Direct Determination of Sugar Cane Quality Parameters by X-ray Spectrometry and Multivariate Analysis

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ABSTRACT: Current methods for quality control of sugar cane are performed in extracted juice using several methodologies, often requiring appreciable time and chemicals (eventually toxic), making the methods not green and expensive. The present study proposes the use of X-ray spectrometry together with chemometric methods as an innovative and alternative technique for determining sugar cane quality parameters, specifically sucrose concentration, POL, and fiber content. Measurements in stem, leaf, and juice were performed, and those applied directly in stem provided the best results. Prediction models for sugar cane stem determinations with a single 60 s irradiation using portable X-ray fluorescence equipment allows estimating the % sucrose, % fiber, and POL simultaneously. Average relative deviations in the prediction step of around 8% are acceptable if considering that field measurements were done. These results may indicate the best period to cut a particular crop as well as for evaluating the quality of sugar cane for the sugar and alcohol industries.

KEYWORDS: portable X-ray fluorescence, multivariate calibration, sugar cane, PLS, sucrose, fiber

■ INTRODUCTION

Sugar cane is an important food crop of the tropic and subtropic areas, cultivated in more than 70 countries located between 40° N and 32°5′ S, encompassing approximately one-half the globe.[1] Raw sugar and ethanol production have been the predominant commodity produced from sugar cane (*Saccharum* spp. hybrids). Worldwide interest in renewable energy has focused attention in total biomass production of energy canes rather than sucrose yield alone.[2]

The maturation process of sugar cane can be defined as the physiological process involving formation of sugars in leaves and their transportation and storage in the stem. From an economic point of view, the cane has to be cut when it reaches the minimum content of 13% sucrose by weight of the stem, which is required to be industrially feasible.[3] In São Paulo State, Brazil, the National Concill of Sugar cane Producers of São Paulo State (CONSECANA) adopts the cane price directly from its sucrose content; thus, the producer needs to combine high agricultural productivity with high sucrose content at harvest time. In this context, quality control parameters, such as % sucrose in the juice, % fiber, and POL (polarization) in sugar cane, are important pieces of information for producers as well as in sugar refineries and food industries because of sucrose continuous evolution during the maturation and later fermentation processes.

Current methods for quality control of sugar cane are performed in extracted juice using several methodologies, such as cutting, milling, pressing, juice clarification, and analysis on a saccharimeter or NIR equipment. These often require appreciable time and chemicals (eventually toxic), making the methods not green and expensive.

Vis/NIR spectroscopy and multivariate calibration is a convenient combination often used for % sucrose determination.[4−11]

This paper proposes the use of X-ray spectrometry as an innovative and alternative technique for sugar cane quality parameter determination. A branch of X-ray spectrometry, called X-ray fluorescence, is an analytical technique based primarily on the photoelectric effect, which reveals qualitative and quantitative aspects of atoms contained in a sample. These aspects can be measured with confidence when the atoms have high enough photoelectric X-ray absorption coefficients, that is, for high-Z elements (metals).[12] Generally, when a sample contains very light elements ($Z < 11$), the incident X-ray beam is mainly scattered and poorly absorbed. However, the scattering regions of similar samples are very informative when combined with a multivariate mathematical tool.[13] This is the basis of the X-ray scattering spectrometry (XRSS) technique,[14] which not only considers characteristic elemental lines but also makes use of other spectral regions including scattering peaks from Rayleigh, Compton, and Raman effects. Hence, by using the spectrum energy interval that covers X-ray source scatter and applying chemometrics tools on it, it has been possible to classify complex organic samples[15] such as vegetable oils,[16] varnishes,[17] plants,[18] polymers,[19] and teas.[20] Quantitative aspects can also be extracted by correlations using multivariate calibrations, common sugars with degrees of sweetness,[21] sucrose inversion monitoring, sucrose content in liquid samples,[11,12] energy
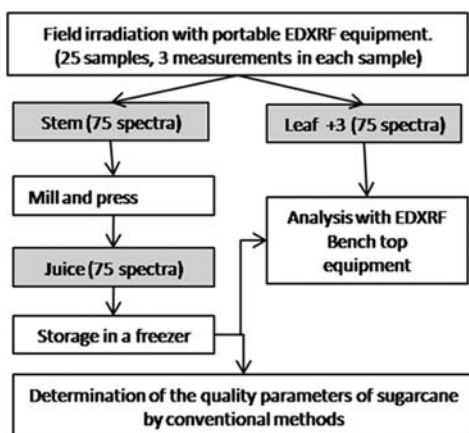
Figure 1. Measurement procedure and number of spectra obtained with portable equipment in each measurement.

values of industrialized foods,[22] and Ti concentration in toothpastes.[23] Thus, XRSS and chemometrics produces excellent results with several organic samples, is essentially nondestructive and fast, requires minimal sample handling and data treatment, and can be used in situ, with portable equipment, without generating any kind of chemical residuals.

Portable X-ray fluorescence with homemade or commercial equipment is actually viable, and its applications have been increasing in recent years.[24] It has been applied in a great variety of issues for environmental and geological interest,[25−29] archaeometry, archeological,[30−34] quality control monitorings,[35−37] among others.

The objectives of this paper are (a) to determine sugar cane quality parameters (% sucrose in juice, % POL of cane, % fiber) using energy-dispersive X-ray fluorescence (EDXRF) together with chemometric methods, allowing quantification of these parameters simultaneously, rapidly, and nondestructively, and (b) to evaluate the best sugar cane matrix (stem, leaf, or juice) to produce this information.

MATERIAL AND METHODS

Instrumentation. Two different EDXRF systems were used. For field measurements, the portable InnovX system model AlphaCam was used, provided with a Ta target X-ray tube and a Si-PIN detector. Measurement conditions were optimized for voltage, current, and filter in the X-ray tube, and the best condition was 20 kV, 20 μA, and 100 μm Al filter. In laboratory measurements, a Shimadzu EDX 700 with a Rh X-ray tube and a Si(Li) detector was used with 50 kV, 100 μA, and 100 s of irradiation, in air atmosphere and no radiation filter.

For conventional analysis of juice, a miller (Dedini-Siemens), a hydraulic press (MA098/cana, Marconi) at 250 kgf/cm^2 for 60 s, a moisture analyzer (IV-2000, GEHAKA), a polarimeter (Propol, Anton Paar with 40 mm cells), and a refratrometer (Abbe, Quimis) were used.

Sampling. Eleven different varieties of sugar cane from Fazenda Areão of Escola Superior de Agricultura Luiz de Queiroz, University of São Paulo, were analyzed. Ninety seven samples were analyzed in the field and subsequently cut for analysis by conventional methods. There were 22 samples collected in August, 24 in September, 26 in October, and 25 in December 2011. The varieties studied (with its codes in parentheses) were *Saccharum officinarum* (SAC), IAC SP95 5000 (IAC95), RB835089 (RB89), RB 835486 (RB86), RB 867515 (RB15), SP 711406 (SP06), SP 813250 (SP50), SP 803280 (SP80), SP 803280 (SP80), SP 701143 (SP43), SP 8642 (SP42).

At each sampling the team traveled to the experimental farm with the portable EDXRF system for field measurements. In August 2011, 2 stalks of each variety were cut with their leaves. After applying a PCA (principal component analysis) with these data, the necessity of more samples from *Saccharum officinarum* was verified, whose points separated sharply from the other in the scores plots.

Irradiations were performed directly in the central stem without any kind of major preparation, just cleaning the region with dry paper. Hand-held equipment was supported over the stem in order to avoid variation in the measurement geometry. The same care was devoted to the leaves, from which the middle front face of +3 leaf was chosen for all measurements. The first leaf from the top to the bottom of the stalk with clearly visible dewlap is designated as +1. Downward, they receive the numbers +2 and +3. The top visible dewlap leaf +3 is provided with a diagnostic tissue that is frequently used in the evaluation of plant nutritional status. Initially the stem and +3 leaf samples were irradiated in the field, directly in the grounded plant. After some tests, it was noted that the results were equivalent for planted samples and for up to 6 h after
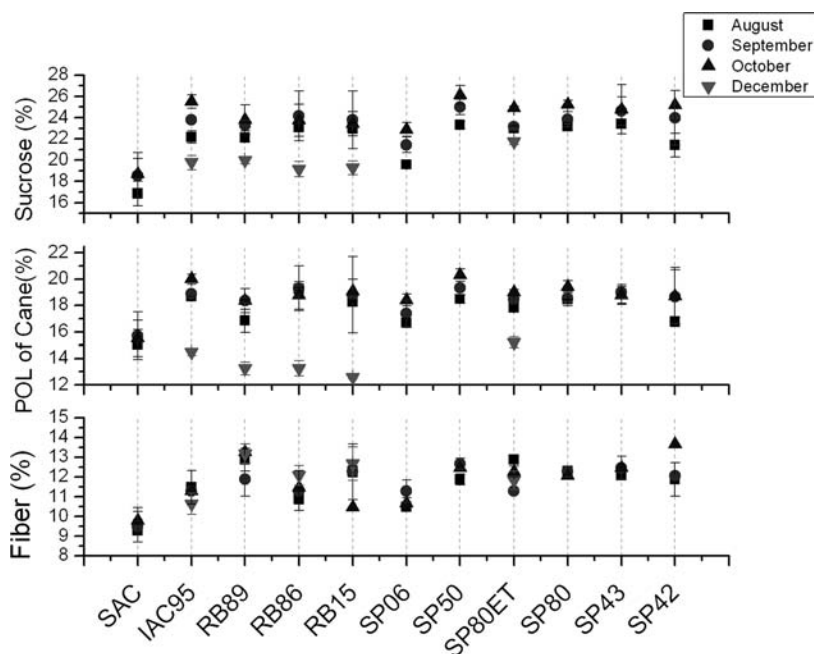

Figure 2. Sugar cane quality parameter for (a) % sucrose, (b) % fiber, and (c) % POL of cane. Values with standard deviation.

cutting. Thus, the samples were cut and analyzed in the laboratory where the procedures of cane processing were performed. The leaves were stored in plastic bags and irradiated at the benchtop equipment in the same day. All samples were measured 3 times by EDXRF.

After EDXRF measurements, sugar cane was milled and pressed to obtain fiber and juice for conventional laboratory analysis of sugar cane quality parameters, as shown Figure 1. Juice was frozen for posterior analysis in both EDXRF equipments, when 3 mL of the liquid was placed in XRF cells covered with a 2.5 μm thick Mylar (polyterphtalate) film.
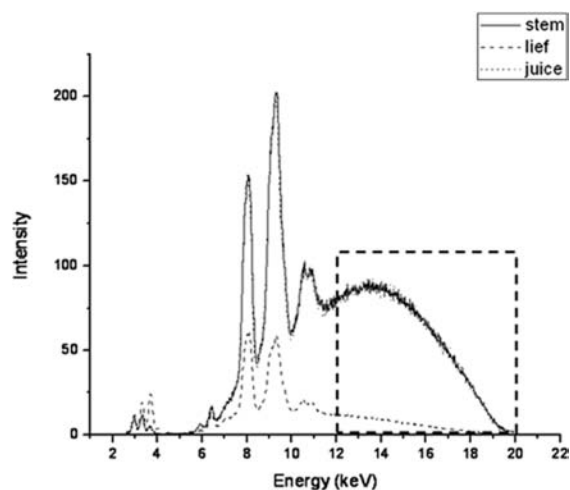

Figure 3. Stem, leaf, and juice sugar cane spectra for IAC95-5000 variety. Dotted square refers to the portion used to calculate the detection and quantification limits.

Table 1. Detection Limit (DL) and Quantification Limit (QL) Values for the Sugar Cane Parameters Determined by Portable EDXRF

	stem		leaf		juice	
	DL	QL	DL	QL	DL	QL
% sucrose	2.4	7.2	6.4	19.3	1.8	5.4
% POL of cane	1.4	4.1	3.5	10.7	1.1	3.2
% fiber	1.5	4.5	4.0	12.2	0.9	2.8

Conventional Methodology for Quality Parameters Determination. Values of % sucrose in the juice, % fiber, and % POL of cane were first obtained by conventional methodologies following the CONSECANA guide.[3] All methods described by CONSECANA are in agreement with the international rules from ICUMSA (International Commission for Uniform Methods of Sugar Analysis),[38] which are recognized by the Codex Alimentarius, European Union, and USA Chemicals Codex.

After cutting the plant, each sample was milled to break the fiber and 500 g of it was pressed to obtain the juice. The wet cake so produced is weighted (PBU) and then dried at 120 °C for 10 min using an infrared moisture analyzer.

For % sucrose (S) quantification, the juice must be clarified using lead subacetate, which was added to 200 mL of sugar cane juice. Clarified juice is analyzed using 40 mm cells at the polarimeter.

Fiber content, in %, was calculated from wet cake weight (PBU) according to the equation[3]

$$\text{Fiber}(F) = 0.08\text{PBU} + 0.876$$

The POL of cane (PC), in %, was calculated considering % sucrose in the juice (S) and fiber content (F) using the equation[3]

$$PC = S(1 - 0.01F)C$$

where C = 1.0313 − 0.00575 F.

Regression Models by Partial Least Squares (PLS). PLS is a well-known factor analysis multivariate method principally applied for prediction.[39,40] It requires a calibration step in which a model is constructed from a number of significant factors that establish a relation between independent variables (**X** matrix, samples spectra, in this case) with physical or chemical properties (**Y** matrix, concentration of the quality parameters of sugar cane, in this case), developing a mathematical model that makes possible the provision of unknown samples. Values for **Y** matrices were obtained from conventional determination of the sugar cane parameters. **X** matrices were prepared using the mean value of 3 measurements performed for each sample.

Models for % sucrose, % fiber, and % POL of cane (PC) were developed, since these are the main parameters used by farmers and refineries for evaluating the degree of maturarion and quality of sugar cane. Otherwise, other parameters can be evaluated using the measured data and equations that are given in the CONSECANA[3] rules.

PLS models were tested with different preprocessing techniques and spectrum region (number of variables in the X matrix). From the 97 samples, 24 were used as external prevision samples. The Kennard−Stone algorithm[41] was applied to obtain a uniform subset selection.

Table 2. PLS Model Parameters for the Set of Internal and External Validation for Stem, Leaf, and Juice of Sugarcane for Portable and Benchtop Equipment[a]

sample (no. of samples versus XRF measurement)	equipment	sugar cane parameter	LV	validation samples[b]	RMSEC	RMSECV	RMSEP	R^2 cal	R^2 pred
stem (97 × 3)	portable	% sucrose	6	14	0.5	2.5	0.7	0.96	0.88
		% fiber	6	10	0.3	1.1	0.3	0.94	0.86
		% POL of cane	6	10	0.1	1.5	0.3	0.99	0.92
leaf (97 × 3)	portable	% sucrose	8	18	0.6	2.8	1.0	0.94	0.74
		% fiber	8	13	0.3	1.3	0.5	0.92	0.63
		% POL of cane	8	15	0.4	1.6	0.6	0.95	0.69
	benchtop	% sucrose	8	14	0.6	2.3	1.0	0.95	0.77
		% fiber	8	20	0.24	1.2	0.9	0.96	0.16
		% POL of cane	8	16	0.4	1.6	1.1	0.95	0.49
juice (97 × 3)	portable	% sucrose	6	16	0.03	2.2	1.7	0.99	0.49
		% fiber	6	16	0.04	1.2	0.7	0.99	0.47
		% POL of cane	6	18	0.05	1.7	0.7	0.99	0.63
	benchtop	% sucrose	4	19	0.4	2.3	1.4	0.98	0.68
		% fiber	4	23	0.2	1.2	0.9	0.97	0.12
		% POL of cane	4	18	0.2	1.5	1.8	0.98	0.10

[a]LV: latent variable. RMSEC: root mean square error of the calibration. RMSECV: root mean squares error of cross validation. RMSECP: root mean square error of the prediction. R2 cal: Correlation coeficient of calibration. R2pred: Correlation coeficient of prediction. [b]Number of validation samples considering 3 times RMSEC.
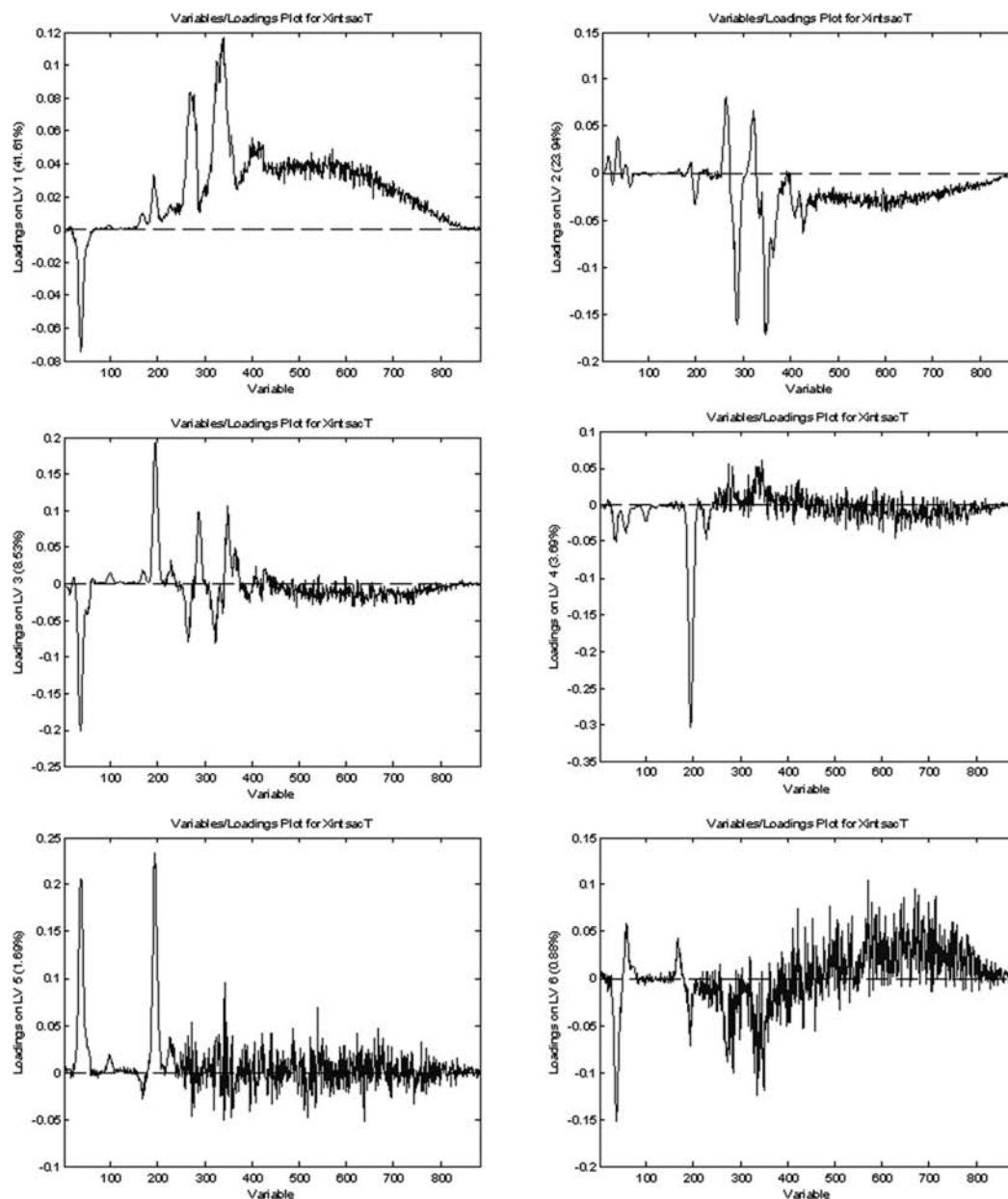
Figure 4. Loadings graphics from all latent variables used in the PLS model for sucrose in the stem with the portable XRF equipment data.

MatLab software with PLS ToolBox version 5.8 was used to execute the multivariate calculations.

Outliers are identified comparing the root mean square error of calibration (RMSEC) with the absolute error of that sample. In this study, a sample presenting a difference between its reference and its estimate values higher than 3 times the RMSEC is considered an outlier.[42]

Detection Limits and Quantification Limits in EDXRF Analysis. To estimate the detection limits (DL) from the parameters of interest in the portable EDXRF system, it is necessary to calculate the blank deviation or background under the region of interest in the spectrum. Considering the example for the % sucrose determination, first, a sugar cane sample without sucrose, in its stem or juice, is not naturally available. Besides this, in the present study, % sucrose is evaluated with X-ray scattering information, i.e., there is no sucrose peak in the obtained spectra. An alternative aproximation for DL and quantification limits (QL) when multivariate calibration is used is to select a region of the spectrum with noise signal or scattering signal and consider it as the net analytical signal

(NAS).[43,44] In this case, the final part of the spectrum often offers enough data for DL and QL calculations[45]

$$DL = 3\delta x \, \| \mathbf{b} \| = 3\delta x / SEN$$

$$QL = 10\delta x \, \| \mathbf{b} \| = 3\delta x / SEN$$

where δx is the standard deviation of the reference signal obtained from a matrix (n, m), with n samples and m variables, $\| \mathbf{b} \|$ is the norm regression vector from the calibration model, and SEN is the sensitivity or the inverse of $\mathbf{b}$ norm.

■ RESULTS AND DISCUSSION

Sugar Cane Quality Parameters. Figure 2 presents the average values of the sugar cane parameters, where the degree of maturation of each variety can be evaluated. *Saccharum officinarum* presented the lowest values of % sucrose compared with others. In general, the varieties reached their peak of sucrose in October, and sucrose inversion to glucose and fructose was
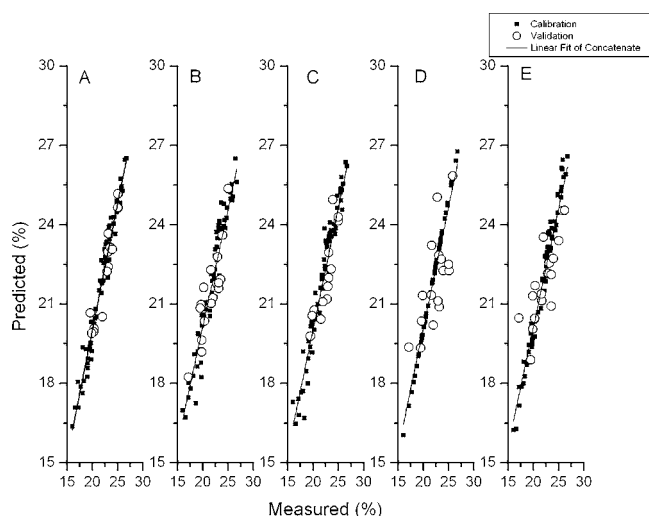
Figure 5. Reference values against the values estimated by PLS regression for sucrose: (A) stem portable EDXRF, (B) leaf portable EDXRF, (C) leaf benchtop EDXRF, (D) juice portable, and (E) juice benchtop.
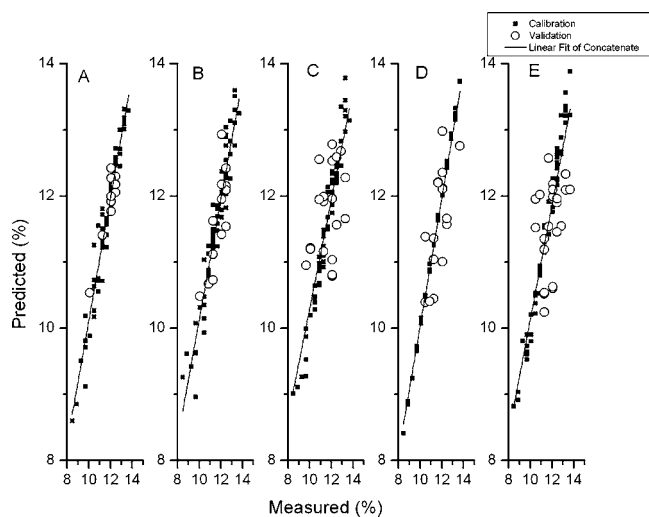

Figure 6. Reference values against the values estimated by PLS regression for fiber: (A) stem portable EDXRF, (B) leaf portable EDXRF, (C) leaf benchtop EDXRF, (D) juice portable, and (E) juice benchtop.

Figure 7. Reference values against the values estimated by PLS regression for POL of sugar cane: (A) stem portable EDXRF, (B) leaf portable EDXRF, (C) leaf benchtop EDXRF, (D) juice portable, and (E) juice benchtop.

The PLS models resulted in correlation coefficients (R^2) from 0.8 to 0.99, with the best values for the stem samples.

The search for outliers, that is, those samples whose reference and predicted values differ higher than three times the RMSEC, showed that some samples have to be disregarded. Newer simulations were then applied, and Table 2 presents the results. Now, R^2 for calibration and validation are between 0.92 and 0.99 and 0.10 and 0.92, respectively. R^2 values for stem samples are more satisfactory. External prediction presents the maximum medium relative standard deviation of 7% for stems, 13% for leaves, and 21% for juices. Considering only leaves and comparing the two types of equipment, for a total of 86 results, only seven have a relative deviation higher than 10%. For juice, with 110 validation results, 14 show a relative deviation higher than 10%.

Evaluating loadings graphics for the models, it is observed that all latent variables have significative information, as shown in Figure 4. Thus, the models are not over fitted,[46] and the data behavior, in this case, presents a validation correlation that is not robust, but satisfactory, considering the easiness of the method. Besides, it is usual that between 20% and 30% of the contributing results falling outside the limits may be considered as acceptable when using portable XRF instruments, according to Kump et al. in 2005.[47]

Figures 5–7 present measured versus predicted values in which paired t tests were applied at the 95% confidence level and mean differences between the populations are not statistically significant.

The results for leaf and juice with the two equipments can be considered equivalent. This conclusion is a guarantee that the use of portable equipment in the field is viable and robust, practically in real time (irradiation time of 60 s). Among the 3 distinct matrices under evaluation, the stem and juice furnished better results than leaves for all parameters.

XRS measurements in stems are extremally advantageous, since it dispenses any previous sample treatment and can be done with the plant still grounded or even after a short period after being cut. A large amount of samples can be processed in a short time and the results obtained still in the field provided that a notebook is avaiable.

clearly noted in December. These data comprise **Y** matrixes used in the PLS regression models.

Detection Limits and Quantification Limits. Detection limits for the portable EDXRF equipment were determined using the final part of the spectra from stem, leaves, and juice of 52 samples from the calibration set. The data comprises 3 matrices of (52×405), related to the spectral region from 12 to 20 keV, as shown in Figure 3. The obtained values are presented in Table 1, indicating that the system has enough sensitivity to estimate the parameters of interest.

PLS Model Results. After several simulations using Matlab, distinct preprocessing methods were tested as well as several number of variables in matrix data. Nevertheless, after evaluating these simulations, the mean centering preprocessing with the whole spectrum (from 2 to 20 keV for portable equipment and from 2 to 40 keV for bench equipment) was considered the best choice. The validation proccess used a total of 24 samples.
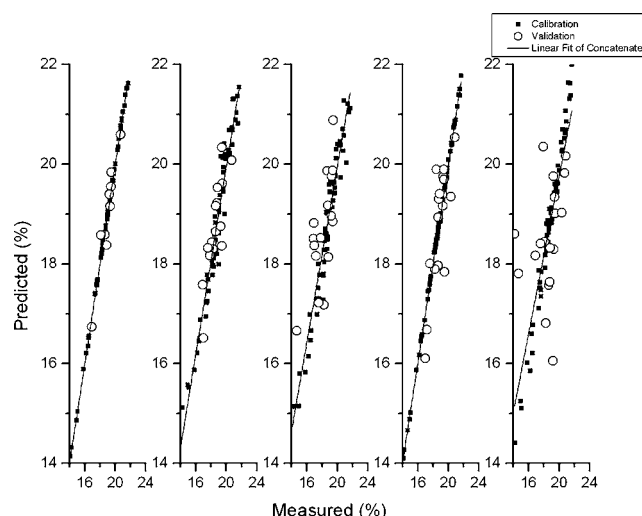
Using the juice to acquire the same parameter values is more troublesome but viable. To do so, it is obviously necessary to extract the juice from the sugar cane and pour it in a specific cell used for XRF irradiation, with the sample sustained on a Mylar film. In such a case, irradiations were necessary to be done in a support provided with the portable equipment. This is caused by the sample being a liquid; a more stable platform is required. In this case, irradiations done inside the laboratory are more adequate.

The mean predicted relative deviations are around 3%, an accetable value. As a final statement, the prediction results can be regarded as excellent, since three essential parameters for quality control of sugar cane can be estimated in a single 60 s irradiation, in the field, with a hand-portable instrument, and also with the plant still grounded. The great profit of this study is the aid in deciding the best time to have the sugar cane ready to be cut off, with a maximum of benefit. Alcohol and sugar factories can also take advantage of it.

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Notes

The authors declare no competing financial interest.

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