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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.

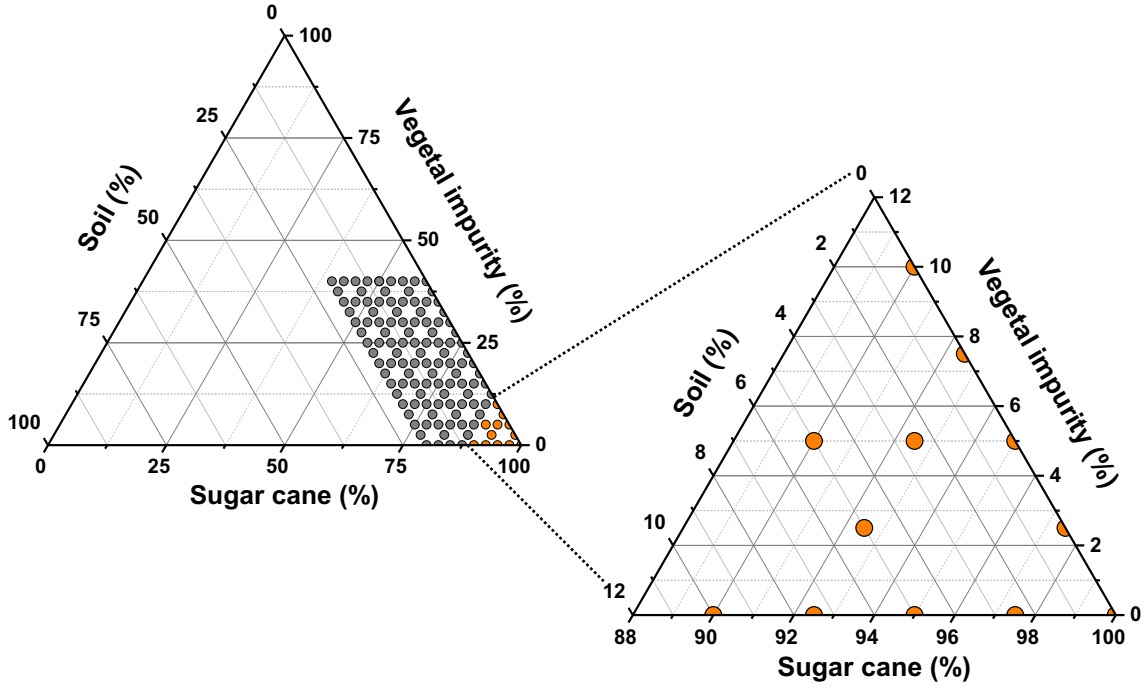

Fig. 1. Mixture design outlined for the study of impurities in raw sugarcane.

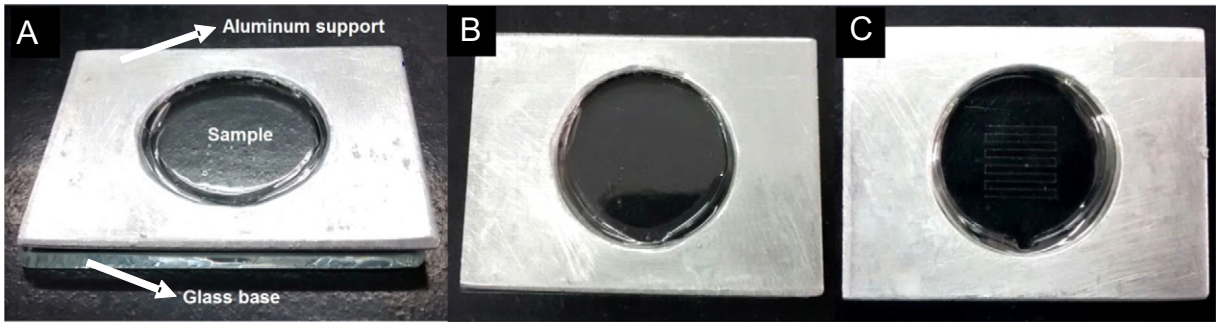

Fig. 2. Solution of the leached sample from (a) a mixture of sugarcane, soil and vegetal parts of the plant immobilized in a solid PVA substrate. (b) The sample before and (c) after analysis with LIBS.

[17] for the suspension of fertilizer. The authors obtained homogeneous polymers with stabilities of at least 28 days after the immobilization of the samples. Accurate determinations of various nutrients (including Cu, K, Mn, Mg, and Zn) in highly concentrated liquid samples were obtained with low standard errors of 0.02% to 0.06% using reference values from inductively coupled plasma optical emission spectrometry (ICP OES) and from a combination of LIBS spectra with chemometrics.

The goal of this study was to verify the elements that characterize two ranges of impurities, (1) 3–5 wt% and (2) 8–10 wt%, which is considered the maximum tolerable amount that does not impact the quality of the extracted sugarcane juice. The dataset was analyzed using an exploratory analysis performed with PCA. Matrices with these datasets were organized that considered the mean or sum of the spectra for each experiment, with the entire profile of the LIBS spectra.

The LIBS spectra of each leached sample immobilized in a PVA substrate are shown in the Supplementary data (Figs. 1S to 12S). A set of typical emission lines was observed: atomic (I) lines for C, Na, H, K and O. Additionally, other ionic (II) lines were reported, including those of Ca and Mg. The mean spectrum for 10% (w/v) PVA with no content of leached solutions was shown in Fig. 3. The average deviation among the signals of five replicate measurements was up 66 to 76 for 507 pulses each. It is important to emphasize that the leached solution of samples had to be mixed to PVA melted and dried together; then it was not possible to measure each PVA before this procedure. Also can be verified in the spectrum of Fig. 3 neither detection of Al emission lines in the support made of 99.99% aluminum alloy (Fig. 2), considering the most intensity Al I atomic lines for following wavelengths 308.22, 309.27, 309.28, 394.40 and 396.15 nm.

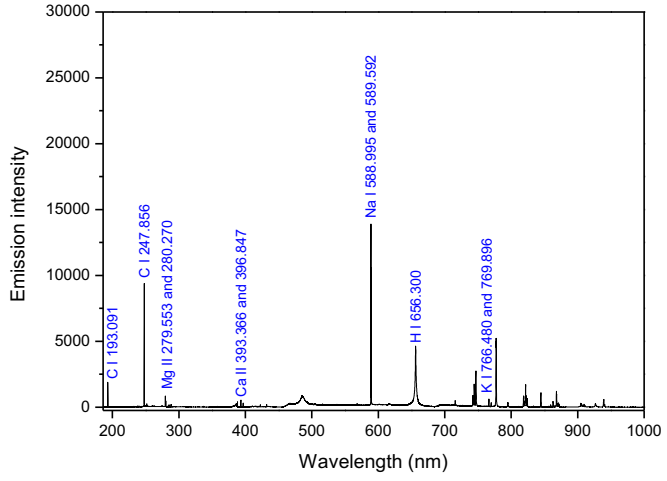

Fig. 3. Mean of the LIBS spectra for 10% (w/v) PVA solution with no content of leached solutions.

Signal fluctuations and sample heterogeneity may impinge measurement accuracy. In this context, dataset standardization can be applied to improve the signal-to-noise ratio [18].

Moreover, before the standardizations it was possible to evaluate whether a spectra was anomalous using the "libs_treat" code. The standard deviation, area, maximum and Euclidean norm were calculated for each sample. An anomalous spectrum would have a suspect value, such as a standard deviation of 0, showing that they can be excluded from the dataset.

Spectra standardizations require replicates to calculate the mean and sum. Then, the "libs_treat" code was used to calculate the following list of standardizations other than the mean and sum: (1) The individual Euclidean norm (vector length) was calculated for each spectrum, and the raw data were divided by this value. (2) The individual spectral area (sum of all the signals) was calculated, and the raw data were divided by this value. (3) The individual spectral maximum (the highest signal) was identified for each spectrum, and the raw data were divided by this value.

Then, the matrices for the mean or sum of the spectra were composed into 60 rows × 12,288 columns (12 experiments × 5 samples each = 60 spectra with 12,288 emission lines). To understand the details of the spectra and their relations to the assessed impurities, each type of standardized dataset was mean-centered and subsequently analyzed by a PCA.

The score plot from the PCA of the mean spectra is shown in Fig. 4a, and the PC1 and PC2 loadings are shown in Fig. 4b and c, respectively. The explained variance due to the first and second principal components (PCs) was 72% (PC1 40%; PC2 32%). The analysis of the score plots shows a predominant segregation in the positive part of PC2 in the experiments with a higher impurity content (between 8 and 10 wt%, white triangles) in the samples. The atomic lines for C I 247.86 and K I 766.48 nm showed remarkably positive values from the analysis of the PC2 loadings.

Moreover, in the experiments with high ranges of impurities, substantial differences were observed in the Mg II 279.55 and Ca II 393.36 in the positive part of PC1. Therefore, the correlation between Mg and Ca and Na must arise from tests 1–3, which had 10 wt% vegetal or soil impurities or 5 wt% of each. The negative part of PC1 contains the samples with lower levels of impurities, 3–5 wt% (gray squares) and 0 wt% (black circles), as shown in Fig. 4a.

The results obtained after standardization by the Euclidean norm, area, and maximum were not different from those from the analysis of the mean standardization (Fig. 4). The score and loading plots are presented in the Supplementary data (Figs. 13S, 14S and 15S).

The spatial distribution of the data after another standardization was calculated using the C atomic line emitted at 193.09 nm and is shown in Fig. 5a. The elements that were most important for the separation of the impurities in clusters were the same as verified above. More of the variance could be explained when the data were standardized using the carbon line: 64% from PC1 and 22% from PC2 (a total of 86%). Therefore, the

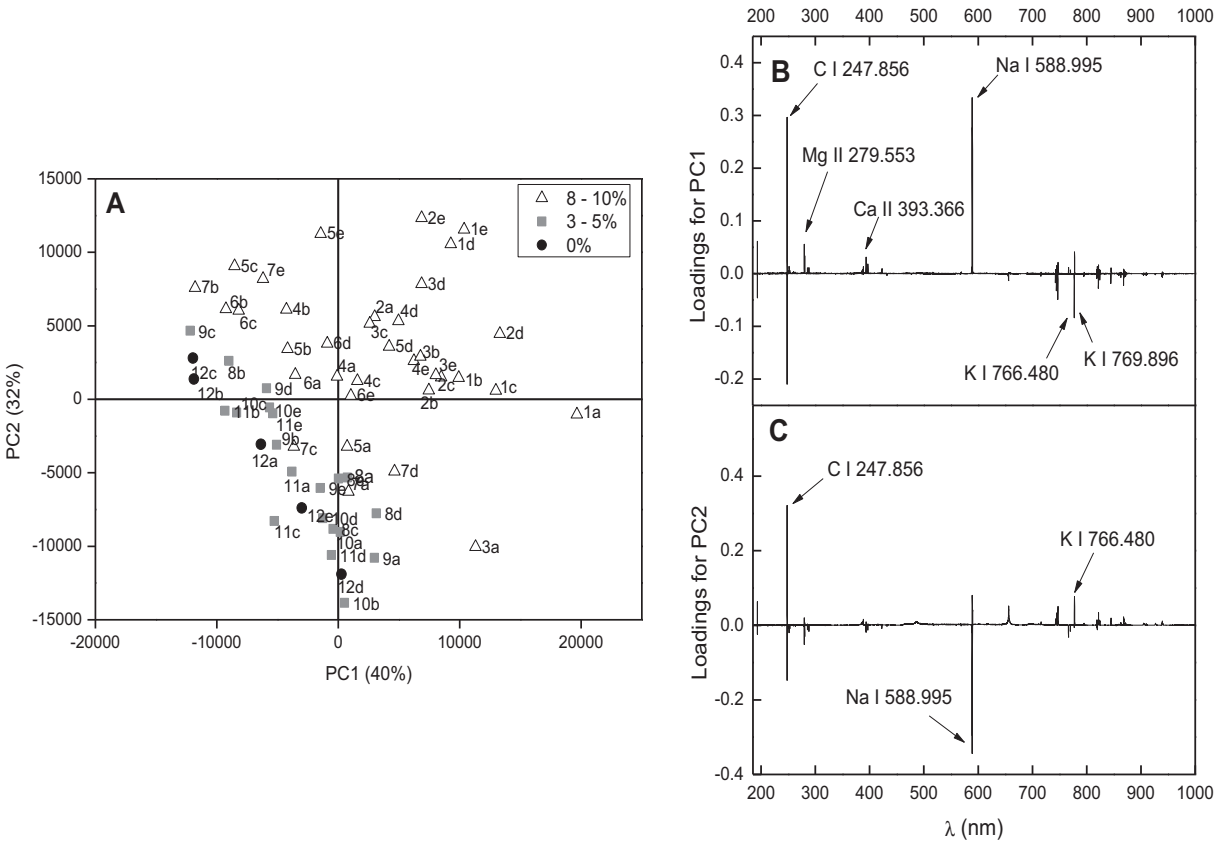

Fig. 4. Scores (a) and loadings for PC1 (b) and PC2 (c) calculated using the mean spectra dataset.

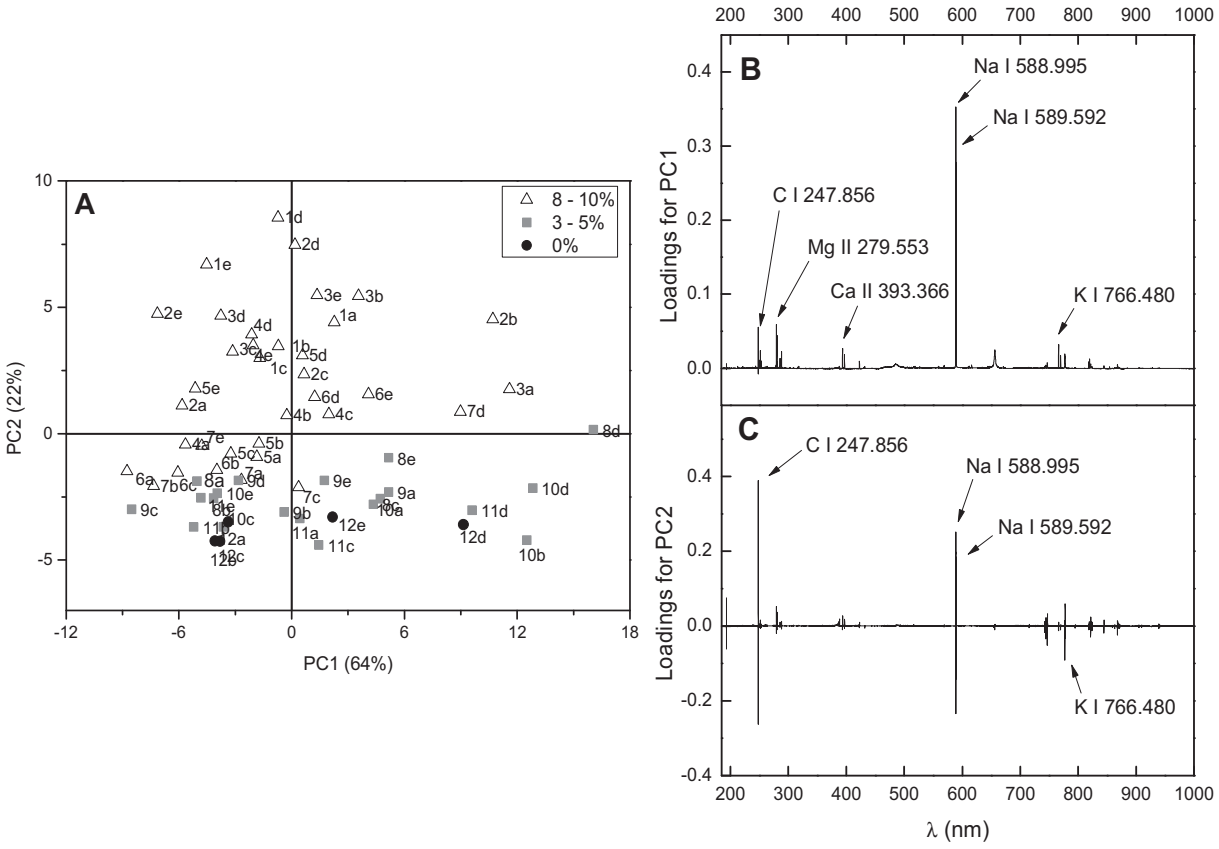

Fig. 5. Scores (a) and loadings for PC1 (b) and PC2 (c) calculated using the mean spectra standardized with the C I 193.09 nm line.

193.09 nm carbon emission line can be used as an internal standard to improve the separation of LIBS data.

Additionally, the spectra were standardized with the C I 247.86 line. Fig. 6 depicts the results from this standardization, which are slightly better to the other standardization, considering better segregation for the cluster with 0 and 3–5 wt% in the negative part of PC2.

The atomic lines of carbon were the best way to standardize the dataset to discriminate high contents of impurities between 8 and 10 wt%. Additionally, using both of the atomic lines for C I, 193.09 and 247.86 nm, a better visualization of the samples was achieved, where no impurities were added (*i.e.*, the samples were 100 wt% sugarcane). The observed C I signals were assigned to the PVA matrix and not raw sugarcane. In this context, the influence of the PVA matrix was minimized, which implies that this is a good alternative for standardizing LIBS spectra of immobilized material in this polymer. However, it was possible to distinguish the LIBS signals of the samples with no-added impurities and to detect the impurities in the immobilized solutions in PVA.

For comparative purposes, this computational code was applied to the aforementioned standardizations, and the corrected spectra were summed. The results from the summed spectra were not significantly different from those of the mean spectra. Further details are shown in Figs. 16S, 17S, 18S, 19S, 20S and 21S in the Supplementary data.

Summarizing, chemical elements with positive loadings, such as Ca and Mg, characterized the samples with the highest range of impurities (8–10 wt%), as shown in Figs. 4b, 5b and 6b. Positive and negative values for loadings were observed in the Na I 588.99 and 589.59 and, K I 766.48 and 769.90 signals (Figs. 4c, 5c and 6c), and were related to all of the level of impurities.

To support the information from PCA analysis, the ratio between the highest intensity of the relevant signals for samples and 10% (w/v) PVA (Fig. 3) was calculated. The values were addressed in Table 1 and values higher than 1.5 were considered relevant for impurities characterization. Calcium, Mg and a small influence of K for both, the mean and the mean spectra standardized with the C I 247.86 nm line were confirmed as responsible to differentiate the levels of impurities as highlighted in gray in Table 1. These data also confirmed that the emission lines of C came from PVA chemical composition, since the magnitude was up 1.0 to 1.2 for most of ratios. Additionally, the samples denoted as 12 had any impurity added and the ratios were 1.0, exception only for line of C I 193.09 nm that was 1.1.

4. Conclusions

The proposed method combining LIBS emission lines, standardization modes and PCA was demonstrated to be a good alternative for detecting impurities in sugarcane samples. The results indicate that after standardizing with the atomic lines of carbon, it was possible to visualize the contents between 3 and 10 wt% better. The ratio between the highest intensity lines for samples and 10% (w/v) PVA corroborated with the chemometric findings. The conversion of the analytical matrix from a liquid to a solid phase produced a viable system for evaluating the impurities in raw sugarcane. All of the results demonstrate that this method provides adequate sensitivity for evaluating a narrow range of impurities between 3 and 10 wt%.

Acknowledgments

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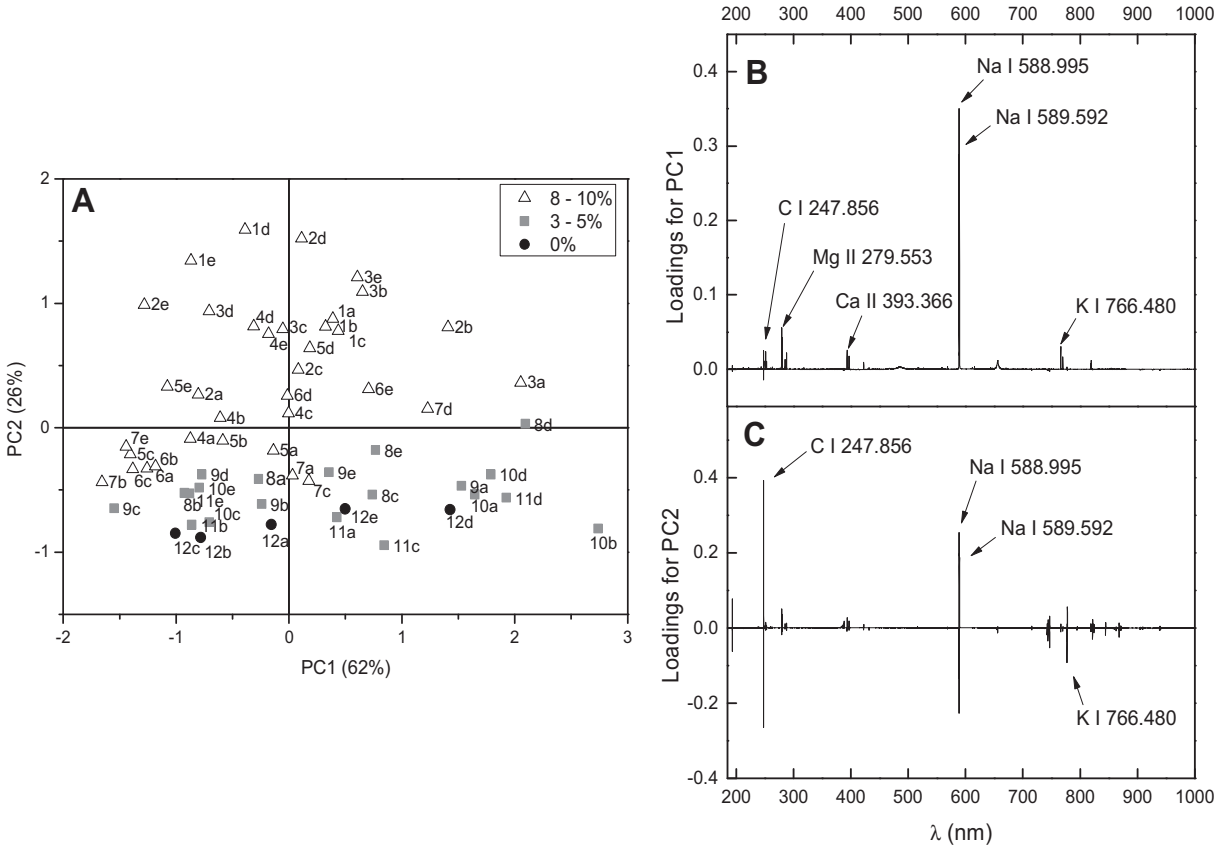

Fig. 6. Scores (a) and loadings for PC1 (b) and PC2 (c) calculated using the mean spectra standardized with the C I 247.86 nm line.

Table 1
Ratio between the maximum intensity of most important LIBS emission lines evidenced using PCA for both datasets, the mean spectra and the mean spectra standardized with the C I 247.86 nm, and 10% (w/v) PVA with no content of leached solutions.

Sample			1	2	3	4	5	6	7	8	9	10	11	12
Impurities (wt%)	Vegetal		10	0	5	8	5	3	0	5	0	3	0	0
	Soil		0	10	5	0	3	5	8	0	5	0	3	0
Sum of impurities (wt%)			10	10	10	8	8	8	8	5	5	3	3	0
Ratio of the highest intensity line	C193	Mean	1.2	1.2	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.0	1.1	1.1
		C247	1.1	1.0	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.0
	C247	Mean	1.1	1.1	1.0	1.1	1.1	1.1	1.1	1.0	1.0	1.0	1.0	1.0
		C247	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Mg279	Mean	2.1	2.0	1.1	1.3	1.0	0.5	0.4	2.0	1.0	1.1	1.2	1.0
		C247	2.0	2.0	1.3	1.2	1.0	0.5	0.4	2.0	2.0	1.3	1.5	1.0
	Mg280	Mean	2.0	2.0	1.2	1.3	1.0	0.5	0.4	2.0	1.0	1.2	2.0	1.0
		C247	2.0	2.0	1.3	1.2	1.0	0.5	0.4	2.4	2.4	1.4	2.1	1.0
	Ca393	Mean	1.5	1.4	1.0	1.0	1.0	0.4	0.3	1.1	1.0	1.0	1.0	1.0
		C247	1.3	1.5	1.0	1.0	1.0	0.4	0.4	1.3	1.3	1.0	1.0	1.0
	Ca396	Mean	1.5	1.5	1.0	1.1	1.0	0.4	0.4	1.3	1.0	1.0	1.0	1.0
		C247	1.3	2.0	1.1	1.0	1.0	0.4	0.4	1.5	1.5	1.1	1.1	1.0
	Na588	Mean	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		C247	1.0	1.0	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.0	1.0
	Na589	Mean	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		C247	1.0	1.0	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.0	1.0
	K766	Mean	1.0	0.1	1.0	1.0	0.4	0.3	0.2	1.0	1.0	1.1	0.2	1.0
		C247	1.0	0.1	1.0	1.0	0.4	0.3	0.2	1.0	1.0	2.0	0.2	1.0
	K769	Mean	1.0	0.1	1.0	1.0	0.4	0.2	0.2	1.0	0.5	1.0	0.1	1.0
		C247	1.0	0.1	1.0	1.0	0.4	0.3	0.2	1.0	1.0	1.5	0.2	1.0

Gray boxes are values above 1.5.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2017.12.005.

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