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Laser-induced breakdown spectroscopy to determine soil texture: A fast analytical technique

Paulino Ribeiro Villas-Boas [a,*], Renan Arnon Romano [a,b], Marco Aurélio de Menezes Franco [a,c], Edilene Cristina Ferreira [d], Ednaldo José Ferreira [a], Silvio Crestana [a], Débora Marcondes Bastos Pereira Milori [a]

[a] Embrapa Instrumentation, R. XV de Novembro, 1452, 13560–970 São Carlos, SP, Brazil
[b] Physics Institute of São Carlos, University of São Paulo, IFSC-USP, Av. Trabalhador Sancarlense, 400 Pq. Arnold Schimid, 13566–590 São Carlos, SP, Brazil
[c] Physics Department, São Carlos Federal University, P.O. Box 676, 13565–905 São Carlos, SP, Brazil
[d] São Paulo State University — UNESP, Analytical Chemistry Department, P.O. Box 355, 14801–970, R. Prof. Francisco Degni, 55, 14800–900 Araraquara, SP, Brazil

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ABSTRACT

The analysis of soil texture is crucial for the proper management of agricultural systems and for environmental studies. Soil texture is important as it affects erosion potential, water retention capacity, organic matter complexation, and the retention of nutrients, among others. It is usually determined by pipette or hydrometer methods, but analysis requires a preparation with chemical reagents, which can take hours and hence is unfeasible for large number of samples. Here we propose the use of laser-induced breakdown spectroscopy (LIBS) to estimate the proportions of sand, silt, and clay in 60 Brazilian soil samples of varying composition. Two calibration models were developed with the partial least square regression method: one considering the spectral region from 188 to 980 nm and the other, emission lines of the elements Si, Na, Fe, Ti, Ca, K, Al, Co, Mg, V, Ba, and Be. The Pearson correlation coefficients for the estimated values were 0.89 and 0.90 on average for the first and second models, respectively. The uncertainties were 6% on average for both models. These results demonstrate the use of LIBS for rapid scanning of the texture of soil samples with distinct composition. The procedure presented here can be extended to other chemical and physical soil properties, which makes LIBS a universal tool for rapid soil analysis without preparation with chemical reagents.

1. Introduction

The relative proportion of sand, silt, and clay – texture – is one of the most important physical properties of soils. It directly affects other critical properties, including susceptibility to erosion, drainage, water-holding capacity, organic matter content, and capacity for leaching nutrients and pollutants (Hassink et al., 1993). Soil texture is, therefore, one of the key components for assessing soil quality and the sustainability of agricultural management practices (Kettler et al., 2001).

In the field, agronomists can estimate soil texture by rubbing a soil sample between their fingers and thumb and feeling its physical characteristics. However, such a technique is of low accuracy and requires skill and experience (Brown, 2003). In the laboratory, sand can be easily separated from soil samples by sieving, and clay and silt can be accurately determined by two well-established conventional methods: pipette and hydrometer. The former is more accurate and is considered the standard method for texture determination. It is based on Stoke's law, which states that denser (i.e. larger) particles sink faster than lighter (i.e. smaller) particles. Therefore, after a predetermined time in water suspension clay particles can be separated from the settled silt. Despite its accuracy, the pipette method is time-consuming and laborious, depends on the operator and requires sample pretreatment to disperse soil aggregates (Gee and Bauder, 1986; Kettler et al., 2001).

Other methods for direct determination of soil particle sizes have been developed, including gamma-ray attenuation (Naime et al., 2001), X-ray attenuation, electroresistance particle counting, photometrical techniques, and laser diffractometry (e.g., McCave and Syvitski, 2007). Prior to analysis, however, all these methods also require a pre-processing step to disperse the aggregates, which usually takes a full day. Furthermore, these methods do not have proper correspondence with the pipette or hydrometer for determining the size of the smallest particles, clay and silt (Taubner et al., 2009). Soil texture can also be indirectly determined by visible or infrared reflectance spectroscopy (e.g., Chang et al., 2001; Madari et al., 2006; Rossel et al., 2006; Curcio et al., 2013). The reflectance spectroscopy does not require the sample pre-processing step and has a good correspondence with traditional methods, but its accuracy depends on the amount and diversity of samples used to build calibration models.

In this article, we propose a method for evaluating the relative proportions of sand, clay, and silt in soils without the need for preparing samples, hence reducing the overall time of analysis to a few minutes.

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* Corresponding author.
E-mail address: paulino.villas-boas@embrapa.br (P.R. Villas-Boas).

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The method consists in using the soil elemental composition assessed by laser-induced breakdown spectroscopy (LIBS) (Miziolek et al., 2006) and building calibration models based on the correlation between emission lines and the relative proportions of sand, silt, and clay. We hypothesized that each relative proportion is mainly constituted by certain elements (e.g., silicon in sand), which are either absent or present in small amounts in the other proportions.

The LIBS is a multi-elemental spectroscopic technique based on emission of plasma induced by laser (Miziolek et al., 2006; Cremers and Radziemski, 2006; Singh and Thakur, 2007). Sample can be analyzed with minimal manipulation (i.e. without reagents) or even directly in situ (Theriault et al., 1998; Harmon et al., 2005; Corsi et al., 2006; Palanco et al., 2006). The LIBS analytic process starts by focusing a highly energetic pulse onto the sample. The laser energy density is so high (~10^9 W cm^{-2}) that it can break molecular bonds, generating a small plasma plume — a gas of unbound atoms, ions, electrons, and photons. During laser interaction, the ablated material can reach a temperature of 100,000 K (Miziolek et al., 2006), whereby its emission is basically composed of continuum radiation. As the plasma cools, the continuum emission reduces, allowing the observation of atomic and ionic lines derived from the excited elements (Singh and Thakur, 2007), which is usually performed at ~10,000 K. The elemental composition of the samples can be determined, and with appropriate calibration models the elemental concentration can be obtained. In the case of soil analysis, the LIBS has been applied to evaluate nutrients (Hussain et al., 2007; Ferreira et al., 2011; Braga et al., 2010; Cremers et al., 2001; Ebinger et al., 2003), contaminants (Bousquet et al., 2007; Senesi et al., 2009), and carbon (Nicolodelli et al., 2014; Ebinger and Harris, 2010; Silva et al., 2008), as well as humification degree of soil organic matter (Ferreira et al., 2014), soil pH (Ferreira et al., 2015), and soil classification (Pontes et al., 2009). However, no applications of LIBS have been reported for the evaluation of any soil physical characteristics.

2. Materials and methods

2.1. Soil samples

A set of 60 samples, collected from farmlands all over Brazil and characterized by the Agronomic Institute of Campinas, São Paulo State, Brazil were used in the following analyses. The relative proportions of sand, silt, and clay were determined by the pipette method and were in the range of 4–92%, 2–35% and 6–66%, respectively. Prior to the texture analysis by the LIBS technique, the soil samples were sieved to remove roots and ground to reduce particle size heterogeneity by a cryogenic mill working with liquid nitrogen at a temperature of −196 °C. For the LIBS analysis, the ground samples were pressed into pellets with 10 tons of hand press.

2.2. Laser-induced breakdown spectroscopy (LIBS)

The LIBS spectra of the soil samples were acquired with a LIBS2500plus spectrometer (Ocean Optics, Dunedin, FL, USA), which utilized a Q-switched Nd:YAG laser at 1064 nm (Quantel, Bozeman, MT, USA) operating at 75 mJ maximum power energy, 8 ns pulse width, and 10 Hz frame rate. The laser pulse was focused on the sample inside an ablation chamber. After the plasma was formed, the emission of excited species was carried by an optical fiber bundle connected to seven spectrometers ranging from 188 to 980 nm, each one coupled with a 2048 element linear silicon CCD array whose resolution was ~0.1 nm (FWHM). The distance from the sample to the collecting optical fiber bundle was approximately 7 mm. All measurements were performed in air, and the LIBS system was set to 50 mJ per laser pulse with a 2.1 ms integration time and a fixed delay time of 2 µs. On each soil sample, 60 measurements were carried out, two accumulated shots each.

2.3. Spectral processing

The LIBS spectra of a sample may vary from one shot to another, since they are strongly affected by acquisition system and plasma instability. The former depends on optical and electronic systems and may impose offset and random noise on the spectra acquired. The latter is caused by several aspects related to radiation–matter interaction – also known as matrix effects – including the composition and aggregation state of the samples, surface roughness, homogeneity, and optical alignment. The plasma formation involves a combination of non-linear dynamics such as radiation–matter interaction, laser-ablation mechanisms, production of free electrons, radiation absorbed by the plasma, and reabsorption of the species (Tognoni et al., 2010). Also, because of the non-linear plasma formation, LIBS measurements follow a generalized distribution of extreme values (Michel and Chave, 2007), instead of a normal distribution. All these issues lead to a non-reproducible background continuum emission of the spectra, which makes quantitative elemental analysis difficult. To develop calibration models for elemental quantification with LIBS, these issues have to be eliminated or reduced. In this study, only offset, random noise, and background continuum emission were corrected.

The offset of each spectrum was corrected separately for each spectrometer by subtracting the minimum value found in each spectral region. To reduce the random noise, the spectra were smoothed with a Savitzky–Golay filter (Savitzky and Golay, 1964), whose parameters were selected according to the genetic optimization algorithm (Mebane and Sekhon, 2011).

The background continuum emission – the spectral baseline – was corrected by two methods. The first one was 4S Peak Filling (Liland, 2015), which was developed for similar spectra found in other spectroscopy techniques, such as NMR and Raman (Liland et al., 2010; Liland and Mevik, 2011). The method estimates the baseline by iteratively suppressing the spectrum with a moving window and is based on four operations: smoothing, subsampling, suppression, and stretching. The parameters of the 4S Peak Filling method were also selected according to the genetic optimization algorithm. The second method estimates a baseline for each peak independently through a linear fit of the points on the left and right sides. It depends on the fact that the baseline approaches a straight line for small spectral regions and considers only spectral points not belonging to peaks (Dawson et al., 1993).

Since finding the elements whose concentration was most correlated to the soil, textural proportions was also important for this study, the intensity of lines was approximated by the area of the fitted function to the experimental points. If the line of interest was interfered by other lines, a deconvolution method was applied, in which a distribution was fitted for each peak in the analyzed range. In this study, only Lorentzian distribution was considered for the peaks.

2.4. Calibration model

Since the sum of the relative proportions of sand, silt, and clay is 100%, it is not necessary to build a calibration model for all relative proportions. For instance, if a model is built to predict the relative proportion of sand and clay, the proportion of silt would be 100% minus the sum of the other two. However, the uncertainty of estimating the relative proportion of silt would be higher than if it was directly predicted by the model (assuming that the model is less accurate than the reference method). One way to improve the predictions using just two variables is to combine the relative proportions of sand, silt, and clay prior to building the calibration model. Thus, we defined two variables as follows:

$$\begin{aligned} e &= a - b - c \\ f &= b - c, \end{aligned} \tag{1}$$

where a, b and c are the relative proportions of sand, clay, and silt, respectively. Such a combination is similar to what is provided by