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Detection of chemical elements related to impurities leached from raw sugarcane: Use of laser-induced breakdown spectroscopy (LIBS) and chemometrics

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ABSTRACT

Impurities in raw sugarcane directly influence the quality of sugarcane juice by compromising its color and affecting the entire sugar manufacturing process. Therefore, the primary objective of this study was to identify the chemical elements related to different levels of impurities, ranging from 3 to 10 wt%, leached from sugarcane using only water. This analysis employed laser-induced breakdown spectroscopy (LIBS) after the sample solutions were immobilized in a polyvinyl alcohol (PVA) polymer. A mixture design was outlined to describe the composition of numerous samples. To treat the data generated by LIBS, 12 different standardization strategies of the dependent variables (LIBS instrumental response) were tested. To identify the chemical elements from the impurities and their relations, a principal component analysis (PCA) was performed using the entire spectra. The analysis of the score plots shows a large segregation in the experiments with the highest amounts of impurities (from 8 to 10 wt%). Calcium, and Mg were highly correlated to the samples in the PCA and the ratio between the highest intensity of these signals for samples and 10% (w/v) PVA confirmed this evidence. LIBS showed advantages in the analysis of impurities from sugarcane after the conversion of the PVA solution into a solid to contain the leached solutions. The method provides a fast, simple and sensitive method for the detection of sugarcane impurities.

1. Introduction

During the sugarcane harvesting process, various parts of the plant, such as green and dry leaves, culms and tops, as well as soil, are incorporated into raw material, compromising the quality of final products, such as sugar or ethanol [1].

In sugar manufacturing, browning of the juice is caused by an excess of soil. Additionally, vegetal impurities can increase the volume of the raw material but not the quantity of the extracted juice [2].

Therefore, the monitoring of impurities in raw sugarcane is of great interest to the sugar and ethanol industries, as there is no analytical method to identify them, and their presence is inherent to mechanical harvesting.

Laser-induced breakdown spectroscopy (LIBS) has been used for the development of several analytical procedures with simple methods, good analytical frequencies and a minimum amount of reagents. LIBS has shown promise for the analysis of plants [3,4] and soil [5,6], the determination of silicon in sugarcane [7], the estimation of fiber content in sugarcane bagasse [8], and the determination of macro- and micronutrients in sugarcane leaves [9,10]. This technique is primarily indicated for the direct analysis of solid samples and materials with complex decompositions. Additionally, LIBS can reduce the measurement time to seconds and enable *in loco* microanalysis with minimum sample preparation [11].

Spectra recorded through LIBS represent a fingerprint of the sample that have a degree of complexity which, in most cases, is challenging to solve using only univariate analysis for data evaluation. For solid matrices, the construction of an analytical calibration curve is labor-intensive. Therefore, one viable alternative with a good success rate for treating LIBS signals is to use multivariate methods [12]. A well-consolidated principal component analysis (PCA) was applied to explore data with higher dimensionality than those from LIBS [13].

Another approach about raw sugar manufacturing process was the study of Silva et al. [14] to determine heavy metal sources in sugarcane Brazilian soils using inductively coupled plasma (ICP-OES) and PCA for visualization of tendencies in the data. The soil samples were mineralized using acid and microwave system. According to the authors, the sources of metals were discriminated using PCA as natural for the chemical elements Cr, Cu, Ni, and Zn, and anthropogenic for Cd. Miranda et al. [15] also applied ICP-OES and a closed-vessel conductively digestion system to determine macro- and micronutrients in sugarcane leaf for diagnosis purposes. Bakir et al. [16] investigated parameters related to composition, cation exchange capacity, and particle size using x-ray

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techniques for characterization of field soils samples in mimetic samples containing ions present in a typical sugarcane juice solution. However, these studies did not perform evaluations in raw sugarcane in presence of interfering material, such as leaves, straw and soil amendments.

Using all of the advantages and potential of LIBS, this study applied LIBS and chemometrics for the investigation of soil and vegetal impurities in raw sugarcane.

2. Materials and methods

2.1. Samples

Samples of raw sugarcane and vegetal and soil impurities were all obtained from the same crop on a farm located in the city of Ibaté, São Paulo, Brazil. Three batches of this material were acquired that sampled different intervals (15 days).

A mixture design was outlined to simulate the presence of impurities in sugarcane from soil and the vegetal parts of the plant, which were combined in different proportions, as shown in Fig. 1.

To prepare each solid mixture, fractions of sugarcane, soil and the vegetal parts of the plant were individually weighed and combined to achieve a final mass of 100 g. For leaching tests, the "range" discussed herein was equal to the sum of both impurities (the vegetal parts of the plants and soil) and was between 0 and 10 wt%, as represented by orange circles in Fig. 1.

Each mixture was placed in a polyethylene plastic bag, and 200 mL of Milli Q™ water was used for the leaching procedure. Occasionally, a manual agitation was performed. Two hours later, a small hole was made in the plastic bag, and 50 mL of the solutions of leached impurities were transferred into Falcon™ flasks.

2.2. Immobilization of leached impurities solutions in polyvinyl alcohol (PVA)

Leached solutions from the solid mixtures described above were converted into solids for instrumental measurements. The conversion of the analytical matrix from a liquid to a solid was performed using polyvinyl alcohol (PVA) (viscosity 28–32, Molar Mass 85,000–124,000, Matheson Coleman & Bell) as substrate [17]. The samples were immobilized in 10% (w/v) PVA solution. The PVA solution was prepared by dissolving the polymer in deionized water under heating to ~90 °C. A mass of 200 mg sample (leached impurities solution) and 800 mg 10% (w/v) PVA were weighed, mixed and transferred to the pre-adapted drying support. After heating for 2 h at 50 °C in an oven, an immobilized sample in solid PVA was obtained and analyzed with LIBS. Fig. 2a, b and c show photographs of the drying support, the sample after immobilization in PVA and the sample after analysis with LIBS, respectively.

2.3. LIBS analysis

The LIBS spectra were collected using a commercial J200 LIBS spectrometer (Applied Spectra, Fremont, CA, USA). This instrument was equipped with a Q-switched Nd:YAG laser (1064 nm) that generated nanosecond pulses up to 100 mJ. Experiments were conducted by recording 50-point scans in 10 horizontal lines, as shown in Fig. 2c, with a total of 500 LIBS emission signals for each sample. The laser was configured as follows: laser fluence of 1000 J/cm^2 (80 mJ of laser pulse energy on a 100 μm spot), at a 5 Hz repetition rate and a 1 mm/s ablation rate. The data acquisition time was 1.05 ms and the delay time was 0.5 μs.

2.4. LIBS dataset

For processing the LIBS data, different standardization or normalization strategies of the dependent variables were used. In this study, a MATLAB code "libs_treat" [18] was used for preliminary data inspection and standardization and was run in Matlab R2015b (The Matworks, Natick, MA, USA). This computational code is able to calculate 12 standardization modes using all of the spectral information (details are in the Supplementary data). Using this approach, dataset evaluation was performed with PCA using the Pirouette (Infometrix, Bothel, WA, USA) software package (version 4.5 rev. 1).

3. Results and discussion

The procedure for the liquid-to-solid conversion of the leached solutions applied in this study was previously developed by Andrade et al.

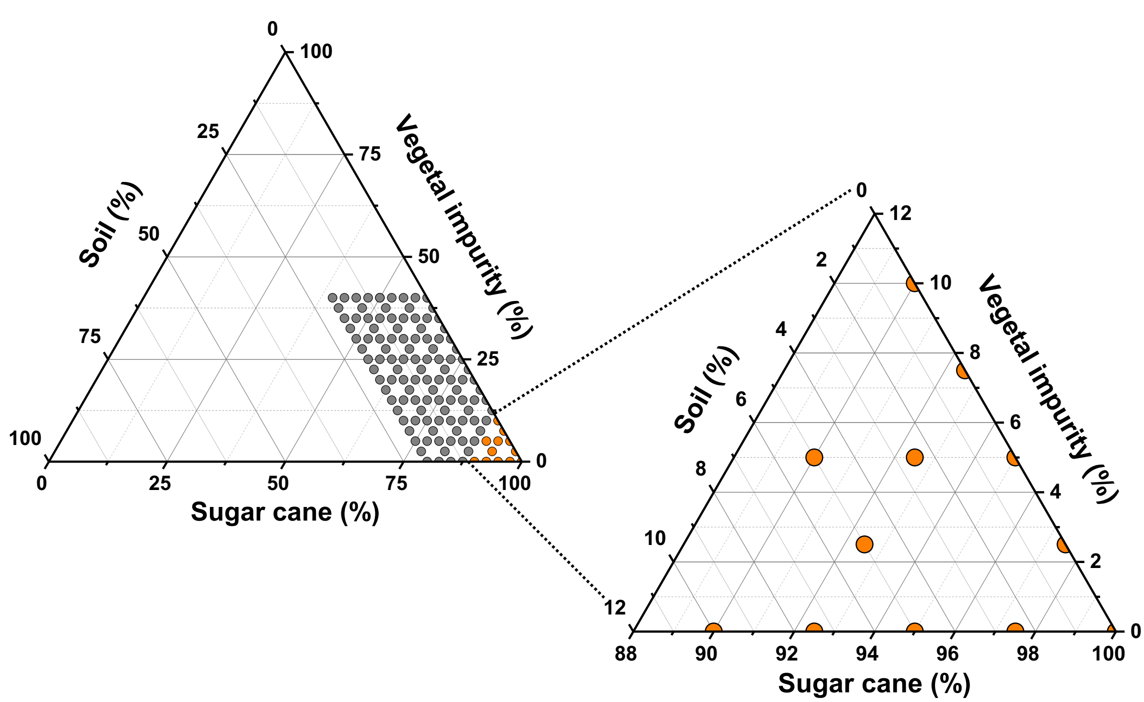

Fig. 1. Mixture design outlined for the study of impurities in raw sugarcane.