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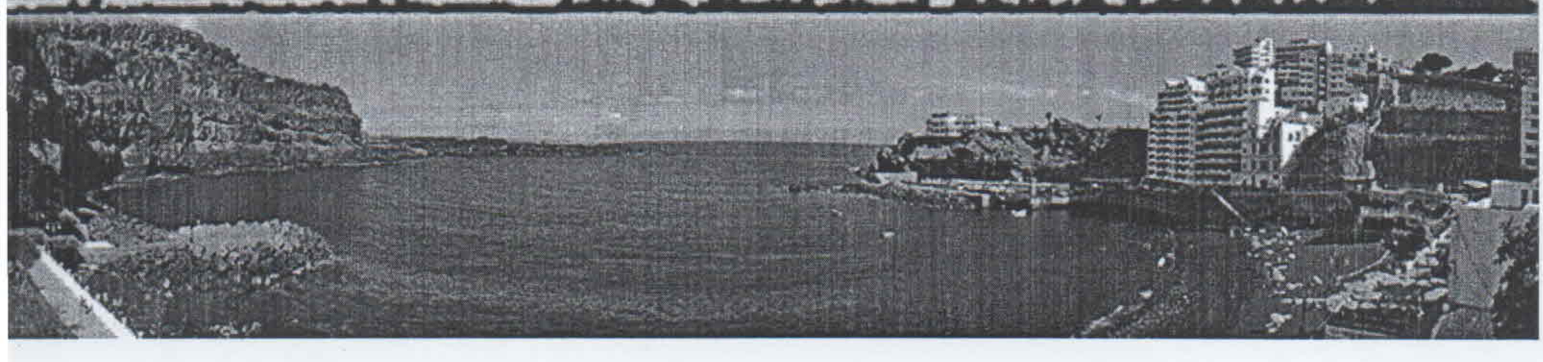

Determination of Organic Matter Humification by Laser Induced Breakdown Spectrometry and Artificial Neural Network

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1. Introduction

The humic substances are the largest reservoir of organic carbon in soil. The carbon that makes up the humic substances can be degraded by the action of different factors, including the practices of soil management. Moreover, the incorporation of carbon in the humic substance constitutes an important soil property, which can contribute significantly to reduce atmospheric CO_2 (a gas causing the greenhouse effect) [1]. Accordingly is highlighted the importance of determining the stability of the humic substances.

Nowadays, Laser-Induced Fluorescence (LIF) can be applied to evaluate the humification of organic matter in whole soil [2]. In this method, the area of the LIF spectrum of each soil sample is divided by the corresponding carbon concentration and then a normalized fluorescence signal is obtained, which is considered being the index of soil organic matter humification (H_{LIF}). However LIF is a clean and simple method, the determination of H_{Fil} depends on another analytical technique able to determine the total carbon.

Laser Induced Breakdown Spectroscopy (LIBS) is spectroscopy technique that has shown great potential for elemental determination and also has found application for organic compounds. This technique is based on the observation of the radiation emitted by atoms, ions and molecular species from a microplasma, which is generated by a laser pulse [3]. In a LIBS spectrum, the identification of the species is based on the wavelength of emission, which is characteristic for each element, and the number of species can be determined by the intensity of the emission signals [4]. The current LIBS potential to perform *in situ* analysis is enthusiastic. The technique presents features such as the possibility of elemental direct analysis, rapid and simultaneous.

In the present study LIBS potential was evaluated to determinate the organic matter humification in whole soil.

2. Materials and Methods

A set of samples was constituted by thirty six samples from Brazilian Cerrado region (Argisoil). The samples were collected in six depths (0–10 cm, 10–20 cm, 20–40 cm, 40–60 cm, 60–80 cm and 80–100 cm) from an experimental area submitted to six distinct treatments: without irrigation and fertilization, irrigation with treated sewage effluent and without nitrogen fertilization, irrigation with treated sewage effluent and fertilization with 171.6 kg ha^{-1} $year^{-1}$ of nitrogen, irrigation with treated sewage effluent and fertilization with 343.2 kg ha^{-1} $year^{-1}$of nitrogen, irrigation with treated sewage effluent and fertilization with 520 kg ha^{-1} $year^{-1}$ of nitrogen and irrigation with water consumption and fertilization with 520 kg ha^{-1} $year^{-1}$ of nitrogen.After collection the samples were transported to the laboratory, where a manual cleaning procedure was carried out to remove parts of roots and leaves. Then, the samples were submitted to a process of cryogenic grinding to reduce heterogeneity and three pellets of each sample were prepared by applying 15 ton of pressure during three minutes. The LIBS spectra of pellets were captured by using the system model LIBS2500, from Ocean Optics.

Twenty spectra were captured from different regions of each pellet, being each spectrum corresponding to two accumulated laser pulses. A previous laser pulse was always used to clean the pellets surface, before capturing a spectrum. The average of spectra was obtained after individual spectrum offset correction.

Aiming to correlate the LIBS spectra with the index of soil organic matter humification (H_{LIF}), LIF was used as reference method [2]. For LIF measurements it was used a portable LIF system, developed at Embrapa Agricultural Instrumentation (a Brazilian research center). Three LIF spectra were obtained for each sample and the ratio between the areas above spectra and the total carbon were calculated. The total carbon content in the samples was previously determined by the method of dry combustion using a Total Organic Carbon (TOC) from Shimadzu, model TOC-V. The average of three measurements of each sample was performed.

Multilayer Perceptron (MLP), a kind of artificial neural network, was used to calibrate and validate the proposed LIBS method. The selected variables from LIBS spectra for MLP training were the following emission lines and ratios between them: Ni, Co, Mn, Mg, Al, C/H, C/O, N/H, S/O, N/O, P/O, H/O, C/N, C/P, N/S, H/(PO), Ca/O.

The Weka system (Waikato Environment for Knowledge Analysis) version 3.5.7 was used for MLP training and validation. The strategy of cross validation in ten folds was used.

3. Results and Discussion

The selection of LIBS variables to be used for calibration was performed based on factors controlling humification and mineralization of soil organic matter [5]. The selected emission lines and ratios between some interesting emission lines were experimented to training the calibration system, built with a MLP. To MLP training it was used the Back-Propagation algorithm and the combinations among Back-Propagation parameters were: training time = 500, momentum= 0.2 and learning rate= 0.3.

In Fig. 1 are showed the results obtained by the correlation among the LIF reference values and LIBS predicted values. The Pearson's correlation coefficient was 0.9, indicating good agreement between the organic matter humification determined by LIF and that obtained by the proposed LIBS method, even though the relative absolute error.

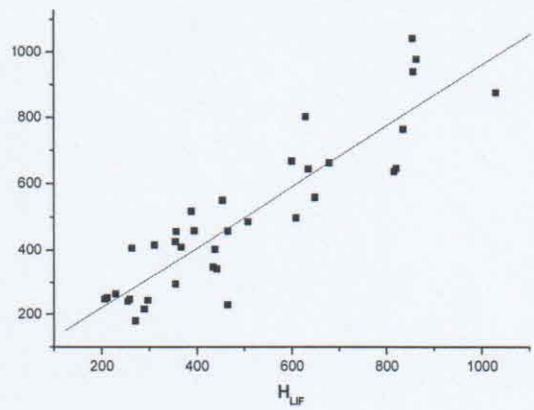

Figure 1: Correlation between the results of organic matter humification determined by LIF reference method and LIBS proposed method

This preliminary result seems to be very promising, since LIBS dispenses the use o another technique for carbon determination. However, future efforts will be spent for improvement of prediction and minimization of errors. These efforts could bring important contribution for soil analysis, since with a single LIBS spectrum many other analytical demands for soil can be satisfied, such as determination of contaminants, nutrients and carbon concentration.

4. Conclusions

A new method using LIBS and MLP is proposed to determinate organic matter humification. The results obtained showed 90% of correlation between LIF reference method and LIBS proposed method. The results are promising due to the LIBS potential to determine organic matter humification dispensing carbon determination. Moreover a single LIBS spectrum can be used to determine other elements in soil.

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