CrossMark

Laser-induced breakdown spectroscopy: Extending its application to soil pH measurements

Edilene Cristina Ferreira [a,*], José A. Gomes Neto [a], Débora M.B.P. Milori [b], Ednaldo José Ferreira [b], Jesús Manuel Anzano [c]

[a] São Paulo State University – UNESP, Analytical Chemistry Department, Rua Prof. Francisco Degni 55, CEP 14800-060, Araraquara, SP, Brazil
[b] Embrapa Agricultural Instrumentation, Rua XV de Novembro 1452, CEP 13560-970, São Carlos, SP, Brazil
[c] Laser Laboratory & Environment, Faculty of Sciences, University of Zaragoza, C/. Pedro Cerbuna 12, 50009, Zaragoza, Spain

ARTICLE INFO

ABSTRACT

Acid–base equilibria are involved in almost all the processes that occur in soil. The bioavailability of nutrients for plants, for instance, depends on the solubilization of mineral nutrients in the soil solution, which is a pH-dependent process. The determination of pH in soil solutions is usually carried out by potentiometry using a glass membrane electrode, after extracting some of the soil components with water or $CaCl_2$ solution. The present work describes a simple method for determining the pH of soil, using laser-induced breakdown spectroscopy (LIBS). Sixty samples presenting different textural composition and pH (previously determined by potentiometry) were employed. The samples were divided into a calibration set with fifty samples and a validation set with ten samples. LIBS spectra were recorded for each pelleted sample using laser pulse energy of 115 mJ. The intensities of thirty-two emission lines for Al, Ca, H, and O were used to fit a partial least squares (PLS) model. The model was validated by prediction of the pH of the validation set samples, which showed good agreement with the reference values. The prediction mean absolute error was 0.3 pH units and the root mean square error of the prediction was 0.4. These results highlight the potential of LIBS for use in other applications beyond elemental composition determinations. For soil analysis, the proposed method offers the possibility of determining pH, in addition to nutrients and contaminants, using a single LIBS measurement.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Acid–base equilibria are involved in almost all soil processes, and the physical, chemical, and biological properties of soil are all influenced by pH [1]. The bioavailability of plant nutrients depends on the solubilization of minerals or other nutrients in the soil solution, and this process is pH dependent. The pH can also affect the activity of microorganisms, altering the rate of decomposition of soil organic matter and consequently the release of nutrients [2]. The determination of soil pH is therefore crucial for agricultural soil use. For example, the correction of soil pH (in the case of soils presenting high acidity) by the application of bases relies on pH measurements.

The pH of mineral soils is normally determined using slurries of water and soil [1]. The use of $CaCl_2$ solution for determining the pH of soils was proposed by Schofield and Taylor [3], with the aim of minimizing interferences due to particles suspended in the soil solution and variable salt contents.

In 1990, the Soil Science Society of America (SSSA) and the Association of Official Agricultural Chemists (AOAC) decided to conduct collaborative studies in order to validate techniques applied to soils. Four potentiometric methods for soil pH measurement were considered, according to the characteristics of the soil: (a) pH measurement in a soil suspension obtained by stirring the sample with distilled or deionized water, applied to mineral soil samples containing less than 17% of organic carbon; (b) pH measurement in a soil suspension obtained by stirring the sample with 0.01 mol L^{-1} $CaCl_2$ solution, applied to mineral soils with variable salt content; (c) pH measurement in a soil paste obtained by moistening the sample with distilled or deionized water, applied to soils containing large amounts of soluble salts and sufficient exchangeable sodium; (d) pH measurement in an aqueous soil extract, applied to soils containing organic carbon at levels equal to or greater than 17%. Based on the results of this study, methods for pH measurements of mineral, saline-sodic, and organic soils were adopted by AOAC International [4].

Although the methods recommended by AOAC are effective, they involve the use of potentiometric measurements, which require the preparation of a soil solution for each sample [5]. Moreover, the dependence of the sample preparation method on the characteristics of the soil

* Corresponding author. Tel.: +55 16 33019616.
E-mail address: edilene@iq.unesp.br (E.C. Ferreira).

requires previous soil characterization, which complicates the analysis of a heterogeneous set of soil samples.

The present work proposes a new and simple method for the determination of soil pH, based on laser-induced breakdown spectroscopy (LIBS). LIBS is an optical technique capable of performing direct multi-element analysis, eliminating the need for the conventional preparation of sample solutions before analysis [6,7]. Moreover, LIBS has potential for use in analyses conducted *in situ*. LIBS measurements are based on recording light emissions from atomic and ionic species present in a sample, after their excitation in a transient plasma produced by a laser pulse. Typically, a LIBS spectrum provides qualitative information about the elemental composition of the sample, although the signal intensities for each wavelength can be used for quantitative determinations [7,8]. In this proposal, the LIBS emission lines of elements related to soil acidity were selected to fit a multivariate model for soil pH determination.

2. Experimental

A set of sixty soil samples with distinct textures was provided by the Agronomic Institute of Campinas (AIC, Campinas, Brazil). The samples were dried at 40 °C in an oven with air circulation and then passed through a sieve with 2 mm mesh openings.

The set of 60 samples was divided into two subsets: calibration and validation sets, containing 50 and 10 samples, respectively. The samples allocated to each group were randomly selected. No heuristics were used to balance the number of the samples in the calibration and validation sets, due to the relatively small number of samples.

As part of an AIC proficiency-testing program, several parameters (including pH) were determined for each soil sample by 89 Brazilian laboratories. The average pH values reported by AIC were used as reference values in the present work. The pH values of the 60 samples were from 4.0 to 6.3, with standard deviations ranging from 0.1 to 0.2 pH units.

For the LIBS analysis, the samples were submitted to cryogenic grinding in order to reduce their heterogeneity, using a SpexCertiprep Model 6750 cryogenic mill operated at liquid nitrogen temperature (−196 °C). The grinding program consisted of two grinding steps of 2 min, 3 min for pre-cooling, and 2 min for cooling between the grinding steps. This procedure produced particles in the 60–120 μm size range. The ground samples were used to prepare pellets by applying 10-ton pressure on a portion (~500 mg) of sample during 3 min. The pellets were analyzed by LIBS, recording ten spectra for each sample. The spectra obtained for each sample were then averaged, without any preprocessing, to obtain a representative spectrum per sample.

The LIBS system comprised a Nd:YAG laser (Brilliant Quantel, Q-Switched) with a second harmonic generator (SHG), an xyz stage carrying the sample (Standa 011957), a spectrograph, and an intensified charge-coupled device (ICCD) detector. The characteristics of the laser were maximum laser pulse energy of 115 mJ (operating at 532 nm), 4.4 ns pulse duration, and 10 Hz repetition frequency. The plasma light was collected and transported to the spectrograph through a lens and an optical fiber. An external collimator was used as the collecting lens. The position of the fiber relative to the collecting lens was adjusted by means of a divergent beam from a diode laser (HE-OPI-0009, Andor) connected to the fiber, which was focused on the sample position by the collecting system. This arrangement ensured that the light emitted by the sample was focused on the fiber. An Echelle spectrograph (Andor Mechelle ME5000, focal length 195 mm, F/7, spectral range from 200 to 975 nm) was coupled to an ICCD detector (Andor iStar DH734, 1024 × 1024 pixels, 13.6 × 13.6 μ^2/pixel, 18 mm intensifier diameter). This system was calibrated using a mercury–argon lamp (Ocean Optics HG-1, 253–922 nm).

The LIBS experimental conditions established for acquisition of the spectra were 115 mJ laser pulse energy, two pulses per site, delay time of 400 ns, and integration time gate of 25 μs.

Wavelengths corresponding to the core lines of Al, Ca, H, and O, and wavelengths in the wings of these core lines, were selected as follows: 373.665 nm (wing of the Ca II line), 373.688 nm (Ca II line), 393.308 nm (wing of the Ca II line), 393.333 nm (Ca II line), 393.357 nm (wing of the Ca II line), 394.419 nm (Al I line), 396.103 nm (wing of the Al I line), 396.128 nm (wing of the Al I line), 396.153 nm (Al I line), 396.178 nm (wing of the Al I line), 396.799 nm (wing of the Ca II line), 396.824 nm (Ca II line), 655.461 nm (O II line), 655.502 nm (wing of the O II line), 655.542 (wing of the O II line), 655.582 (wing of the O II line), 655.622 nm (wing of the O II line), 655.662 nm (wing of the O II line), 656.065 nm (wing of the H I line), 656.105 nm (H I line), 656.145 nm (wing of the H I line), 656.306 nm (wing of the H I line), 656.346 nm (wing of the H I line), 656.387 nm (wing of the H I line), 656.427 nm (wing of the H I line), 656.467 nm (wing of the O II line), 656.507 nm (O II line), 656.991 (wing of the O II line), 657.031 nm (wing of the O II line), 657.071 nm (wing of the O II line), 657.112 nm (O II line), and 657.152 nm (wing of the O II line). Using the selected lines, a partial least squares (PLS) model for the prediction of soil pH was constructed using centralization of the data on the average, with five latent variables. The calibration model took account of at least nine sources of variability, considering only the centers of the selected lines. The Weka v. 3.5.7 system (Waikato Environment for Knowledge Analysis) was used to build and validate the calibration model [9].
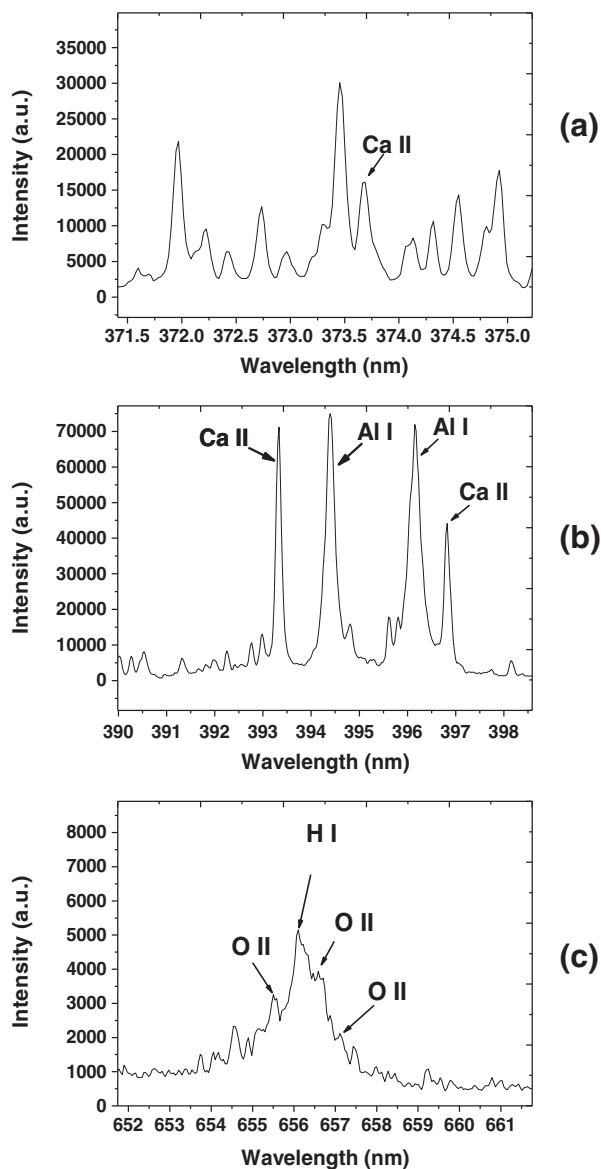
3. Results and discussion

A heterogeneous set of soils (in terms of texture) was used in order to obtain a robust model for pH determination, independent of the sample matrix. The proposed model could therefore offer important advantages compared to the AOAC method, where different textural classes of soils require separate extraction procedures [4].

The influence of pH on processes occurring in the soil is complex. Some well-known processes in which the pH varies as a function of exchangeable cations were therefore used as criteria to select independent variables for the calibration model. Soil liming, a procedure employed to increase soil pH, is performed by adding limestone derived from calcareous sedimentary rock containing calcium carbonate at levels exceeding 30% [10]. The presence of calcium in the soil can therefore be directly correlated to the pH. At acid pH, exchangeable aluminum predominates, while with liming, Al^+ is progressively precipitated and remains in the form of $Al(OH)_3$ in alkaline soil [11]. Considering these processes, wavelengths corresponding to the emission lines of Ca, Al, H, and O were selected. Additionally, with the aim of circumventing matrix effects and self-absorption, which could affect the cores of the selected emission lines, several wavelengths in the wings of the peaks were also selected. It is important to mention that although organic acids influence soil pH, the carbon line at 247.856 nm showed an unresolved iron interference (247.857 nm). Since the samples presented high iron contents, this carbon line could not be included. The spectral regions of the selected lines are shown in Fig. 1. The labeled peaks correspond to Ca II (373.688 nm) (Fig. 1a); Ca II (393.333 nm), Al I (394.419 nm), Al I (396.153 nm), and Ca II (396.824 nm) (Fig. 1b); and O II (655.461 nm), H I (656.105 nm), O II (656.507 nm), and O II (657.112 nm) (Fig. 1c).

An average spectrum was calculated from the ten replicates measured for each sample. The coefficients of variation observed for the selected lines ranged from 8% to 30%, depending on the sample composition and the wavelength used. Bousquet et al. [12] reported variability ranging from 10% to 25% in LIBS signals resulting from the ablation of a typical soil prepared as a pressed pellet. On this basis, the present data were considered acceptable for the construction of a multivariate calibration model.

To build the calibration model, the emission intensities at each selected wavelength for each calibration sample (independent variables) were organized in line vectors to obtain the X matrix (50 × 32), while pH values (dependent variables) corresponding to each calibration

Fig. 1. Extracts of a typical LIBS spectrum of a soil sample, highlighting the cores of selected emission lines: (a) Ca II 373.688 nm, (b) Ca II 393.333 nm, Al I 394.419 nm, Al I 396.153 nm, Ca II 396.824 nm, (c) O II 655.461 nm, H I 656.105 nm, O II 656.507 nm, and O II 657.112 nm.

Table 1
Reference and predicted pH values, and absolute errors of prediction, for ten samples of the validation set.

pH reference value	pH predicted value	Absolute error*
6.2	4.9	1.3
5.4	5.0	0.6
4.5	4.4	0.1
5.4	5.3	0.1
5.0	5.1	0.1
4.5	4.5	0.0
5.6	5.6	0.0
4.1	4.4	0.3
4.8	4.7	0.1
5.9	5.7	0.2

* Mean absolute error (MAE) = 0.3

The variances observed for the dependent variable (pH), of around 6%, were lower compared to those for the independent variables (wavelengths), which ranged from 8% to 30%. This indicates that despite the difficulties that high signal variability can cause for quantitative analysis of soil by LIBS, calibration models that use multiple variables (such as PLS) can minimize the influence of the variances as well as matrix and self-absorption effects.

These findings highlight the potential of LIBS for obtaining other important sample information, in addition to elemental composition, demonstrating that the technique can make a significant contribution to soil science.

4. Conclusions

A clean and simple method for the determination of soil pH by LIBS is proposed, using a PLS calibration model and taking into account variables corresponding to elements that influence soil pH. The pH values obtained by the LIBS and reference methods were positively correlated, with low MAE (0.3 pH units). The results show the potential of LIBS for evaluating soil acidity, with advantages over traditional potentiometric methods including low analytical cost, no chemical waste generation, and a single analytical procedure irrespective of the soil composition. Furthermore, the proposed method offers the possibility of determining pH, as well as nutrients and contaminants, in a single LIBS measurement.

Future studies should be carried out to obtain a better understanding of the effects of the selected variables and their contributions to the performance of the calibration model.

Acknowledgements

sample were organized in a column vector to obtain the Y matrix (50 × 1). From these matrices, a partial least squares (PLS) model was built and optimized with respect to the numbers of latent variables. The optimization results indicated that the use of five latent variables provided the best model fitting (R = 0.8661).

After obtaining the calibration model, it was applied for prediction of the pH of the 10 validation set samples. The results of the method validation are shown in Table 1. The values predicted by the proposed model showed a positive correlation with the reference pH values, with a root mean square error of prediction (RMSEP) of 0.4. The mean absolute error (MAE) was 0.3 pH units, which can be considered acceptable for this type of determination. Furthermore, the sample with pH 6.2 showed the largest absolute error of prediction (AE = 1.3), which acted to increase the MAE. It is important to mention that this same sample showed the largest relative standard deviation calculated from determinations using the reference method (RSD = 3.2%, n = 89). These results suggest that the physical characteristics of this sample interfered with the pH measurements made using both methods.

References

[1] E.O. McLean, Soil pH and Lime Requirement, in: A.L. Page, R.H. Miller, D.R. Keeney (Eds.), Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties, American Society of Agronomy, Soil Science Society of America, Madison 1982, pp. 199–224.
[2] J.B. Jones Jr., Plant Nutrition and Soil Fertility Manual, 2nd ed. CRC Press, Taylor & Francis Group, Boca Raton, 2012.
[3] R.K. Schofield, A.W. Taylor, The measurement of soil pH, Soil Sci. Soc. Am. Proc. 19 (1955) 164–167.
[4] Y.P. Kalra, Determination of pH of soils by different methods: collaborative study, J. AOAC Int. 78 (1995) 310–324.
[5] D.A. Skoog, D.M. West, F.J. Holler, Fundamentals of Analytical Chemistry, 6th ed. Saunders College Publishing, New York, 1992.
[6] A.W. Miziolek, V. Palleschi, I. Schechter, Laser Induced Breakdown Spectroscopy—Fundamentals and Applications, Cambridge University Press, Cambridge, 2012.

[7] D.W. Hahn, N. Omenetto, Laser-induced breakdown spectroscopy (LIBS). Part II: Review of instrumental and methodological approaches to material analysis and applications to different fields, Appl. Spectrosc. 66 (2012) 347–419.

[8] D.A. Cremers, L.J. Radziemski, Handbook of Laser-Induced Breakdown Spectroscopy, Wiley & Sons, Chichester, 2006.

[9] M. Hall, E. Frank, G. Holmes, B. Pfahringer, P. Reutemann, I.H. Witten, The WEKA data mining software: an update, SIGKDD Explor. 11 (2009) 10–17.

[10] S.L. Tisdale, W.L. Nelson, Soil Fertility and Fertilizers, 2nd ed. Macmillan, New York, 1966.

[11] N.T. Coleman, D. Craig, The spontaneous alteration of hydrogen clay, Soil Sci. 91 (1961) 14–18.

[12] B. Bousquet, G. Travaillé, A. Ismaël, L. Canioni, K. Michel-Le Pierrès, E. Brasseur, S. Roy, I. le Hecho, M. Larregieu, S. Tellier, M. Potin-Gautier, T. Boriachon, P. Wazen, A. Diard, S. Belbèze, Development of a mobile system based on laser-induced breakdown spectroscopy and dedicated to in situ analysis of polluted soils, Spectrochim. Acta Part B 63 (2008) 1085–1090.