonstrated the technique of laser-induced breakdown spectroscopy (LIBS) in the determination of the total concentration of carbon and nitrogen in soils. We have obtained a linear calibration curve for carbon in 15 soil samples directly correlated to the soil combustion technique.

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## Introduction

Carbon reservoirs at the earth's surface comprise the atmosphere, biomass, and organic and inorganic carbon in soils, lakes, rivers and ocean surfaces. These reservoirs interact with the atmosphere and affect its CO<sub>2</sub> content. Knowledge that CO<sub>2</sub> is stored within and exchanged between the atmosphere and vegetation and soils has led to the suggestion that soils and vegetation could be managed to increase their uptake and storage of CO<sub>2</sub>, and thus become 'land carbon sinks'. Uncertainty in the scientific understanding of the causes, magnitude and permanence of the land carbon sink is of utmost concern and hence in need of instrumentation and technology development to accurately measure baseline amounts of carbon sequestered in land masses<sup>1</sup>. Soil organic matter (SOM) is the sum total of all organic carbon containing substances in soils. SOM influences plant growth through its effects on the physical, chemical, and biological properties of soils. SOM consists of humic substances that are amorphous, dark-colored, complex, polyelectrolyte-like materials<sup>2</sup>. The very complex structure of humic and fulvic acid makes it difficult to obtain a spectral signature for all soils in general<sup>3</sup>. The percentage of the humus that occurs in the various humic fractions varies considerably from one soil type to another. The humus of forest soils is characterized by a high content of fulvic acids while the humus of peat and grassland soils is high in humic acids.

Laser spectroscopic techniques are well established for their versatility in environmental chemical analysis because they offer real-time monitoring capabilities with high analytical sensitivity and selectivity<sup>4</sup>. FT-IR, FT-Raman, dispersive Raman, surface-enhanced Raman, and <sup>1</sup>H-NMR spectroscopies<sup>5,6</sup> have been applied to investigate molecular changes in SOM. These techniques are valuable for in-laboratory research. However, to take an instrument or technology into the field requires another level of research and development to ensure ruggedness, stability, reliability, small footprint, and calibration algorithms that have been tested for a variety of matrices. The choice of particular laser technique is decided by the specific problem at hand. For example, in the elemental characterization of airborne particles, if simultaneous *in situ* multielement determination is desired then laser-induced breakdown spectroscopy (LIBS) is the technique of choice. We have applied this technique to the determination of total carbon and nitrogen in various soils<sup>7</sup>.

## The LIBS technique

The ability of LIBS to provide rapid multielemental microanalysis of bulk samples (solid, liquid, gas, aerosol) in the parts-per-million (ppm) range with little or no sample preparation has been widely demonstrated. LIBS induces the vaporization of a small volume of sample material with sufficient energy for optical excitation of the elemental species in the resultant sample plume. The vaporized species then undergo de-excitation and optical emission on a microsecond time scale, and time-dependent ultraviolet-visible spectroscopy fingerprints the elements associated with the spectral peaks. LIBS is typically a surface analytical technique, with each laser pulse vaporizing microgram or submicrogram sample masses. However, the rapidity of sampling (typically 10 Hz laser repetition rate) and ability to scan a sample surface, ablate a hole into a solid sample with repeated laser pulses, for depth profiling or focus the laser spark below the surface of a liquid sample permits more versatile analyses and provides sufficient statistics for bulk sampling. The greatest advantage of LIBS is its capability for remote chemical analysis of samples with minimal handling and little or no sample preparation, which minimizes generation of waste to the microgram per pulse of ablated material. Although calibration standards are required for quantitative analysis, the generation of a single calibration curve will suffice for analysis of samples in a similar matrix.

## Experimental setup

The experimental setup employs a Spectra Physics™ laser, model INDI-50. This is a Q-switched Nd: YAG laser that has output wavelengths at the fundamental wavelength of 1064-nm, frequency doubled to 532-nm, and frequency quadrupled to 266-nm. For these experiments, we used the 266-nm laser wavelength with 23 mJ/pulse as the excitation energy. The laser pulsewidth is 6-8 ns and the repetition rate is 10 Hz. All the processes such as plasma formation, emission, gated detection, data collection, and analysis are completed within 100 milliseconds until the next pulse arrives in the sample volume. The pulsed laser beam is focused onto a soil sample that has been pressed into a pellet. The light emitted by the resulting plasma is collected by an optical collection system situated at ~ 45° angle to the axis of the sample and the laser excitation beam and is delivered to an Acton Research Inc. spectrometer (SpectraPro-500) via a carbon-core fiber-optic cable bundle. The resolved spectrum is detected by an intensified charge coupled device (ICCD) built by Andor Technology with the ICCD delayed and gated by a Stanford Research Systems model SRS535 delay generator. Figure 1 shows the characteristic elemental carbon peak that occurs at 247.9 nm.

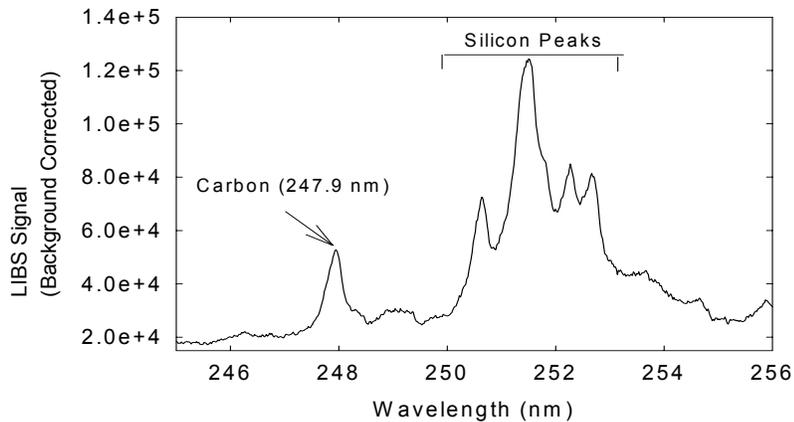
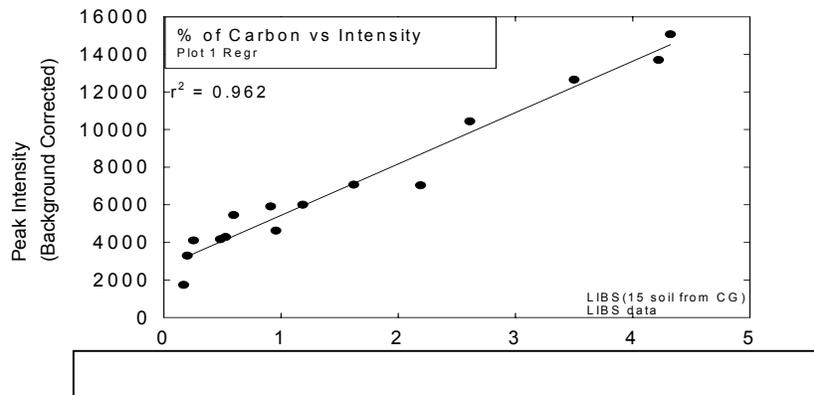


Figure 1. LIBS Signal for Carbon in Soil

The numerous peaks around 252 nm wavelength are silicon peaks, with silicon very abundant in most soils.



The LIBS signal as a function of carbon content in different soil samples is shown in figure 2. From the data shown in figure 2, it is observed that the linearity of the calibration extends from < 0.2 % to > 4 % of carbon contained in

15 soil samples. These fifteen soils were obtained from Oak Ridge National Laboratory's, Natural and Accelerated Bioremediation Research (NABIR) Field Research Center (FRC).

We have also taken four different soils from SW Virginia mined lands and have analyzed each soil at least twenty times using LIBS to obtain the standard deviation in those soils for the carbon and nitrogen concentrations, and compared to LECO carbon-nitrogen-2000 elemental analyzer. The data for the same soils was obtained before and after acid washing of the soils. It has been observed that after acid washing the amount of total carbon signal decreased significantly (50%-60%), while the amount of nitrogen remained within the percentage of standard deviation before being washed in acid. This is to be expected since the acid washing of the soils eliminates the inorganic carbon and will not affect the organic carbon (bound to the nitrogen in the soils).

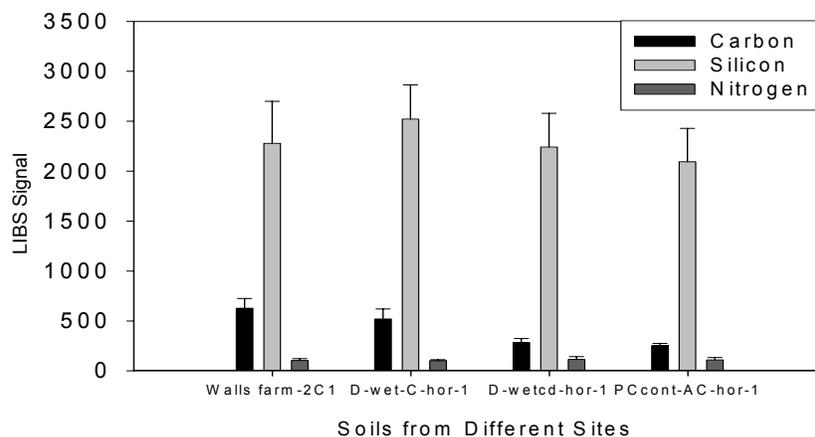


Figure 3. Concentration of carbon, silicon, and nitrogen in the four soils from SW Virginia mined lands.

## Conclusions

In this research we have shown LIBS to be a viable technique in the determination of total carbon and nitrogen concentrations. The variability has been reduced by increasing the number of spectra over which the data is averaged. In case of certain soils the ratio C/Si can be used to reduce this variability. The LIBS technique can be used to determine the total concentration of carbon and nitrogen *in situ* in field measurements.

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