

Environmental and biological applications of laser-induced breakdown spectroscopy

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Abstract

Laser-induced breakdown spectroscopy (LIBS) was used to determine the total amount of carbon and nitrogen in soils, and it was also used to determine the total amount of palladium and silver metal in biofilms. These results were correlated to standard laboratory based techniques such as soil combustion technique for carbon and nitrogen analysis and atomic absorption spectroscopy in the case of calibrating metals in biofilms. 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. The ultimate goal is the development of field portable instrumentation using this technique.

Introduction

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 [1,2]. Laser spectroscopic techniques are very versatile for environmental chemical analysis because they offer real-time monitoring capabilities with high analytical sensitivity and selectivity [3,4]. These techniques are valuable for laboratory research. However, to take an instrument or technology into the field requires another level of research and development to ensure ruggedness, stability, reliability, a small instrument footprint, and calibration algorithms that have been tested for a variety of matrices that is the ultimate goal. The instrumentation and operation of a LIBS system is simpler than some of the more sensitive techniques, and analysis times on the order of minutes for LIBS make it more amenable for real-time analyses of chemical processes. 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

The first step in LIBS is occurrence of breakdown followed by plasma formation. Breakdown can occur when a laser beam of sufficient energy is focused onto a small volume ($\sim 10^{-8} \text{ cm}^3$), creating a power density inside the volume exceeding 10^{15} W/cm^3 . 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 is used to fingerprint 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, LIBS provides rapid sampling (typically 10 Hz laser repetition rate) and has the ability to scan a sample surface, ablate a hole into a solid sample with repeated laser pulses, or focus the laser spark below the surface of a liquid sample. These capabilities permit versatile, multiphase analytical sampling with sufficient statistics to obtain representative analyses for bulk sampling. The experimental configuration is shown in Figure 1. The details are reported in reference 2.

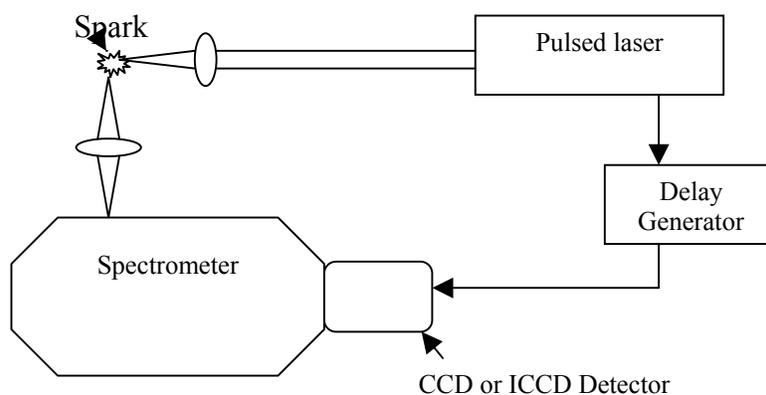


Figure 1. Schematic of a LIBS Experimental System

Results and Discussions

Fifteen different soil samples, with total carbon concentrations varying from 0.16 % to 4.3 %, were analyzed by the combustion method (LECO® CN-2000) and compared to the LIBS technique. A typical LIBS spectrum depicting the carbon peak at 247.9 nm, along with fingerprint peaks for elemental silicon (250-253 nm), is shown in Figure 2.

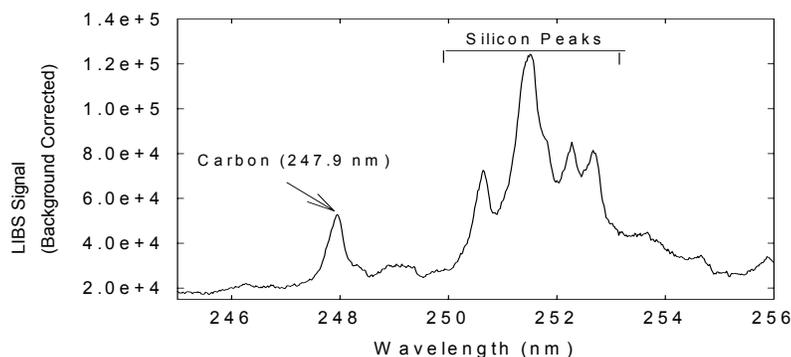


Figure 2. LIBS Signal for Carbon in Soil

Nitrogen is also an important component of SOM and is a significant constituent of proteins, nucleic acids, porphyrins, and alkaloids [5]. Preliminary LIBS data of nitrogen concentrations in soils indicated that this technique could be used successfully to measure total soil nitrogen. The nitrogen has characteristic ionic transitions at 498.2, 498.9, 499.9, 500.6, 501.6, and 503.0 nm.

The biofilms were synthesized by bacteria of the genus *Gluconoacetobacter* which is a gel-like skin or pellicule formed at the surface of the culture medium. The special properties of this cellulose enable it to catalyze deposition of palladium nanoparticles from solution inside the hydrated cellulose matrix (Evans et al., submitted). Such palladium-treated cellulose can be easily dried to thin membranes for application in membrane electrode assemblies and other electronic devices (Evans et al., patent pending). Dried samples of palladium-treated and control cellulose were prepared by drying the cellulose pellicules to a thin membranes on a laboratory gel drier with application of vacuum. We have tested wet and dry films and have found that it is easier to detect the palladium in the cellulose matrix when the film has undergone a drying process. The typical spectrum for metallic palladium deposited on a cellulose membrane starting with a 10 mM solution of $[(\text{NH}_4)_2\text{PdCl}_6]$ is shown in figure 2.

Numerous cellulose membranes with varying concentrations of palladium were used to construct the calibration curve shown in figure 3. The concentrations of Pd in the cellulose membranes tested with the LIBS method were 2, 4, 6, 8 and 10 mM. There seems to be a decrease in the deposition of palladium

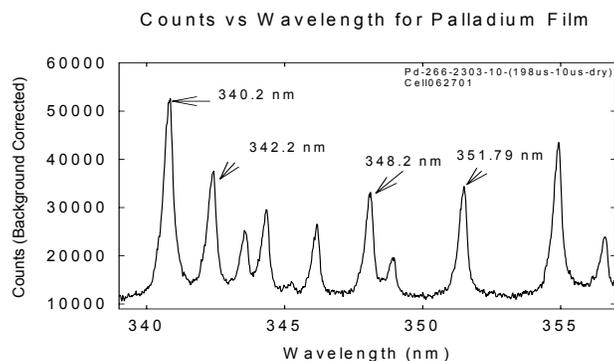


Figure 3. LIBS spectra obtained from Pd metal incorporated in a cellulose film.

metal by the bacteria when the concentration of $[(\text{NH}_4)_2\text{PdCl}_6]$ solution goes above 8 mM. It has been correlated to the calibration curve obtained for the same samples that were used to obtain the calibration curve using a well-established laboratory technique of atomic absorption spectroscopy (AAS).

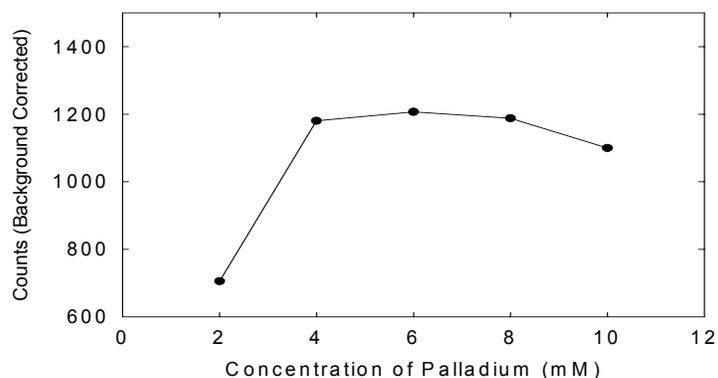


Figure 4. Calibration of the LIBS signal to the concentration of Pd

We have also used the LIBS technique to identify the metallic contaminants in invertebrates such as hydrophsychadaea. Numerous samples of these types of invertebrates were collected from different sites (at varying distances from the hazardous wastes release sites) and tested to see if these organisms when excited with the laser would show any kind of metal contaminants in their bodies (external shell compared to their guts). We did find a significant amount of metal contaminants in the samples that were tested when sampled close to highly contaminated sites. Another application of LIBS is its use in depth profiling. We obtained some iron filings that were used in creating a reactive barrier such that subsurface contamination e.g., VOCs (volatile organic compounds), TCE (trichloroethylene), PCE (tetrachloroethylene), and DNAPL (dense non-aqueous phase liquids) were prevented from migration under the surface area. These iron filings showed a coating layer of CaCO_3 for $\sim 20 \mu\text{m}$ and under that we were able to detect the iron peak. Hence we could detect a calcium peak for the first $20 \mu\text{m}$ and once we had profiled over this depth the iron peak started increasing and the calcium peak diminished. This is the first time that LIBS has been demonstrated in such an application.

Acknowledgements

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