

Potential of Laser Induced Breakdown Spectroscopy for analyzing the quality of unroasted and ground coffee

Tiago Varão Silva^a, Silvine Zanni Hubinger^b, José Anchieta Gomes Neto^a,
Débora Marcondes Bastos Pereira Milori^b, Ednaldo José Ferreira^b, Edilene Cristina Ferreira^{a,*}

^a São Paulo State University - UNESP, Analytical Chemistry Department, P.O. Box 355, 14801-970 Araraquara, SP, Brazil

^b Embrapa Instrumentation, P.O. Box 741, 13560-970 São Carlos, SP, Brazil

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ABSTRACT

Coffee is an important commodity and a very popular beverage around the world. Its economic value as well as beverage quality are strongly dependent of the quality of beans. The presence of defective beans in coffee blends has caused a negative impact on the beverage Global Quality (GQ) assessed by cupping tests. The main defective beans observed in the productive chain has been those *Blacks*, *Greens* and *Sours* (BGS). Chemical composition of BGS has a damaging impact on beverage GQ. That is why analytical tools are needed for monitoring and controlling the GQ in coffee agro-industry. Near Infrared Spectroscopy (NIRS) has been successfully applied for assessment of coffee quality. Another potential technique for direct, clean and fast measurement of coffee GQ is Laser Induced Breakdown Spectroscopy (LIBS). Elements and diatomic molecules commonly present in organic compounds (structure) can be assessed by using LIBS. In this article is reported an evaluation of LIBS for the main interferents of GQ (BGS defects). Results confirm the great potential of LIBS for discriminating good beans from those with BGS defects by using emission lines of C, CN, C₂ and N. Most importantly, some emission lines presented strong linear correlation ($r > 0.9$) with NIRS absorption bands assigned to proteins, lipids, sugar and carboxylic acids, suggesting LIBS potential to estimate these compounds in unroasted and ground coffee samples.

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1. Introduction

For many years coffee has been one of the most consumed beverages in the world. The International Coffee Organization estimated a world consumption of coffee around 144.8 million of 60 kg bags in 2015 and the coffee exports in May 2016 in 9.32 million bags [1]. Due to this widespread consumption, the quality is no longer a simple differential to become an essential prerequisite [2,3].

The quality of coffee is related to its organoleptic properties which are result of several factors oscillating from planting to processing post-harvest [4]. One of the most important factors for expert tasters (and consumers) is related to bean variety. In general, a high quality coffee is essentially composed by flawless beans from Arabica specie [5], i.e., avoiding excessively blends. Blends of different species and defective beans are the cause of coffee quality depreciation [6].

Among several types of bean defects notable in the Brazilian processing agro-industry, three of them are the most frequent and can be categorized as: Black, Green and Sour (BGS). Black beans are commonly originated from over-ripened beans. Greens are immature fruits known by increasing beverage astringency. Sour beans have the cause of water

scarcity during development of the fruits or by abnormal fermentation [7]. The presence of BGS defects has a direct impact on demeaning the final beverage quality. The more BGS defects, the less the final beverage quality.

In order to aggregate value and expand internal consumption, the Secretary of Agriculture of São Paulo/Brazil, through the normative resolution (called as: SAA-28) of June 1, 2007 [8] established a technical standard for Brazilian coffee quality certification, based on a score, called Global Quality (GQ), assessed by a panel of experts (experienced tasters), using a very similar methodology to that one recommended by Technical Standards Committee of the Specialty Coffee Association of America (SCAA) for standards for cupping coffee [9]. From GQ, coffees are classified as: Traditional (GQ score: 4.5 to 6.0) Superior (GQ score: 6.1 to 7.2) and Gourmet (score 7.3 to 10) [10]. Additionally, SAA-28 establishes the maximum contents of BGS defects for Gourmet (0%), Superior (up to 10%) and Traditional (up to 20%) classes [8]. The method for assessing GQ by a panel of experts is expensive, time consuming, demands drink preparation and is rather subjective [11]. Therefore, a simple, fast, low-cost and reliable analytical method is still an essential (important and desirable) tool for an efficient, highly standardized, competitive and modern coffee industry.

Aiming to verify coffee quality authenticity and prevent fraud, several analytical methods have been developed for monitoring and

* Corresponding author.

E-mail address: edilene@iq.unesp.br (E.C. Ferreira).

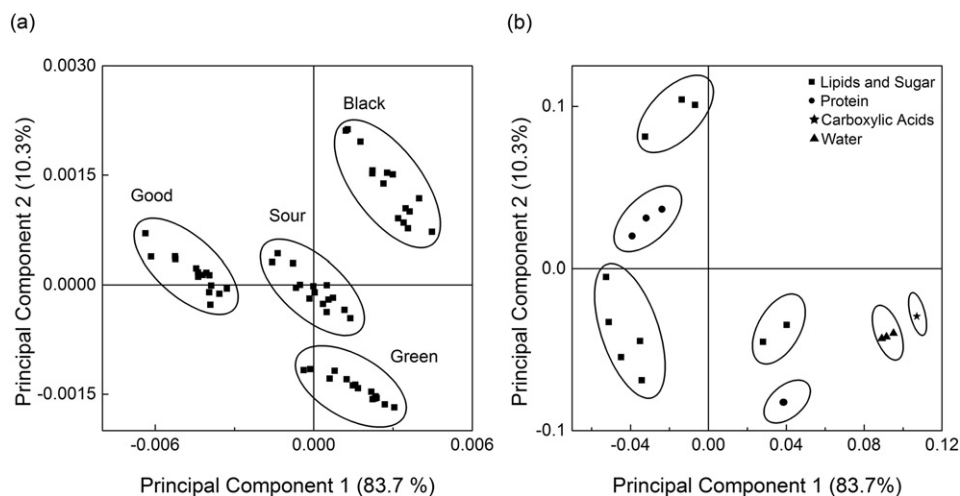


Fig. 1. Results of Principal Component Analysis (PC1xPC2) from NIRS derived spectral data: a) scores plot b) Wavenumbers contributions for discrimination among classes (see Table 2).

classifying the coffee beans [12,13]. Among the analytical techniques commonly applied to that purpose, Near Infrared Spectroscopy (NIRS) has been outstanding with good results [14–16]. The NIRS shows advantages over others dedicated to organic composition analysis (e.g. chromatography), since it performs direct, fast and low-cost analysis, dispensing complex procedures for samples (minimal pretreatment). Absorption bands in NIRS spectrum provide information about organic molecular compounds present in sample [17]. Thus, NIRS has an enormous potential for discriminating

different coffee classes, since there exist organic composition differences among them [5].

On the other hand, a more complete chemical profile for different coffee beans (including BGS defects) can extend current knowledge to beyond the molecular comprehension, providing scientific novelty and making technological development viable for analyzing quality tasted in coffee cupping.

Different methods based on atomic absorption and emission spectroscopy have been used to determine concentrations of elements in

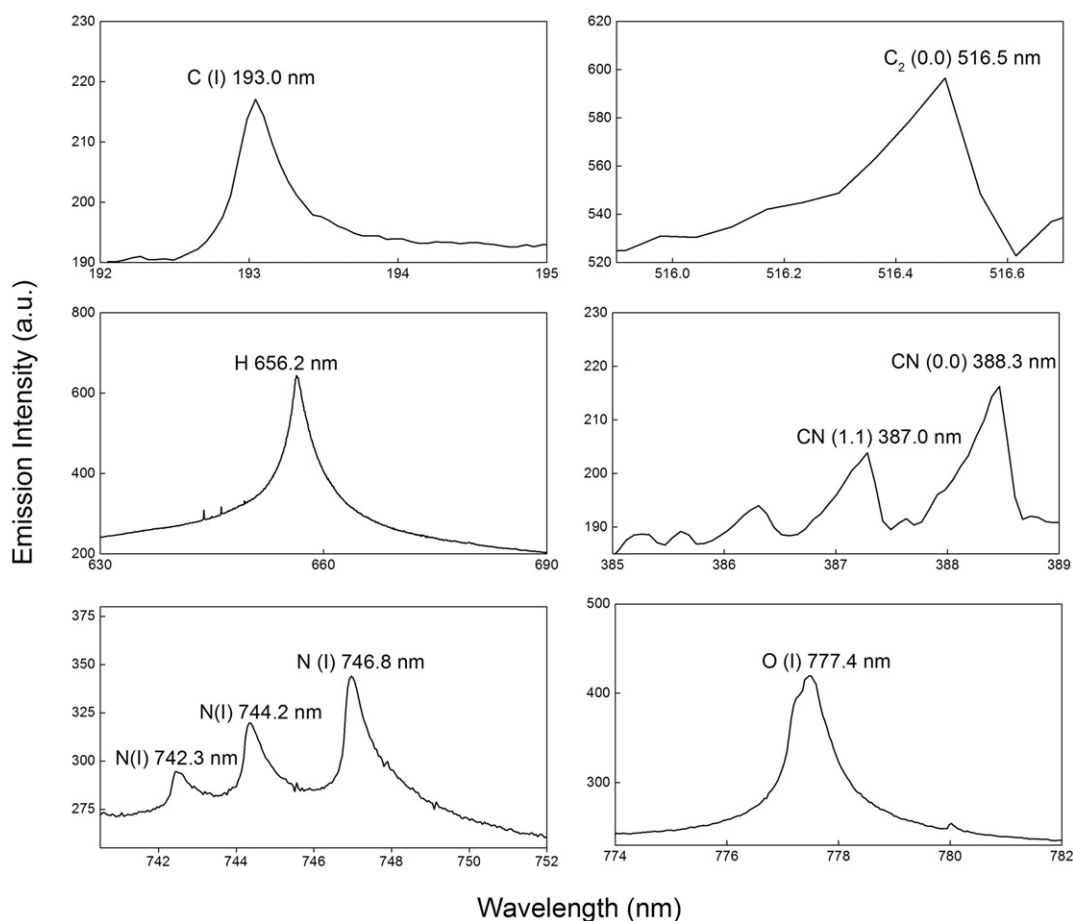


Fig. 2. Fragments of medium LIBS spectrum ($n = 40$) of good coffee sample in different spectral regions of the selected lines.

coffee samples [18]. In general, these techniques need an adequate sample preparation, some of them involving complicated procedures of acid decomposition in high temperatures. In this context, the technique Laser Induced Breakdown Spectroscopy (LIBS) stands out as an interesting alternative. LIBS is based on application of short energetic laser pulses, directly in sample surface. Laser pulse removes a reduced mass of sample, vaporizes it and produces a plasma. Breakdown of sample compounds and species excitation occurs as a result of laser pulse and the plasma action. The evaluation of the recorded light emission intensity, arising from the de-excitation processes, permits a qualitative and sometimes quantitative sample characterization [19]. As LIBS is directly performed on solid samples, a sample pretreatment is practically unnecessary. Although direct analysis may result in precision reduction, speed and lower cost per analysis make viable a high number of analyses per sample, which improves representativeness [20,21].

LIBS potential has also been exploited for classification of organic compounds in biological materials [20], oils [22] and explosives [23]. These applications are possible because of emission lines of major elements present in organic compounds, such as C, H, N and O [22,23] as well as lines corresponding to emission bands of diatomic molecules, such as CN [24] and C₂ [23]. Additionally, LIBS has also been investigated for determination of other samples properties such as pH and soil texture with high correlation among properties and emission lines [25,26].

Ferreira et al. (2011) [27] applied LIBS for classification of roasted coffees according to their respective GQ classes (Gourmet, Superior, Traditional and Inferior). According to them, wavelengths in the region of the hydrogen emission line (close to 680 nm) were useful to build a high accurate ensemble of decision trees for classification of roasted and ground coffees (commercially available).

An increasing demand for coffee quality certification in the world market brings with it an emergent necessity of techniques endowed with features like those immanent in LIBS. Thus, the aim of this study was investigating elemental and molecular compositions by using LIBS (establishing LIBS-NIRS correlations) to thereby demonstrate its potential for distinguishing classes of coffee beans, especially among good beans and BGS defects, as previous discrimination task intrinsically (and strongly) linked to the GQ of the resultant coffee drink. Elemental and molecular emission lines were analyzed by observing the highest correlations to molecular bands of C—H, C=O and O—H assessed through NIRS spectrum.

2. Material and methods

Samples of coffee beans (Arabic specie from the same crop) classified by an expert as “good” (good quality/no defects), “black”, “green” and “sour” were provided by a Brazilian coffee cooperative of Minas Gerais state. All samples were submitted to a cryogenic grinding, using grinding cycle of 2.0 min, followed by 3.0 min of sample refreezing and other grinding cycle of 2.0 min.

2.1. Sample analysis

The NIRS instrument used for analysis was a near infrared spectrometer, model Spectrum 100 N (Perkin-Elmer Corp., Norwalk, CT) covering 4000–10,000 cm⁻¹ range of wavenumbers with spectral resolution of 2 cm⁻¹. Masses around 2.0 g were placed in a glass cuvette, which was introduced over the sample holder of the spectrometer. For each of one of the five sample repetition per class, three measurements were carried. Each measurement corresponded to 32 averaged spectra.

For LIBS analysis, five pellets of each coffee class were prepared by applying 10 tons in 200 mg of ground samples. The pellets were placed in sample holder of a LIBS system. The mentioned equipment comprises seven spectrometers (model LIBS2500 from Ocean Optics, USA) with resolution around 0.1 nm (FWHM) for

the spectral analysis ranging from 188 to 980 nm, a Q-switched Nd:YAG laser at 1064 nm, manufactured by Quantel (Big Sky Laser Ultra50), an ablation chamber, a lens for laser focalization (10 cm of focal distance) and an optical system to collect plasma emission and to conduct it the spectrometers made up of a lens and a fiber optic bundle. All measurements were acquired by setting a pulse energy of 50 mJ with 8 ns duration, resulting in an output laser fluency around 0.3 J cm⁻² and an irradiance in focal point around 10¹² W cm⁻². The delay time (relative to a Q-switch delay) used was 11 μs and the fixed system instrumental conditions of integration time 2.1 ms. Laser pulses were spread on both sides of each pellet. Forty spectra were obtained from each prepared pellet resulting in 200 spectra per class of samples, since five pellets of each class were analyzed.

2.2. Data processing

NIRS spectra show undesirable effects like light scattering, which can account negatively to the results interpretation. Then an adequate spectral treatment is important to minimize these effects [17]. First derivative was chosen for this proposal considering its simplicity [17,28]. Therefore each mean spectrum (average of 32 spectra) acquired by the instrument was differentiated. A Principal Component Analysis (PCA) was carried on considering derivative spectra. Pirouette® 4.5 (Infometrix) software was used for PCA and the data were mean centering. The spectral bands responsible for separating the coffee classes

Table 1
Coffee classes discrimination according to LIBS emission lines.

Emission line	Significant difference between classes (<i>p</i> -value < 0.05)	No significant difference between classes (<i>p</i> -value > 0.05)
C (I) 193.0 nm	Green – Good Black – Good Sour – Good	Green – Black Green – Sour Black – Sour
CN (1.1) 387.0 nm	Green – Good Black – Good Sour – Good	Green – Black Green – Sour Black – Sour
CN (0.0) 388.5 nm	Green – Good Black – Good Sour – Good Green – Sour Black – Sour Green – Black	
C ₂ (0.0) 516.6 nm	Green – Good Black – Good Sour – Good Green – Sour Black – Sour	Green – Black
H 656.2 nm	Green – Good Black – Green	Green – Sour Black – Good Black – Sour Sour – Good Green – Sour Black – Sour
N (I) 742.3 nm	Green – Black Green – Good Black – Good Good – Sour	
N (I) 744.2 nm	Green – Black Green – Good Black – Good Good – Sour Green – Sour	Black – Sour
N (I) 746.8 nm	Green – Black Green – Good Black – Good Good – Sour Green – Sour	Black – Sour
O (I) 777.4 nm	Green – Black Green – Good Green – Sour Black – Sour	Black – Good Sour – Good

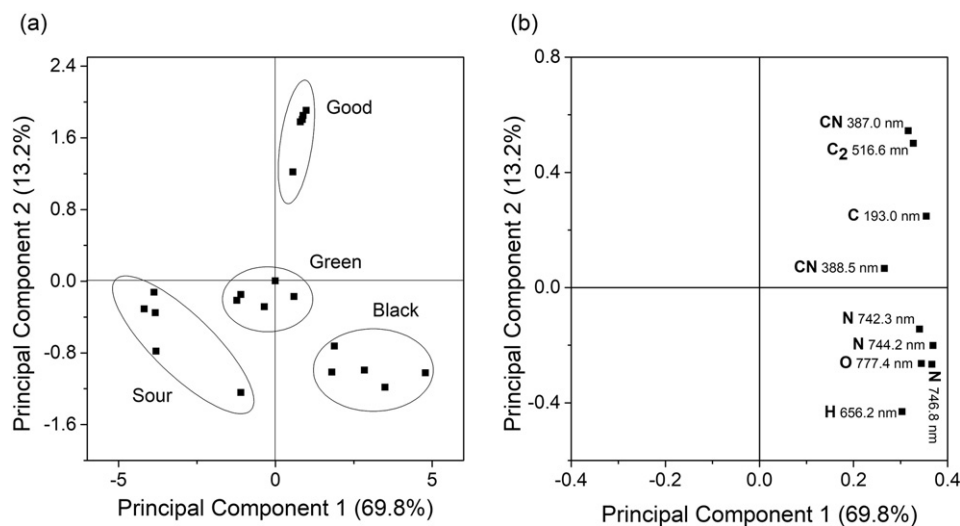


Fig. 3. Results of Principal Component Analysis (PC1xPC2) from LIBS derived spectral data: a) scores plot b) Species contributions for discrimination among classes (see Table 1).

were identified and associated with the compounds present in the samples.

In LIBS spectra, emission lines corresponding to species commonly present in organic molecules were selected: C (I) 193.0 nm, CN (0.0) 387.0 nm, CN (1.1) 388.5 nm, C₂ (0.0) 516.6 nm, H 656.2 nm, N (I) 742.3 nm, N (I) 744.2 nm, N (I) 746.8 nm and O (I) 777.4 nm. For all selected lines, Voigt functions were fitted and then integrated (area under the curve). An average spectrum corresponding to each coffee class was obtained (average of 200 spectra). Significant differences among means from coffee classes were assessed by using Analysis of Variance (ANOVA) with Tukey test (significance level equal to 0.05) for pairwise comparisons. Additionally a PCA was applied to the autoscaled data.

Afterwards, LIBS spectra were processed by first derivative only to get the same mathematical transformation applied to NIRS spectra, making possible a direct correlation (rate of change in LIBS vs. rate of change in NIRS). Derivative spectra from each coffee class for both analytical techniques were averaged, and then linear correlations between narrow ranges (peak interval) of emission lines (LIBS) and NIRS bands (C—H, C=O and O—H) were assessed exactly on inflection points (minimum value of the first derivative) of the interest regions.

3. Results and discussion

Discrimination of coffee classes from the NIRS results were clearly observed by PCA plot. The results of this analysis are shown in Fig. 1, where PC1 represents 83.7% and PC2 10.3% of total data variance. Ellipses were drawn to guide the eyes for the clustering of the classes. In Fig. 1b can be observed contributions for PCs. There are strong indications that main absorption bands are contributing for a clear discrimination among classes, i.e., C—H at 4244–4350 cm⁻¹ from lipids, sugars and proteins, C=O at about 5260 cm⁻¹ from carboxylic acid and O—H at 5280–5286 cm⁻¹ from water [2]. The Fig. 1b indicates that good beans, distinct by PC1, contain higher amounts of lipids, sugars and/or proteins. The green class, discriminated from the black and sour shows also proteins, lipids and sugars besides of the highest amounts of water and carboxylic acids. The sour class shows intermediate amounts of the mentioned compounds while black class shows lower amounts of these compounds. The color of black beans is result of a non enzymatic browning known as Maillard reactions, i.e. reactions between carbonyl groups of the sugars with the nucleophilic amino group of the amino acids [29]. As carboxylic acids and proteins are consumed in Maillard reaction these compounds were lower in black class.

Table 2

Linear correlation coefficient (in module) for differentiated minimum inflections of LIBS and NIRS signals.

Wavenumber attribution	NIRS wave number (cm ⁻¹)	LIBS wavelength (nm)								
		C (I) 193.0	CN (1.1) 387.2	CN (0.0) 388.5	C ₂ (0.0) 516.6	H 656.2	N (I) 742.3	N (I) 744.2	N (I) 746.8	O (I) 777.4
Protein	4244	0.894	0.821	0.815	0.663	0.948	0.935	0.922	0.898	0.872
	4246	0.958	0.908	0.902	0.766	0.881	0.885	0.852	0.830	0.779
	4248	0.990	0.962	0.956	0.839	0.799	0.818	0.768	0.748	0.675
Lipids, sugars and oils	4256	0.903	0.955	0.951	0.924	0.348	0.415	0.315	0.309	0.175
	4266	0.970	0.802	0.796	0.640	0.958	0.942	0.933	0.908	0.887
	4270	0.965	0.919	0.913	0.782	0.868	0.874	0.838	0.816	0.761
	4314	0.289	0.157	0.162	0.020	0.859	0.763	0.845	0.810	0.916
	4318	0.745	0.650	0.652	0.507	0.980	0.927	0.950	0.914	0.942
Protein	4324	0.993	0.997	0.996	0.923	0.651	0.579	0.613	0.592	0.501
	4326	0.964	0.993	0.992	0.944	0.510	0.482	0.472	0.457	0.345
	4328	0.910	0.961	0.960	0.939	0.362	0.379	0.326	0.315	0.188
	4330	0.816	0.892	0.892	0.904	0.182	0.251	0.147	0.141	0.003
	4348	0.803	0.711	0.704	0.538	0.986	0.915	0.965	0.939	0.940
Carboxil acids	4350	0.800	0.707	0.701	0.536	0.986	0.907	0.965	0.938	0.940
	5264	0.990	0.961	0.941	0.793	0.768	0.640	0.754	0.752	0.647
Water	5280	0.983	0.945	0.923	0.764	0.801	0.653	0.790	0.788	0.689
	5284	0.980	0.940	0.919	0.758	0.811	0.657	0.800	0.798	0.701
	5286	0.979	0.937	0.916	0.754	0.817	0.661	0.806	0.803	0.708

The above results suggest that proteins, lipids, sugar and carboxylic acids besides the water are important chemical compounds for discrimination of coffee classes and these compounds can be measured by NIRS to infer the coffee quality.

Whereas proteins, lipids, sugar, water and carboxylic acids are relevant for discrimination among coffee classes, emission lines of elements or diatomic species mostly present in the structures of these compounds were selected from LIBS spectra for evaluation. The selected lines in LIBS spectra can be observed in Fig. 2.

The coffee classes were compared considering medium areas of each selected emission lines. The significant differences (p -value < 0.05) among the classes in function of selected emission lines are shown in Table 1. For clarifying result visualizations a PCA was performed. Scores and loading plots are shown in Fig. 3. Except for the H 656.2 nm and O (I) 777.4 nm lines, the other lines are suitable to be used for discrimination of good beans. These results emphasize LIBS potential for detecting improper blends of BGS defects in Gourmet coffees (100% good beans). Furthermore, it is highlighted the potential of the lines of CN (0.0) 388.5 nm, C₂ (0.0) 516.6 nm, N (I) 744.2 nm and N(I) 746.8 nm for discrimination of the mostly studied classes.

A study was carried out to check the correlations between NIRS absorption bands and LIBS emission lines. All pairwise correlation (using linear correlation as a metric) were applied to values extracted from inflection points. The results of linear correlation (in module) are shown in Table 2.

Absorption bands corresponding to proteins, lipids, sugar and carboxylic acids and emission lines of C(I) 193.0 nm, CN (1.1) 387.0 nm, CN (0.0) 388.5 nm showed correlation coefficient higher than 0.9 suggesting the potential of these emission lines to estimate classes of compounds in coffee samples by using only LIBS technique. The triplet of nitrogen, N (I) 742.3 nm, 744.2 nm and 746.8 nm, have potential for a linear modeling capable of estimating protein contents as well as C₂ (0.0) 516.6 nm for lipids, since these lines showed high correlation with respective NIRS absorption bands ($r \geq 0.9$). It is highlighted that CN emission band at 388.5 nm provided the best class discriminations and it was strongly correlated to coffee proteins (Table 2), suggesting that CN monitored lines are predominantly from protein molecular fragmentations.

The LIBS and NIRS techniques show similar features in terms of analytical simplicity, direct and fast analysis and portability potential. On the other hand, results suggest that LIBS can be capable of performing some kind of analysis similarly to NIRS, besides its ability to analyze the elemental composition, which is not feasible by using NIRS.

4. Conclusion

The quality of coffee is strongly linked to blends with defective beans. Black, Green and Sour beans damage beverage quality. Thus, the development of tools for detection of coffee quality adulteration is very important for world coffee agro-industry. LIBS technique showed a high potential for discriminating good beans from BGS defects from unroasted ground coffee. Emission lines of elements and emission bands of diatomic molecules derived from organic compounds showed good discriminant power. The high correlations ($r > 0.9$) observed for N, CN, C and C₂ LIBS emissions and NIRS absorption bands of proteins, lipids, sugars and carboxylic acids also suggest the potential of LIBS for estimation of these compounds. Finally, more than a multielemental determination, LIBS has shown a capacity for aggregating information on molecular and organic aspects (a particular feature attributed to NIRS) related to quality of coffee beans, and consequently coffee beverage resultant from them. These findings confirm LIBS as a promising tool for analyzing food quality in many agro-industry branches.

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