

# Laser-induced breakdown spectroscopy for the environmental determination of total carbon and nitrogen in soils

Madhavi Z. Martin, Stan D. Wullschleger, Charles T. Garten Jr., and Anthony V. Palumbo

Soils from various sites have been analyzed with the laser-induced breakdown spectroscopy (LIBS) technique for total elemental determination of carbon and nitrogen. Results from LIBS have been correlated to a standard laboratory-based technique (sample combustion), and strong linear correlations were obtained for determination of carbon concentrations. The LIBS technique was used on soils before and after acid washing, and the technique appears to be useful for the determination of both organic and inorganic soil carbon. The LIBS technique has the potential to be packaged into a field-deployable instrument. © 2003 Optical Society of America

OCIS codes: 140.3440, 300.6210, 300.2140, 300.6360, 120.6200.

## 1. Introduction

Research indicates that atmospheric greenhouse gases, such as CO<sub>2</sub>, influence climate change.<sup>1</sup> As a result, international efforts are now focused on the reduction of anthropogenic emissions of greenhouse gases, particularly CO<sub>2</sub>. Since CO<sub>2</sub> is cycled between the atmosphere and vegetation and soils, it may be possible to increase carbon storage in *terrestrial carbon sinks*. There is some uncertainty, however, in how the magnitude of these carbon sinks can be reliably measured, which necessitates the development of instrumentation that can be used to quantify and verify the concentration of carbon present in soil.<sup>1</sup>

Soil organic matter (SOM) is the sum of all organic carbon-containing substances in soils and is usually subdivided into humic and nonhumic substances. The very complex structure of soil humins makes it difficult to obtain a general spectral signature for all soils.<sup>2</sup> The characterization of SOM is important because organic matter serves as a soil conditioner, nutrient source, and substrate for microbial activity. SOM influences plant growth through the physical, chemical, and biological properties of soil.<sup>3</sup>

Laser spectroscopic techniques are very versatile for environmental chemical analysis because they offer real-time monitoring capabilities with high analytical sensitivity and selectivity.<sup>4–6</sup> Fourier-transform-(FT-)IR, FT-Raman, dispersive Raman, surface-enhanced Raman, and hydrogen–nuclear magnetic resonance spectroscopies<sup>7–13</sup> have been applied to investigate molecular changes in SOM. Recently a new technique, pyrolysis molecular beam mass spectrometry, has also been developed for the measurement and characterization of carbon in soils.<sup>14,15</sup> 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, which is the ultimate goal. In this paper we apply the laser-induced breakdown spectroscopy (LIBS) technique under controlled laboratory conditions in the determination of total carbon and nitrogen in various soils.<sup>16</sup> Our study builds upon and extends the preliminary observations of Cremers *et al.*,<sup>17</sup> who have also demonstrated the unique capabilities of LIBS to detect soil carbon.

## 2. Experiment

### A. Laser-Induced Breakdown Spectroscopy Technique

This technique requires a pulsed laser as the excitation source. A plasma can be formed when a laser beam of sufficient energy is focused onto a small area,

The authors are with the Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6038. M. Martin's e-mail address is martinm1@ornl.gov.

Received 21 May 2002; revised manuscript received 12 July 2002.

0003-6935/03/122072-06\$15.00/0

© 2003 Optical Society of America

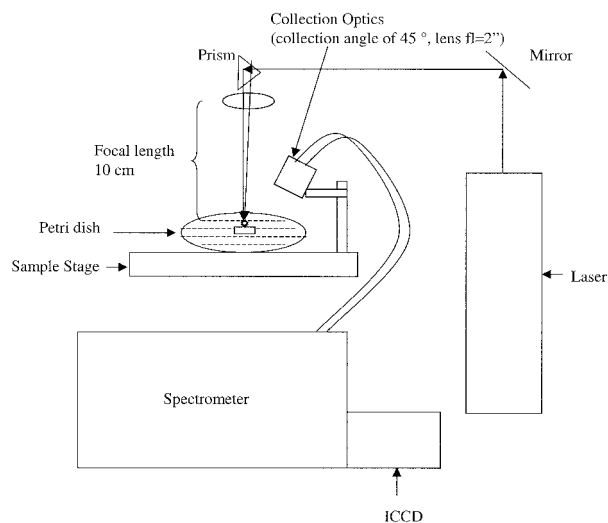


Fig. 1. LIBS experimental setup for carbon and nitrogen detection.

creating a power density inside the sampling volume ( $\sim 14 \times 10^{-9} \text{ cm}^3$ ) exceeding tens of gigawatts per cubic centimeter. This vaporizes material in the focal volume into its elemental constituents. This plasma appears as a spark accompanied by an audible crack as the plasma expands outward at supersonic speed in all directions, with an initial rate of expansion of the order of  $10^5 \text{ m s}^{-1}$ . The experimental setup used to determine the concentration of carbon and nitrogen in soils is shown in Fig. 1. In the experimental configuration we use a Spectra Physics model Indi-HG laser that is a Q-switched Nd:YAG laser with output wavelengths of 1064, 532, and 266 nm. The laser was used at 266 nm with typically 23 mJ/pulse. The light emitted by the plasma at the focal volume was collected by a set of collection optics and focused into a low O-H silica fiber bundle consisting of 19 fibers. This fiber bundle (N.A. = 0.22; diameter, 4.66 mm) delivered the light to a 0.5-m Acton Research model SpectraPro-500 spectrometer (spectral bandwidth at 40 nm for 1200-g/mm grating and slitwidth of spectrometer at 25  $\mu\text{m}$ ); which was then detected by an intensified charge-coupled detector (ICCD) made by Andor Technologies. The advantage of using an ICCD is that the detection can be delayed with respect to plasma formation, and the detector can be gated in order to prevent high background light intensity from the plasma in its early stages of formation from entering the detector. Thus gating and delay of the gate serves to optimize the signal-to-noise ratio of the acquired spectrum. The smallest gate width that the ICCD detector can achieve is 2.2 ns. Thus, time-resolved LIBS was used.

#### B. Carbon-Nitrogen Analysis by Sample Combustion

In the combustion method, 0.5–0.6 grams of soil is weighed in a ceramic sample boat. The sample is inserted into the combustion chamber in a LECO CN-2000 elemental analyzer (LECO Corporation, St.

Joseph, Mich.) that heats the sample to a temperature of 1350 °C in the presence of oxygen. Combustion converts SOM containing nitrogen and carbon into  $\text{N}_2$ ,  $\text{NO}_x$ , and  $\text{CO}_2$ . Hydrogen and oxygen combine to form water vapor. The combustion gases are analyzed for  $\text{CO}_2$  (infrared spectroscopy) and  $\text{N}_2$  (thermal conductivity detector). A LECO CN-2000 elemental analyzer was used to determine carbon and nitrogen in all soils that were used to calibrate the LIBS technique. The elemental analyzer was calibrated with standards traceable to the National Institute of Standards and Technology, Gaithersburg, Md.

#### C. Acid Washing to Remove Inorganic Soil Carbon

The soils were obtained from two different sites: (1) Oak Ridge National Laboratory's Natural and Accelerated Bioremediation Research (NABIR) Field Research Center (FRC) and (2) southwest Virginia mined lands. A few grams of homogenized soil was mixed with  $\sim 10 \text{ ml}$  of deionized water in a vial, and the solution was heated until close to boiling. Ten ml of 3 M HCl acid was carefully added to this solution while the sample was held near boiling temperatures for 1 h and swirled intermittently.<sup>18</sup> After 20 ml of deionized water was added, the sample was placed in a shaker for 30 min. The supernatant was poured off after centrifugation at 2500 rpm for 10 min. The vial and the solid mass were placed in an oven at 60 °C and allowed to dry overnight. The dried soil sample was crushed with a mortar and pestle in order to obtain a homogeneous sample for analysis.

Pellets were formed from these homogeneous soil samples by use of the following technique. The homogenized soils were weighed and placed in disposable glass culture tubes. Ultrapure deionized water (0.5 ml) was mixed with the 0.5-g soil sample tubes, and the mixture was heated at 60 °C for 24 hr or until dry. The tubes were then turned upside down and gently tapped to release the pellets. The pellets were stored in airtight vials to prevent absorption of moisture from the atmosphere.

### 3. Results and Discussion

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 with results from 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 Fig. 2. The carbon peak was very distinct, but in soils that contain a significant amount of iron there may be a problem in resolving the nearly overlapping iron (248.4 nm) and the carbon peaks. Thus the resolution of the spectrometer is an important parameter to be remembered during configuration of an instrument for analysis of soils that have a high iron content with the LIBS technique. So too are complications associated with soil water content and attenuation of carbon signal in moist soils (data not shown).

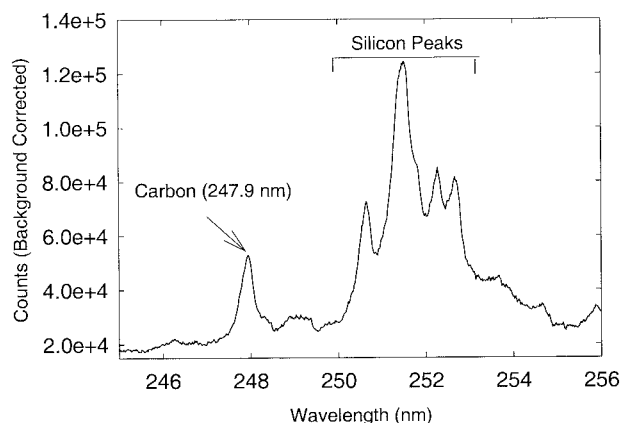


Fig. 2. LIBS spectrum for carbon in soil.

The LIBS signal and the carbon content concentration obtained from the combustion method were highly correlated (Fig. 3) with a coefficient of correlation of 0.962. Fifteen soils were sampled from Oak Ridge National Laboratory's NABIR FRC with carbon percentages, by weight, of 0.16, 0.2, 0.25, 0.48, 0.52, 0.85, 0.91, 0.95, 1.18, 1.62, 2.19, 2.61, 3.57, 4.22, and 4.32% used in the comparison. The standard deviation from the slope of the regression curve calculated for the soil carbon content is in the 10–15% range. Ten laser shots were used for each soil sample analysis. As expected, the standard deviation was higher for the soils with low carbon concentration. This is because, in the LIBS measurement, at lower carbon concentrations the iron peak is dominant, which in turn smears the carbon peak, making it difficult to calculate the area under the carbon peak and determine the peak intensities. Also, the small sample of soil present in the plasma is not necessarily a good representation of the whole soil. To deal with this problem, the pellets were prepared from the homogenized soil samples and 20 pellets from each homogenized soil sample were prepared. The LIBS measurements were made with a ten-shot averaging for each soil measurement in which the ten shots were taken while each pellet was moved around to cover a larger area while the pellet is sampled. The standard deviation can be reduced if multiple sam-

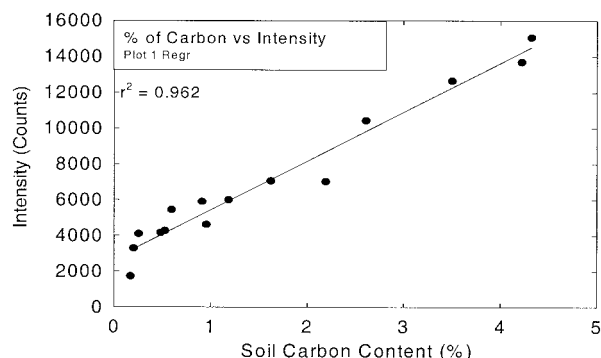


Fig. 3. LIBS signal versus soil carbon content measured with the LECO CN-analyzer.

Table 1. Measurement of Standard Deviation for Two Soils with Two Techniques for Carbon Determination<sup>a</sup>

Soil	Combustion Method (std. dev.) (sample size of 0.5–0.6 g) (%)	LIBS Technique (std. dev.) (sample size of 50–80 ng) (%)
Synthetic LECO soil	0.5	4.56
DOE-FRC soil <sup>b</sup>	3.6	6.7

<sup>a</sup>Ref. 1.

<sup>b</sup>U.S. Department of Energy Field Research Center.

ples of each soil are measured and more laser shots are averaged.

To test whether we can reduce the variation of the soil carbon LIBS signal, two different soils were analyzed at least ten times with the LIBS technique and compared with data from the LECO CN-2000 analyzer. One of the soils was supplied by the LECO Corporation as a calibration standard. The calibration standard has a carbon concentration of 2.61% and was traceable to NIST 8704, which is Buffalo River sediment @3.351% of carbon. This means that the LECO CN-analyzer was initially calibrated by use of the Buffalo River sediment, which contained 3.351% of carbon, and then a synthetically prepared soil standard by the manufacturer was measured with the instrument that had a carbon concentration of 2.61%. This was done to ensure that carbon and nitrogen concentrations measured with the LECO CN-analyzer were highly accurate and correlated to the NIST measurements. The other soil was obtained from a U.S. Department of Energy (DOE) field research site at Oak Ridge. The percent variation in carbon determinations in the two soils by the two different techniques is tabulated in Table 1. This table shows reduced variation in carbon measurements with the LIBS technique with the greater number of shots, but the variation was still noticeably greater than with the combustion method. The reason for a larger variation in measurements with the LIBS technique is explained by the amount of soil that is sampled by each laser shot. In the case of the combustion method, the amount of sample tested is 0.5–0.6 g. For LIBS measurements, the laser was focused to a spot diameter of 10  $\mu\text{m}$ , corresponding to only tens of nanograms of material tested in one shot. Increasing the number of shots for each measurement can reduce the standard deviation in carbon measurements with the LIBS technique. The number of shots typically used in the measurements shown above is only ten, totaling less than 6 s at a repetition rate of 1.65 Hz. If we accumulate 100 shots, the measurements would take only ~60 s, which is still considered to be a near-real-time measurement. Even though carbon concentrations in soils change slowly, the mapping for carbon concentration in all of the terrestrial areas would be a mammoth task to undertake with traditional carbon combustion techniques. Well-established techniques that can accomplish quick verification of base-

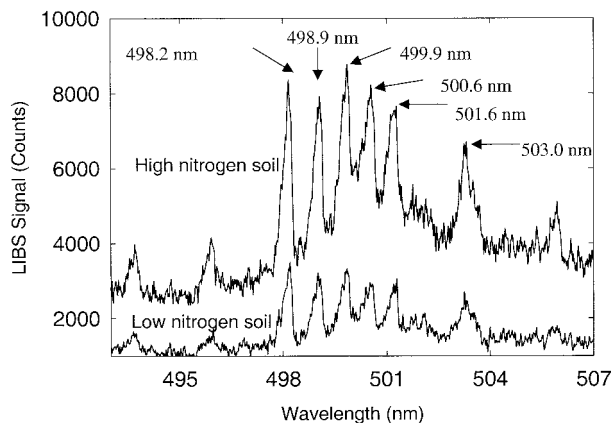


Fig. 4. LIBS signal for nitrogen in soils.

line amounts of sequestered quantities of carbon are needed.

Nitrogen is also an important component of SOM and is a significant constituent of proteins, nucleic acids, porphyrins, and alkaloids;<sup>21</sup> and LIBS has potential to measure the nitrogen component of soil. The major nitrogen forms present in SOM are protein-N, peptide-N, amino-acid-N, amino sugar-N, ammonia-N, nitrogen in purines and pyrimidines, and nitrogen in heterocyclic ring structures—many of which have yet to be identified.<sup>18</sup> One additional advantage of the LIBS technique is the simultaneous measurement of nitrogen and carbon concentrations in soils. Preliminary LIBS data of nitrogen concentrations in soils indicated that this technique could be used successfully to measure total soil nitrogen. Figure 4 shows the typical spectra for elemental nitrogen for two different kinds of soil. The nitrogen peaks are characteristic of their ionic transitions at 498.2, 498.9, 499.9, 500.6, 501.6, and 503.0 nm.

Since air contains 78% nitrogen, care was taken to ensure that these peaks were not due to atmospheric nitrogen (i.e., the plasma formed at the soil surface will engulf the surrounding atmosphere, and nitrogen from the air will also be excited in the plasma plume). The laser power was reduced (usually 35 mJ of laser energy/pulse is used, but in this case only 23 mJ was used) so that no plasma was formed in the air above the soil sample. The nitrogen peaks shown in Fig. 4 were obtained only when the laser beam was focused on the surface of the soil sample. Another sample of similar consistency, which did not contain nitrogen, was placed at the focus of the laser beam. After plasma formation at the sample's surface, these nitrogen peaks did not appear. Hence it was concluded that the nitrogen peaks observed in Fig. 4 were due to the presence of soil nitrogen. In this experiment only five shots were used for data accumulation, which means that each spectrum was acquired in approximately 3 s.

Figure 5 shows the concentration of carbon and nitrogen for three different soil types from mined lands in southwest Virginia. These mined soils are very rocky, ranging from 40% to 80% coarse frag-

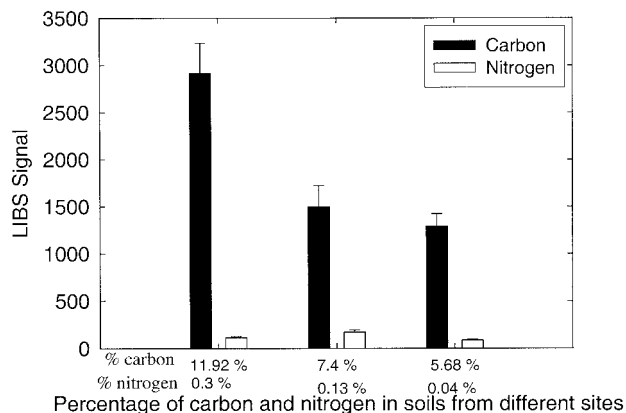


Fig. 5. LIBS signal as a function of carbon and nitrogen in non-acid-washed soils.

ments at all depths sampled. The carbon and nitrogen contents obtained with LIBS correlated well with concentrations obtained by use of the LECO CN-2000 analyzer. The soils were not acid washed; thus the concentrations of carbon in Fig. 5 reflect total soil carbon concentrations (i.e., inorganic and organic soil carbon). LIBS spectra of 10 shots were obtained for 20 pelletized samples of each soil type. The standard deviation associated with these samples was in the range of 7–10%. Three of the same soil samples were washed with acid to dissolve the inorganic carbon, and LIBS data were obtained for 20 pellets of each soil type, again averaged over 10 shots each. The LIBS signal due to carbon, nitrogen, and silicon present in the acid-washed soils is plotted in Fig. 6. The amount of silicon present in the mined land soils was similar but not equal for each soil type. The carbon concentrations for the acid-washed soils varied from 1.6% to 7.4%. Acid washing reduced the LIBS carbon signal by almost 60% (shown in the inset in Fig. 6). However, the LIBS signal for nitrogen was unchanged, indicating that the acid treatment removed only the inorganic soil carbon. The nitrogen is usually bonded to the organic carbon, and thus the signal for nitrogen does not change. The standard deviation for the acid-washed soils increased to 15% from a variation of 7% for pre-acid-washed soils, which was attributed to the change in the soil matrix after acid washing. Acid-washed soils had a different packing density (i.e., they appeared to have more porosity) and were more difficult to pelletize than untreated soil samples. There are three ways in which we can improve the reproducibility and reliability of soil analysis: (1) increasing the number of shots and averaging of the spectra over more shots (100 instead of 10), (2) applying the method intensity ratios of two elements present in all soils (e.g., silicon or aluminum), and (3) using the linear correlation technique.<sup>19,20</sup>

Incorporation of increase in spectral averaging has proven to be quite successful as discussed above. The ratio of carbon to silicon has been used to improve the reliability of the soil carbon and nitrogen data and to reduce the standard deviation in carbon



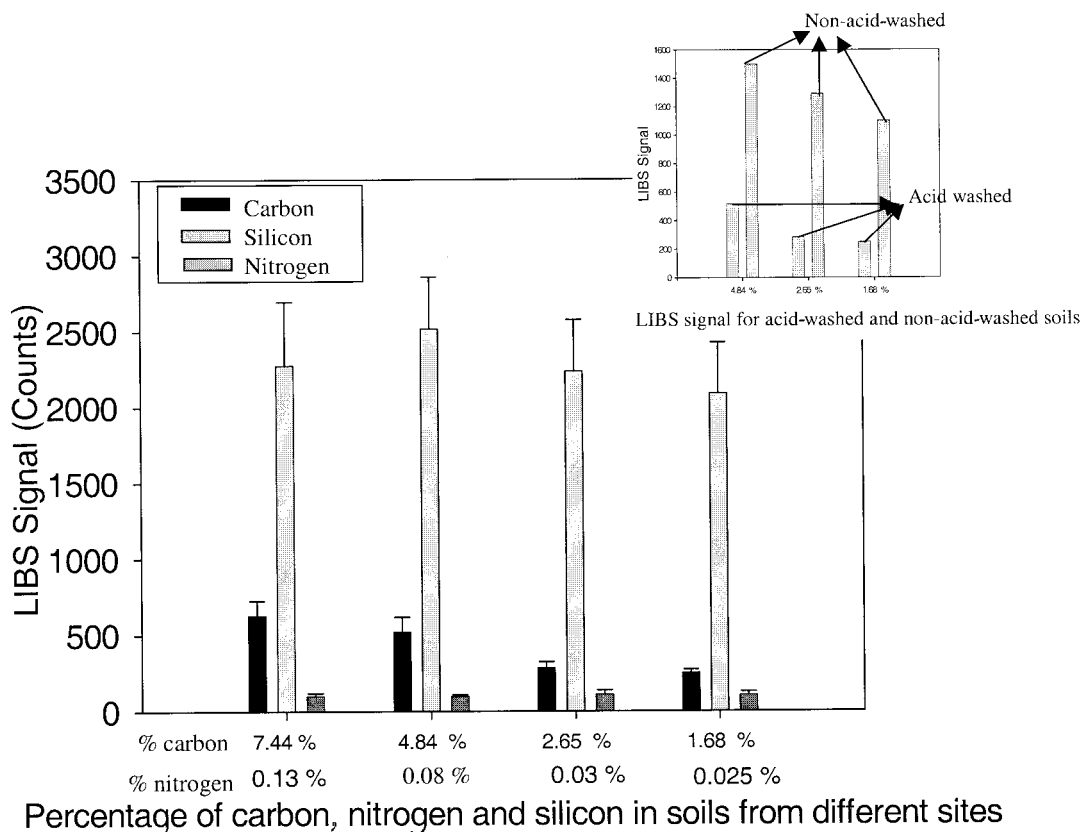


Fig. 6. LIBS signal for different non-acid-washed (inset) and acid-washed soils.

and nitrogen measurements using LIBS. The standard deviation was reduced to  $\sim 8\%$  for the acid-washed soils after the carbon signal was normalized to the silicon signal. The ratio of carbon to silicon (C/Si) was used in the calibration for the acid-washed soils (Fig. 7). The small variation in the silicon contents of each soil type was used very effectively to reduce the standard deviation in soil carbon analysis. Other authors<sup>21</sup> have used the C/Si ratio method when LIBS was used to determine carbon in soils. The third way to reduce variation of the carbon signal in soil matrices is done by applying a technique of linear correlation that uses the theory of covariance.

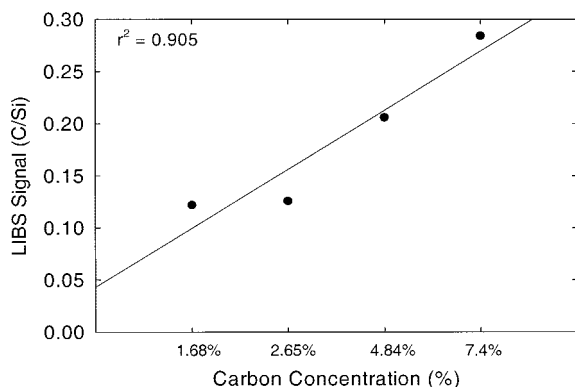


Fig. 7. LIBS signal (ratio of C/Si) as a function of the percentage of carbon in acid washed soils.

Covariance is a measure of the tendency of two variables to vary together (to co-vary). It has been established that shape and position of the calibration curve are not affected by detector sensitivity or baseline-level variations, as long as the whole spectrum is affected uniformly. The outcome of the linear correlation technique is that it successfully suppresses the effect of signal-intensity fluctuations.

In conclusion, carbon measurements by conventional combustion methods and LIBS were determined to be in good agreement in 15 different soils. LIBS was also used successfully to determine the nitrogen content of various soils. Comparing the LIBS signals for carbon, nitrogen, and silicon before and after acid washing suggests that a strategy to determine the inorganic and organic carbon present in the soils can be established for future experiments. The ratio of two elements (C/Si) was used to improve the correlation between the LIBS signal and conventional soil carbon measurements.

In this study we have shown that instrumentation and operation of a LIBS system is simpler than with some of the more sensitive laser-based techniques (for example, induced by coupled plasma-mass spectrometry), and analysis times of the order of minutes make it amenable for real-time, *in situ* analysis and environmental monitoring of soil carbon and nitrogen. Furthermore, this technique requires little or no sample preparation, thus making it an attractive

alternative to existing methods of soil carbon and nitrogen analysis.

We acknowledge Bonnie Lu for analyzing the 15 soils using the LECO CN-2000. A special thanks goes to Jena Tarver, who did all the acid washing and the task of making pellets of the soil samples. We also extend our thanks to Deanne Brice, who helped with the LIBS measurements and made sure that the soil pellets were sampled in a reproducible and repeatable manner. This research has been sponsored by the Laboratory Directed Research and Development (LDRD) program of Oak Ridge National Laboratory, managed by University of Tennessee-Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725. Additional support was provided by the DOE Office of Fossil Energy though the National Energy Technology Laboratory.

## References

1. D. Read, D. Beerling, M. Cannell, P. Cox, P. Curran, J. Grace, P. Ineson, Y. Malhi, D. Powlson, J. Shepherd, and I. Woodward, in *The Role of Land Carbon Sinks in Mitigating Global Climate Change* (The Royal Society, London, 2001), pp. 1–27.
2. M. Schnitzer and U. Khan, *Humic Substances in the Environment* (Marcel Dekker, New York, 1972), pp. 2–3.
3. F. J. Stevenson, *Humus Chemistry* (Wiley, New York, 1982), pp. 1–25.
4. S. J. Weeks, H. Haraguchi, and J. D. Winefordner, "Improvement of detection limits in laser-excited atomic fluorescence flame spectrometry," *Anal. Chem.* **50**, 360–368 (1978).
5. S. Sjöström and P. Mauchien, "Laser atomic spectroscopic techniques—the analytical performance for trace element analysis of solid and liquid samples," *Spectrochim. Acta Part B*, **15**, 153–180 (1991).
6. S. Rudnick and R. Chen, "Laser-induced fluorescence of pyrene and other polycyclic aromatic hydrocarbons (PAH) in seawater," *Talanta* **47**, 907–919 (1998).
7. C. M. Preston, S.-E. Shipitalo, R. L. Dudley, C. A. Fyfe, S. P. Mathur, and M. Levesque, "Comparison of  $^{13}\text{C}$  CPMAS NMR and chemical techniques for measuring the degree of decomposition in virgin and cultivated peat profiles," *Can. J. Soil Sci.* **67**, 187–198, (1987).
8. O. Francioso, S. Sanchez-Cortes, V. Tugnoli, C. Ciavatta, L. Sitti, and C. Gessa, "Infrared, Raman, and nuclear magnetic resonance ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ) spectroscopy in the study of fractions of peat humic acids," *Appl. Spectrosc.* **50**, 1165–1174 (1996).
9. O. Francioso, S. Sanchez-Cortes, V. Tugnoli, C. Ciavatta, and C. Gessa, "Characterization of peat fulvic acid fractions by means of FT-IR, SERS, and  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy," *Appl. Spectrosc.* **52**, 270–277 (1998).
10. O. Francioso, C. Ciavatta, S. Sanchez-Cortes, V. Tugnoli, L. Sitti, and C. Gessa, "Spectroscopic characterization of soil organic matter in long-term amendment trials," *Soil Sci.* **165**, 495–504 (2000).
11. Y. Yang and H. A. Chase, "Applications of Raman and surface-enhanced Raman scattering techniques to humic substances," *Spectrosc. Lett.* **31**, 821–848 (1998).
12. T. Wang, Y. Xiao, Y. Yang, and H. A. Chase, "Fourier transform surface-enhanced Raman spectra of fulvic acid from weathered coal adsorbed on gold electrodes," *J. Environ. Sci. Health A* **34**, 749–765 (1999).
13. E. J. Liang, Y. Yang, and W. Kiefer, "Surface-enhanced Raman spectra of fulvic and humic acids adsorbed on copper electrodes," *Spectrosc. Lett.* **32**, 689–701 (1999).
14. K. A. Magrini, R. J. Evans, C. M. Hoover, C. C. Elam, and M. F. Davis, "Use of pyrolysis molecular beam mass spectrometry (py-MBMS) to characterize forest soil carbon: method and preliminary results," *Environ. Poll.* **116**(Suppl. 1), S255–S268 (2002).
15. C. M. Hoover, K. A. Magrini, and R. J. Evans, "Soil carbon content and character in an old-growth forest in northern Pennsylvania: a case study introducing pyrolysis molecular beam mass spectrometry (py-MBMS)," *Environ. Poll.* **116**(Suppl. 1), S269–S275 (2002).
16. M. Martin, S. Wulfschleger, and C. Garten Jr., "Laser-induced breakdown spectroscopy for environmental monitoring of soil carbon and nitrogen," in *Advanced Environmental Sensing Technology II*, T. Vo-Dinh and S. Buettgenbach, eds., *Proc. SPIE* **4576**, 188–195 (2002).
17. D. A. Cremers, M. H. Ebinger, D. D. Breshears, P. J. Unkefer, S. A. Kammerdiener, M. J. Ferris, K. M. Catlett, and J. R. Brown, "Measuring total soil carbon with laser-induced breakdown spectroscopy (LIBS)," *J. Environ. Qual.* **30**, 2202–2206 (2001).
18. S. E. Trumbore and S. Zheng, "Comparison of fractionation methods for soil organic matter  $^{14}\text{C}$  analysis," *Radiocarbon* **38**, 219–229 (1996).
19. M. Schnitzer, *Humic Substances in Soil, Sediment and Water* (Wiley New York, 1985), pp. 303–325.
20. I. B. Gornushkin, B. W. Smith, H. Nasajpour, and J. D. Winefordner, "Identification of solid materials by correlation analysis using a microscopic laser-induced plasma spectrometer," *Anal. Chem.* **71**, 5157–5164 (1999).
21. G. Galbacs, I. B. Gornushkin, B. W. Smith, and J. D. Winefordner, "Semiquantitative analysis of binary alloys using laser-induced breakdown spectroscopy and a new calibration approach based on linear correlation," *Spectrochim Acta Part B* **56**, 1159–1173 (2001).