

Analysis of total nitrogen and total phosphorus in soil using laser-induced breakdown spectroscopy

Cuiping Lu (鲁翠萍)*, Liusan Wang (汪六三), Haiying Hu (胡海瀛), Zhong Zhuang (庄重),
Yubing Wang (汪玉冰), Rujing Wang (王儒敬), and Liangtu Song (宋良图)

Laboratory of Intelligent Decision, Institute of Intelligent Machines,
Chinese Academy of Sciences, Hefei 230031, China

*Corresponding author: lcphu1983@126.com

Received December 3, 2012; accepted February 25, 2013; posted online April 24, 2013

Laser-induced breakdown spectroscopy (LIBS) is used to determine the total nitrogen (TN) and total phosphorus (TP) in soil. Quantitative determinations are conducted using the line intensity of the analyte element and element concentration. Calibration models are obtained using ten samples for TN and seven samples for TP. The rest samples are used to validate the results. Strong linear correlations are obtained from the determined TN and TP concentrations. LIBS is a powerful tool for analyzing soil samples to determine nutrient elements by selecting calibration and validation samples with similar matrix composition.

OCIS codes: 300.6365, 300.6210, 140.3440.

doi: 10.3788/COL201311.053004.

The rapid determination of soil organic matter (SOM), total nitrogen (TN), total phosphorus (TP), and total potassium concentrations is a key factor for analyzing soil fertility and reducing the agricultural costs. Traditional analytical chemical methods and different spectroscopic techniques, such as inductively coupled plasma (ICP) optical emission spectrometry, ICP mass spectrometry, and flame atomic absorption spectrometry, are used to determine element concentrations in soil. These analytical methods require time consuming and costly collection and pretreatment of samples prior to analysis. Furthermore, these techniques cannot detect *in situ*. Thus, a reliable analytical method in precision agriculture should be developed to provide quality information of soil fertility in real time.

Laser-induced breakdown spectroscopy (LIBS), a type of atomic emission spectroscopy, is based on the spectral analysis of characteristic emission from micro-plasma generated by focusing a high-power pulsed laser beam onto the surface of a sample. The characteristic emission plasma is then analyzed to determine the constituents of the sample^[1–7]. Compared with conventional analytical techniques, LIBS exhibits several advantages such as negligible sample pretreatment, high sensitivity, real-time response, simultaneous multi-elemental detection of major and trace elements, and low detection limit. However, compared with conventional analytical techniques that generally provide better detection limits and accuracy, LIBS has some constraints on the quantitative analysis of elements in chemically complex matrices. On the analytical point of view, LIBS is a well-established technique for elemental analysis. Different analytical approaches may be used for this technique, such as calibration curve method with matrix-matched standards, calibration-free method, and multivariate analysis. Furthermore, the LIBS apparatus can be easily assembled for portable instrumentation.

LIBS is used in various fields^[8–13]. In particular, the application of LIBS in agriculture for heavy metal pollution, soil fertility, plant materials, and fertilizer has

attracted great interest^[14–17]. Capitelli *et al.*^[14] used LIBS to analyze heavy metals in soil samples. Important nutrient elements (Ca, K, P, Mg, S, Ni, and Ba) were determined by Hussain *et al.*^[15] in soil from a greenhouse. Groisman *et al.*^[16] used LIBS to measure K, Na, and Mg in raw material of potassium fertilizer. The application of LIBS for determining macro and micronutrients in plant materials has recently been reported by Nunes *et al.*^[17].

The analysis of several studies that used LIBS to analyze soil nutrients^[18–21] focused on total C, inorganic C, organic C, and TN in soil. Few studies have focused on TP in soil. This letter mainly concerned on the fast and accurate analysis of TN and TP in soil samples using LIBS. Thirty-three fine powder soil samples were compressed into pellets and prepared for LIBS measurements. The results of the measurement of TN and TP under argon atmosphere conditions are shown and discussed. This letter provides technical support for precision agriculture.

The LIBS instrument used for this letter is shown in Fig. 1. A 1064-nm Q-switched Nd:YAG laser (5-ns pulse width, 50 mJ; Ultra, Quantel, France) with 1-Hz repetition rate was used in the experiment. The laser beam diameter was 6 mm with quality factor M^2 lower than 2. The laser pulse was focused with a 2.54-cm diameter and 10-cm focal length lens to create microplasma on the soil surface. The plasma emission was collected by a coupling lens with 50-mm focal length at 30° to the incident laser beam and fiber-coupled (1.5 m, 50 μ m in core diameter) to an Andor spectrometer. The spectrometer was equipped with Echelle optics with focal length of 19.5 cm, 1:7 numerical aperture, and 13.3×13.3 (mm) flat image plane. The spectral range was from 200 nm to 850 nm, and the spectral resolution was 0.1 nm at 500 nm. The detector was an intensified charge-coupled device (CCD) array. A micro-channel plate image intensifier, with 18-mm diameter, coupled to an ultraviolet (UV)-enhanced photocathode was used. DG 535 was

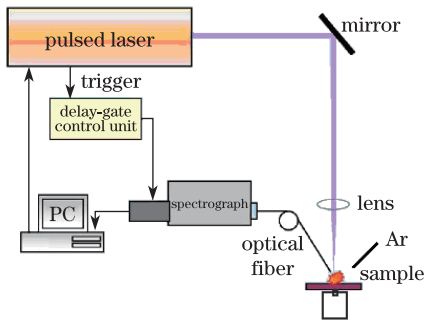


Fig. 1. LIBS experimental system.

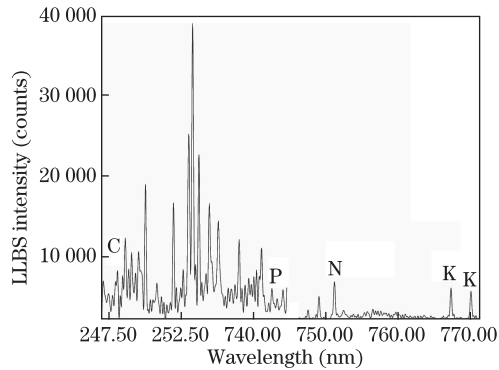


Fig. 2. LIBS spectrum of soil sample.

Table 1. Reference Concentration Range of the Soil Samples

Element	Concentration Intervals (mg/kg)
TP	812-1513
TN	2 040-3 200
Available K	188-336
SOM	50.3-69.7

used to control the delay time between the laser and spectrometer. The spectrometer generated a pulse to excite the laser, which triggered the DG 535. After a delay time, the DG 535 triggered the spectrometer to begin collecting spectra. Based on previous studies, the delay time between the laser beam and beginning scan of the spectrometer was set at 1 μ s with a gate width of 5 μ s.

This letter primarily aims to analyze the TN and TP concentrations in soil. Thirty-three soil samples were collected from a farmland in China. In principle, the concentration of the selected calibration samples should cover the range of variation of the TN and TP concentrations in soil. The reference concentrations of TN and TP in these soil samples were analyzed by standard analytical chemical methods, and the concentration ranges are presented in Table 1. The N and P calibration models were established using 10 and 7 soil samples, respectively. The N and P calibration models and accuracy of LIBS were validated using 23 and 26 soil samples, respectively.

All collected soil samples were ground to reduce heterogeneity. After grinding, the samples were sieved using a wire sieve with <1 mm particle size. Soil pellets were prepared using 5 g of each sample. The sample powder was transferred to a 30-mm-diameter and 50-mm-high pellet die. The sample was then compressed with 10 tons

of pressure to 2-mm thickness.

All measurements were conducted in argon atmosphere to avoid N in air. The soil pellet was mounted on an x - y rotary stage, which was constantly rotated with a stepper motor to minimize soil heterogeneity. Twenty spectra were averaged from each pellet to improve the signal/noise and reduce statistical error caused by laser shot-to-shot fluctuation. Each soil pellet was measured eight times.

Figure 2 represents the average spectrum from 20 spectra of the soil pellets from 247 to 256 nm and from 740 to 772 nm, which includes the emission lines of C, P, N, and K elements in soil. The spectrum was intensity-calibrated. Strong elemental emission lines of N are observed in the spectrum, but the emission lines of P are relatively weak.

The LIBS spectrum depicting the P peak at 255.5 nm is shown in Fig. 2. The main atomic emission lines of P at the UV spectral region are 253.4, 253.6, 255.3, and 255.5 nm. The Fe concentration in the soil samples is relatively high, and the characteristic lines of Fe are rich. The 253.4 and 253.6 nm peaks of P are interfered by the emission lines of Fe (253.4 and 253.6 nm). Thus, the identified line P I 255.5 nm was selected as the analytical line.

Soil composition is very complex, and spectral overlap is common. Thus, the resolution of the spectrometer is an important parameter when LIBS is used to analyze the soil samples. The triple lines of N at 742.4, 744.2, and 746.8 nm are clearly visible in the spectrum. The emission line N I 746.83 nm is selected to analyze the soil samples because this line is not interfered by the emission lines of other elements. Considering that air contains 78% N, the N in air and soil are simultaneously measured when LIBS is used to analyze the soil samples in air. The aim of this study is to measure the TN in soil, so the measurement is conducted in argon atmosphere. Given that total C and K concentrations are unknown, this study does not study the measurement of total C and K. For future studies, C I 247.9 nm and K I 766.5 nm should be selected as analytical lines.

The characteristic line of the elements is fitted by Lorentz profile. The peak intensity was used as the LIBS signal and normalized from peak to base. Generally, the LIBS quantitative analysis is based on the relationship between the elemental emission line intensity and its concentration. Ten soil samples with TN concentrations varying from 0.204% to 0.32% were used for the calibration model. Seven soil samples were used for the calibration model of P, with TP concentrations varying from 0.081% to 0.151%. The correlation between the elemental line intensity and N and P concentrations are shown in Figs. 3 and 4, respectively. Line intensity and concentration are obviously correlated. The correlation coefficients (R) for N and P are 0.989 and 0.981, respectively.

The intercept of the P calibration curve is larger than that of N, which is attributed to the weak signal of P in the UV range. Moreover, the linear correlation of the line intensity and concentration is affected by matrix effects.

The TN and TP concentrations of the 23 and 26 soil samples, respectively, are unknown. These samples were used to estimate the ability and prediction accuracy of

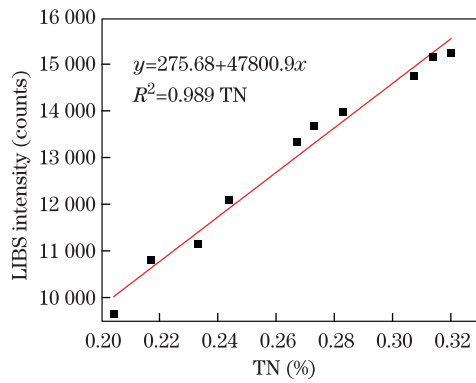


Fig. 3. LIBS intensity as a function of the percentage of TN in soil.

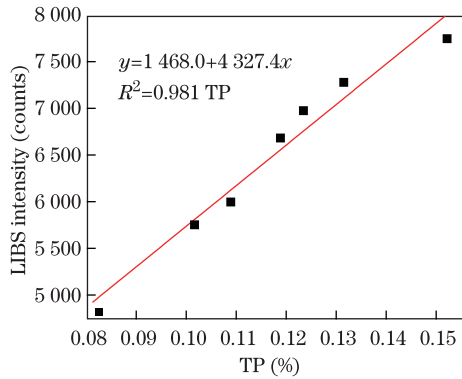


Fig. 4. LIBS intensity as a function of the percentage of TP in soil.

LIBS for analyzing TN and TP concentrations. Each sample was measured eight times under similar conditions as the calibration samples to examine the repeatability of LIBS. Twenty spectra were averaged for each measurement.

The relation between the LIBS-predicted concentration and reference concentration for TN and TP are shown in Figs. 5 and 6, respectively. The correlation coefficient of N is 0.981, but the slope of calibration curve is 0.976. For P, the slope of calibration curve is 0.993, but the correlation coefficient is 0.868.

Humus-N, protein-N, peptide-N, amino-acid-N, ammonia-N, and nitrate-N, the primary forms of N in soil, can be easily excited by laser. Preliminary results indicate that LIBS can be successfully used to measure TN in soil. TN and C concentrations in soil are important. In this letter, the analytical chemical method provided the concentration of organic C but not the total C content in soil. Therefore, the relevance between TN and C is not discussed in this letter.

The primary forms of P in soil include water-soluble phosphorus compounds, acid-soluble P compounds, insoluble phosphate compounds, inositol phosphate, nucleic acids, and phospholipids. The characteristic lines of P are in the UV spectral range, and the concentration of P in soil is low. Thus, the signal of P is weak. The correlation coefficient of the prediction model is low, which may be ascribed to the other elements present in the soil matrix. The line intensity of P may be affected by Ca, Mg, Al, Fe, K, and Na. To improve the prediction correlation coefficient, multivariate quantitative

method should be conducted. This quantitative method is performed using chemometric tools such as partial least squares, interval partial least squares, and artificial neural networks. This quantitative method will be discussed in future studies.

For measurements, the absolute error is the difference between the measured and true values, whereas the relative error is the absolute error divided by the true value. The absolute errors between the reference and averaged measurement concentrations of N range from 0.0002% to 0.0144%. The relative errors for N range from 0.06% to 5.39%. For P, the absolute and relative errors range from 0.00006% to 0.0207% and from 0.06% to 17.48%, respectively. The average absolute and relative errors of N are 0.0053% and 2.07%, respectively, whereas those of P are 0.0068% and 6.07%, respectively. These results indicate that the accuracy of the quantitative analysis and reproducibility of TN are better than those of TP. These characteristics may have resulted from soil complexity, sample inhomogeneity, and different matrix effects of each element. The global error of the prediction results is attributed to the calibration model, uncertainties on the reference concentrations measured by analytical chemical methods, and LIBS.

In conclusion, the calibration models of TN and TP are developed. The model successfully predicts the TN concentration with high coefficient correlation. The prediction correlation coefficient of TP is lower than that of TN, indicating that other elements in the soil affected the line intensity of P. Validation with the unknown samples for TN and TP concentrations show that LIBS has high measurement accuracy and reproducibility. The

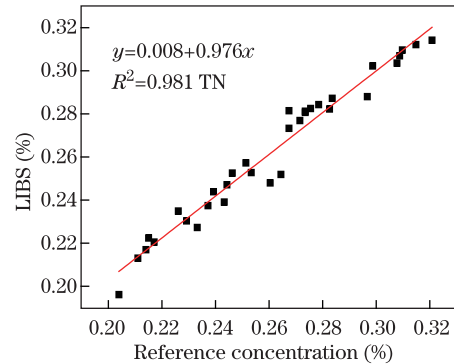


Fig. 5. Comparison of TN predicted by LIBS and chemical analysis.

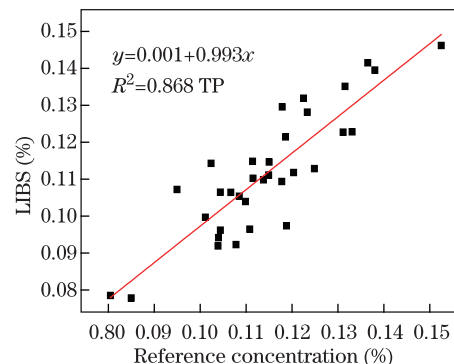


Fig. 6. Comparison of TP predicted by LIBS and chemical analysis.

analysis results confirm that LIBS has good potential for the development and implementation of instruments for *in situ* and on-line measurement of soil fertility.

The authors gratefully acknowledge Anhui University of Traditional Chinese Medicine (Hefei, China) for the analysis of elemental concentration in soil. This work was supported by the National Natural Science Foundation of China under Grant No. 61205146.

References

1. L. J. Radziemski, *Microchem. J.* **50**, 218 (1994).
2. D. A. Rusak, B. C. Castle, B. W. Smith, and J. D. Winefordner, *Crit. Rev. Anal. Chem.* **27**, 257 (1997).
3. A. W. Miziolek, V. Palleschi, and I. Schechter, *Laser-Induced Breakdown Spectroscopy (LIBS): Fundamentals and Applications* (Cambridge University Press, Cambridge, 2006).
4. L. J. Radziemski, *Spectrochim. Acta B* **57**, 1109 (2002).
5. I. B. Gornushkin, A. Y. Kazakov, N. Omenetto, B. W. Smith, and J. D. Winefordner, *Spectrochim. Acta B* **59**, 401 (2004).
6. D. A. Cremers and L. J. Radziemski, *Handbook of Laser-Induced Breakdown Spectroscopy* (Wiley, Chichester, 2006).
7. J. P. Singh and S. N. Thakur, *Laser-Induced Breakdown Spectroscopy* (Elsevier, Amsterdam, 2007).
8. D. K. Ottesen and J. C. F. Wang, *Appl. Spectrosc.* **43**, 967 (1989).
9. Y. Feng, J. Yang, J. Fan, G. Yao, X. Ji, X. Zhang, X. Zheng, and Z. Cui, *Appl. Opt.* **49**, c70 (2010).
10. G. G. A. de Carvalho, L. C. Nunes, P. F. de Souza, F. J. Krug, T. C. Alegrec, and D. S. Jr, *J. Anal. At. Spectrom.* **25**, 803 (2010).
11. K. E. Eseller, M. M. Tripathi, F. Yueh, and J. P. Singh, *Appl. Opt.* **49**, c21 (2010).
12. H. Hakkanen, J. Houni, S. Kaski, and J. Korppi-Tommola, *Spectrochim. Acta B* **56**, 737 (2001).
13. X. K. Shen, H. Wang, Z. Q. Xie, Y. Gao, H. Ling, and Y. F. Lu, *Appl. Opt.* **48**, c75 (2009).
14. F. Capitelli, F. Colao, M. R. Provenzano, R. Fantoni, G. Brunetti, and N. Senesi, *Geoderma* **106**, 45 (2002).
15. T. Hussain, M. A. Gondal, Z. H. Yamani, and M. A. Baig, *EnvFe. Monit. Assess.* **124**, 131 (2007).
16. Y. Groisman and M. Gaft, *Spectrochim. Acta B* **65**, 744 (2010).
17. L. C. Nunes, J. W. B. Braga, L. C. Trevizan, P. F. de Souza, G. G. A. de Carvalho, D. S. Junior, R. J. Poppi, and F. J. Krug, *J. Anal. At. Spectrom.* **25**, 1453 (2010).
18. M. Z. Martin, S. D. Wullschleger, C. T. Garten Jr, and A. V. Palunbo, *Appl. Opt.* **42**, 2072 (2003).
19. K. K. Ayyalasomayajula, F. Yu-Yueh, J. P. Singh, D. L. McIntyre, and J. Jain, *Appl. Opt.* **51**, B149 (2012).
20. M. V. Belkov, V. S. Burakov, A. De Giacomo, V. V. Kiris, S. N. Raikov, and N. V. Tarasenko, *Spectrochim. Acta B* **64**, 899 (2009).
21. R. S. Bricklemeyer, D. J. Brown, J. E. Barefield, and S. M. Clegg, *Soil Sci. Soc. Am. J.* **75**, 1006 (2011).