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Total Carbon and Nutrient Quantification in Brazilian Soils Using LIBS Technique with One-Point Calibration

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This study applies OPC-LIBS approach to quantify total C, K, Ca, Mg, Cu, Fe, and Na in Brazilian soils. A Boltzmann-based correction model was used to reduce Al interference in the C I 193.03 nm line. While matrix effects limited the correction model across different samples, OPC-LIBS using Al as an internal standard improved the accuracy (>90%) for all elements, comparable to CHNS and AAS. The results demonstrate LIBS as a fast, accurate, and environmentally sustainable alternative for large-scale multielement soil analysis.

Keywords**—*****LIBS, One-point calibration, soil analysis, carbon quantification, nutritional quantification***

I. INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) has gained prominence as a versatile analytical tool for soil characterization [1], [2], [3], [4]. Its successful applications include the quantification of nutrients and contaminants, as well as the estimation of key physicochemical properties such as texture, pH, and humification index. However, accurately quantifying carbon (C) in soils remains challenging due to strong matrix effects and spectral interferences. Soil heterogeneity and the spectral overlap of iron (Fe) and aluminum (Al) lines with critical carbon emission lines complicate the establishment of a direct linear relationship between emission intensity and carbon concentration.

In LIBS, matrix effects result from variations in the physicochemical properties of the sample, which influence laser ablation and plasma parameters. These variations cause signal fluctuations and nonlinear relationships between concentration and emission intensity, thus limiting calibration accuracy. These matrix effects are not limited to carbon analysis. The quantification of essential soil nutrients—including potassium (K), calcium (Ca), magnesium (Mg), copper (Cu), iron (Fe), and sodium (Na)—is also affected by matrix effects. Physical and chemical variability among soil samples alters the emission response, undermining traditional calibration models that rely solely on emission line intensities without accounting for matrix-specific influences.

Furthermore, while routine soil analyses often focus on the available nutrient fraction—those immediately accessible to plants—quantifying total nutrient content offers a more comprehensive perspective on soil fertility. Total nutrients represent the entire elemental reservoir within the soil, including forms that are not immediately bioavailable but can become so over time through mineral weathering, organic matter decomposition, or shifts in soil chemistry. This broader view is essential for sustainable fertility management, long-term fertilization planning, rehabilitation of degraded soils, and risk assessment related to nutrient imbalances.

In this study, we propose a correction model for Al interference in the C I 193.03 nm emission line, leveraging the Boltzmann equation and the correlation between Al and C emission features. To address matrix effects in the quantification of both carbon and other nutrients, we adopt a hybrid approach that integrates Calibration-Free LIBS (CF-LIBS) [5] with One-Point Calibration LIBS (OPC-LIBS) [6], [7], [8].

CF-LIBS estimates elemental concentrations by calculating plasma parameters under the assumption of local thermodynamic equilibrium (LTE) and stoichiometric ablation. However, this method can be affected by uncertainties in atomic parameters and experimental variability. OPC-LIBS enhances CF-LIBS by applying an empirical correction based on a single calibration sample with known concentrations and an internal standard to normalize the data.

The integration of CF-LIBS and OPC-LIBS significantly minimizes matrix effects by incorporating both spectroscopic emissions and fundamental plasma properties. This hybrid method allows for more reliable and reproducible quantification, even in soils with high compositional diversity. As such, it represents a significant advancement toward fast, accurate, and scalable elemental analysis for agricultural and environmental monitoring.

II. MATERIALS AND METHODS

A. Soil Samples and Preparation

Three sets of soil samples with diverse physicochemical characteristics were used. Set 1 (36 samples) was collected from the Cerrado region in Mato Grosso do Sul, Brazil; Set 2 (48 samples) from the Atlantic Forest in São Carlos, Brazil; and Set 3 (192 samples) from pasture areas (degraded, recovered, and native) in São Carlos. Set 3 was used for model development and cross-validation, while Sets 1 and 2 were used for validation and OPC-LIBS quantification.

All samples were oven-dried at 36 °C for 72 hours, manually ground, and sieved to 100 mesh ($\leqslant 150\ \mu m$). Pellets (12.5 mm diameter, 500 mg) were prepared by pressing the powder under

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2.4 kBar for 30 seconds and stored under controlled humidity in sealed plastic bags until analysis.

B. LIBS Measurements

LIBS analysis was performed using an OceanOptics LIBS2500+ system equipped with a Q-switched Nd:YAG laser (1064 nm, 8 ns, 50 mJ, 20 Hz, 119 J/cm²). The system features a CCD detector and seven spectrometers covering 180–960 nm at 0.1 nm resolution. Spectra were acquired with a 1 µs delay and 1000 µs gate width. For each sample, 60 spectra were collected, each as the average of two successive shots, after a single cleaning pulse.

C. Reference techniques

C content was determined using a Perkin-Elmer 2400 Series II CHNS analyzer. Approximately 10 mg of each sample (sieved to 100 mesh) was sealed in tin capsules and combusted in the furnace. Analyses were performed in triplicate to ensure analytical accuracy and reproducibility.

In sets 1 and 2, nutritional concentrations were measured by atomic absorption spectrometry (AAS). Samples underwent a 4-hour digestion in HNO_3 at 140 °C, followed by a 4-hour H_2O_2 oxidation step. The resulting solution was filtered, diluted with Milli-Q water, and analyzed using a PerkinElmer PinAAcle™ 900T AAS in flame mode. Data were acquired with background correction and averaged over three replicates.

D. Calibration-Free LIBS (CF-LIBS)

CF-LIBS [5], [9] determines elemental concentrations based on plasma parameters, assuming local thermodynamic equilibrium (LTE) [10],[11] and stoichiometric ablation. The line intensity I_λ^s is calculated using the Boltzmann equation:

$$I_\lambda^s = \frac{N_s}{U_s(T)}\frac{hc}{4\pi}\frac{g_k^s A_{ki}^s}{L_s(\lambda)}e^{-\frac{E_k}{K_B T}} \qquad (1)$$

Where variables represent N_s emitter density, $U_s(T)$ partition function, E_k energy level, K_B is Boltzmann constant, h is Planck's constant, c is the speed of light, g_k^s is the degeneracy of state k, A_{ki}^s is Einstein's spontaneous transition probability, and F is the unknown spectrometer function and T plasma temperature.

E. One-Point Calibration LIBS (OPC-LIBS)

One-Point Calibration [6], [7] is an empirical correction applied to CF-LIBS to improve quantification by addressing uncertainties in emission parameters, self-absorption, and spectrometer response. Only one calibration sample is required, and an internal reference element is used for normalization. Elemental concentration C_α is calculated as:

$$C_\alpha = N_\alpha A_\alpha \chi_p \qquad (9)$$

where A_α is the α atomic mass and χ_p is the plasma normalization constant obtained using an internal standard.

III. RESULTS AND DISCUSSION

Quantifying elements in soil samples using LIBS poses significant analytical challenges, primarily due to spectral interference and the matrix effect. In this study, the quantification of C, K, Ca, Mg, Cu, Fe, and Na was investigated, as these are key elements involved in soil fertility and biogeochemical processes. These nutrients are essential for plant growth, microbial activity, and chemical stability of the soil. Moreover, their total quantification allows for the assessment of long-term nutrient supply potential and the identification of imbalances or contamination in agricultural and degraded environments.

Among the elements evaluated, carbon quantification proved particularly challenging. The C I emission line at 193.03 nm exhibited a weak correlation with the carbon content determined by CHNS, considering the three sets, (r² = 0.29; Fig. 1a), which was mainly attributed to the interference from nearby Al I and Al II emission lines, especially Al II at 193.04 nm. Additionally, the matrix effect—arising from variations in the chemical and mineralogical composition of the soil samples—directly affected plasma parameters such as electron temperature and density, compromising the linear relationship between emission intensity and actual concentration.

To address these interferences, a correction model based on the Boltzmann equation (Eq. 1) was applied to estimate the contribution of Al lines to the total emission observed at 193.03 nm. For this purpose, set 3 was used to build the model, and sets 1 and 2 were used for validation. The corrected calibration curve showed a significantly improved performance, with r² = 0.73 (Fig 1b), considering the three sets.

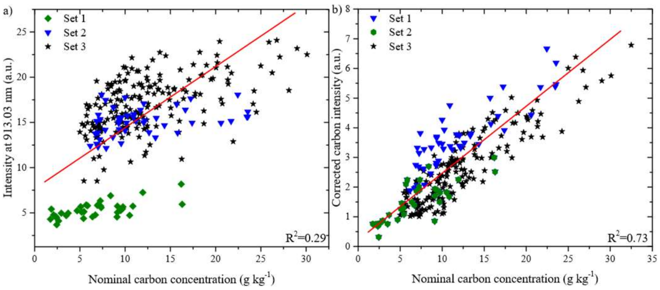

*Fig 1. a)*Calibration curve of the peak area at 193.03 nm and *b)* Calibration curve with the corrected C I area.

However, when the model was applied to samples from different geographic regions (Sets 1 and 2), a decline in performance was observed (Fig 1b), indicating that variations in soil composition affect plasma behavior and limit the generalizability of the correction model.

To overcome this limitation, the OPC-LIBS method was employed using Al as an internal standard. By combining empirical calibration with plasma-based physical parameters, OPC-LIBS enabled robust carbon quantification in sets 1 and 2, with r² = 0.95, accuracy of 91%, and RMSE of 1.3 g/kg (Fig. 2a). These results confirm the model's effectiveness in compensating for both spectral interference and matrix variability, leading to high precision even in heterogeneous soil samples. For the other elements, OPC-LIBS also demonstrated excellent performance. All validations yielded accuracies above 90%, with r² values ranging from 0.91 to 0.97, when compared to concentrations obtained by AAS, as shown in Table 1 and Fig 2b.

Despite the well-known limitations of LIBS, such as sensitivity to matrix effects and spectral interferences, the application of the OPC-LIBS approach proved capable of achieving analytical performance comparable to established laboratory methods like CHNS and AAS. The high accuracy obtained for carbon and nutrient quantification in soils with varied properties demonstrates that these obstacles can be effectively overcome, enabling reliable quantitative analysis even in compositionally complex samples. Beyond its precision, LIBS offers substantial operational advantages: rapid analysis, no chemical preparation, low environmental impact, and potential for automation and portability. These features make the proposed approach particularly promising for large-scale applications in agriculture, environmental monitoring, and soil quality assessment. Scientifically, the findings contribute to advancements in soil science, analytical spectroscopy, and sustainable diagnostic technologies, while also reinforcing LIBS as a robust and accessible tool for multielemental analysis in complex matrices.

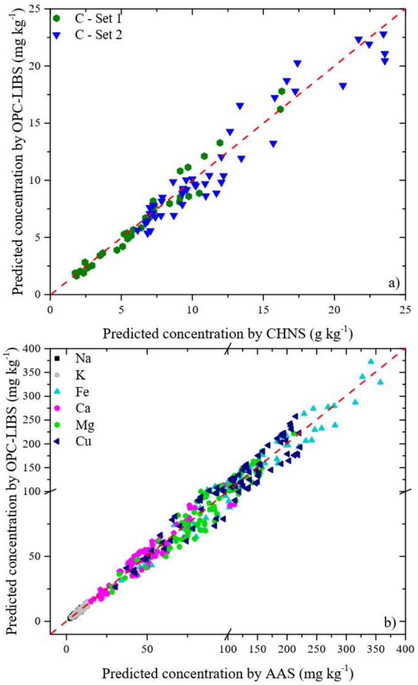

Fig 2.*Validation of LIBS-predicted values against a)CHNS and b) AAS measurements.*

TABLE I. METRICS OF VALIDATION

Element	Accuracy (%)	r²	RMSE (mg/kg)
C	91	0.95	1,300
Na	91	0.89	0.57
K	90	0.85	0.75
Fe	92	0.92	9.5
Ca	92	0.91	4.5
Mg	90	0.97	12.7
Cu	90	0.92	14.9

IV. CONCLUSIONS

This study demonstrated that the OPC-LIBS approach effectively quantifies C, K, Ca, Mg, Cu, Fe, and Na in soils, overcoming limitations from spectral interferences and matrix effects. The correction model for Al interference improved carbon quantification, and the integration with OPC-LIBS using Al as an internal standard further enhanced accuracy across diverse samples.

The method achieved results comparable to CHNS and AAS, with over 90% accuracy for all elements. In addition to its precision, OPC-LIBS offers advantages such as rapid analysis, reagent-free sample preparation, and potential for field deployment, making it a promising tool for large-scale soil monitoring in agriculture and environmental management.

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