

Article

Authentication of Roasted Coffee Beans via LIBS: Statistical Principal Component Analysis

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Abstract: Great efforts are constantly being made by industry-specific coffee agencies to standardize the certification of coffee quality. In consequence, international trade requires quick and reliable analyses because of their high cost, the risk of misclassification, the difficulty of large-scale analysis, and, most importantly, the subjectivity generated by tasters. A powerful analytical method that can be used to accurately evaluate and identify coffee varieties is Laser-Induced Breakdown Spectroscopy (LIBS). In this study, it provided a quick, cost-effective, and residue-free method commonly used in laboratories for direct analysis, determining multi-elemental composition, and exploring the organic composition of roasted coffee. The mineral composition of eight varieties of pure roasted coffee was determined using a pulsed nanosecond laser produced from a Nd:YAG laser at 1064 nm. The most important spectral variables for coffee variety identification were sequestered using LIBS coupled with a chemometric-tool-based principal component analysis (PCA). The nine main wavelengths chosen corresponded to the elements of C(I), Mg(II, I), Ca(II), Fe(I), K(I), H(I), and O(I), in addition to the CN group. The overall findings indicated that using LIBS to identify coffee varieties is feasible based on a simple, quick, and eco-friendly strategy without the requirement for complex preparation or wasting time in preparation. Such studies can help to protect the coffee market and businesses by certifying product quality. Using LIBS and full statistical illustrations with PCA, the prevention of unfair competition, protection of consumers, and determination of coffee quality can be achieved.

Keywords: laser-induced breakdown spectroscopy; principal component analysis; roasted coffee beans; optical properties; laser ablation; detection method; chemical analysis



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1. Introduction

All over the world, roasted coffee is a mandatory part of the morning routine. It is a staple in many societies and is consumed by millions of people every day [1,2] as freshly roasted coffee beans have an enticing aroma and a bold, complex flavor [3]. According to the International Coffee Organization (ICO)'s statistics, coffee consumption increased by 4.2% during 2021/22, which is expected to completely increase by 1.7% during 2022/23 [4,5]. This highlights the significance of coffee in international trade, as it is the second most traded commodity in the world after oil [6]. As a result of this widespread acceptance, quality has evolved from a differentiating factor to a prerequisite as the organoleptic qualities of coffee are affected by a number of variables, from planting to post-harvest

treatment [7,8]. The structure of coffee shows that its flavor and aroma come from a variety of compounds, including caffeine, trigonelline, chlorogenic acid, amino acid (COOH-RNH), peptide (-CO-NH-), citric acid, malic acid, and others [6,9]. Coffee's complex composition makes it hard to pinpoint its precise ingredients. Additionally, the mixing process of roasted coffee, which attracts the attention of gourmets, is characterized by the addition of coffee husk and stems, maize, barley, wheat, soybeans, rye, etc., which lower coffee quality. This is related to DNA-based coffee adulteration detection. Roasted ground coffee is often examined under a microscope to detect adulterants because visual inspection is insufficient. The dark color and small particle size make it hard to detect roasted adulterants in the original sample.

The use of spectroscopic methods for characterization paves the way for the establishment of objective parameters that characterize coffee's quality. There is ample room for an investigation to establish a reliable set of parameters that distinguish coffee's nutritional value, because until now, there have been no standardized techniques available. For this reason, in today's homogeneous, competitive coffee industry, an easy, fast, cheap, and reliable analytical method is still needed. Many analytical methods for tracking and categorizing coffee beans have been developed to ensure quality and prevent fraud [10]. Recent research has focused on how FT-MIR spectroscopy and multivariate analysis can be used to improve food quality control [11]. This does not, however, imply that utilizing IR spectroscopy achieves the study's goal without destroying samples and/or losing time. Microscopy, chromatography with sophisticated statistical tools, and DNA-based methods are all examples of assessment techniques that are not always appropriate. Microscopy and DNA-based methods may be prohibitively expensive in terms of time and money as advanced statistical tools that can provide detailed information, but they are not perfect [12].

Laser-Induced Breakdown Spectroscopy (LIBS) can be analytically used to vaporize a small portion of the coffee sample before it breaks down, releasing radiation at specific wavelengths that can be analyzed to determine its chemical composition and physicochemical properties, which cannot be easily evaluated using other techniques. LIBS's ability to measure constituents quickly and accurately without disrupting the product is one of its main strong points as a regular coffee analysis tool, as well as its high sensitivity and specificity. This method is based on using Q-switched nanosecond laser pulses to induce a laser-matter interaction with the sample's surface, forming a plasma plume containing ions and swirling electrons at extremely high temperatures that reach more than 6000 K. After that, the appropriate optical system collects the emitted light and feeds it into the entrance slit of a spectrometer equipped with a light detector (typically an ICCD) for the dispersion and detection of the light spectrum. Taking self-absorption and the matrix effect into account, the emission spectrum obtained from stoichiometric ablation includes the characteristic spectral lines of the elements presented in the plasma plume of the sample material [13–17].

In order to obtain more precise and trustworthy results from LIBS analysis, chemometric methods like principal component analysis (PCA) are widely used in tandem with LIBS [18–20] to better see patterns and connections [21]. By applying PCA to the data obtained from LIBS analysis, researchers can determine which variables are most important in determining the composition of a sample and use this information to develop more accurate models for predicting the composition of unknown samples. Furthermore, spectral interferences and other sources of measurement errors during the LIBS analysis can be correlated and corrected using chemometric methods as applied in materials science, environmental monitoring, and forensic analysis. All of these applied fields show the successful incorporation of chemometric methods like PCA with LIBS analysis [4].

In 2017, Zhang et al. [4] investigated coffee varieties and identified their main elements using LIBS and chemometric methods. In 2018, Sezer et al. [22] investigated the feasibility of using LIBS in conjunction with multivariate data analysis techniques such as PLS and PCA as a rapid method for distinguishing coffee arabica, *triticum aestivum*/Triticum

durum wheat, maize, and chickpea samples, as well as determining adulteration ratios. In 2019, Silva et al. [23] presented a novel work investigating the spectral responses of LIBS for some coffee compounds in conjunction with linear regression modeling in order to solve the coffee value chain problem. A few studies have used LIBS to analyze parameters intrinsically related to coffee quality [4,7,24–26], which demonstrated how LIBS can be used to solve various problems related to coffee authentication by building calibration curves for detecting the degree of simulated adulteration in coffee and applying the ANN methodology. In 2020, Bilge et al. used PCA analysis to evaluate the variations in spectra by considering the physicochemical changes of coffee beans in order to determine the most effective factor in the physicochemical changes of samples [22].

The purpose of this study is to determine how well LIBS and PCA collaborate in classifying and authenticating eight samples of roasted coffee beans. PCA can be used to analyze the chemical makeup of coffee and isolate the factors that truly distinguish each variety. We demonstrate that the PCA approach is a preferred method for delivering LIBS-based product classification and can identify the most significant chemical constituents supporting the classification results under realistic and demanding conditions. As a result, using PCA in conjunction with LIBS, the complex world of roasted coffee can be more understood and appreciated.

2. Material and Method

2.1. Coffee Samples

Figure 1 shows the eight different cultivars of roasted coffee beans collected from bean producers present in Egypt. These coffee samples are Arabica medium, Ethiopian dark, Robusta medium, Colombian medium, Colombian dark, Brazilian light, Brazilian medium, and Brazilian dark which are imported from Ethiopia, India, Colombia, and Brazil.



Figure 1. The eight different cultivars of roasted coffee beans: (a) Brazilian light, (b) Brazilian medium, (c) Brazilian dark, (d) Colombian medium, (e) Colombian dark, (f) Arabica medium, (g) Robusta medium, and (h) Ethiopian dark, respectively.

2.2. Preparation of the Samples

The experiment was performed with the total number of each coffee bean type up to 20 beans to ensure the correction of the studied samples. As the first step of the experiment, the studied bean samples were ground and roasted at 250 °C for 15 min. Then, the samples were prepared as pellets by using 10-ton force with a hydraulic pellet press machine. Each pellet was analyzed as five replicates. After that, for qualitative analysis with high accuracy with high precision, the samples were prepared by mixing each sample group within itself to represent the general sample type.

2.3. Experimental LIBS Setup and Procedure

The LIBS experimental setup is a Q-switched Nd: YAG laser (Continuum Laser, Surelite II, Santa Clara, CA, USA), which has a pulse duration of 10 ns and typically employs a laser wavelength of 1064 nm, energy of 100 mJ/pulse, 10 Hz repetition rate, and a 0.5 mm effective beam diameter (Figure 2). Experiments are conducted on a sample mounted on an air-pressure-operated holder. The same laser source generated a plasma plume from the interaction of the focusing laser beam with the studied sample. With the X-Y-Z motorized stage at atmospheric pressure, the studied samples were placed on a sample holder with a 70 mm plano-convex quartz lens. The plasma plume is transported using Czerny-Turner spectrometer fiber optics (0.6 mm diameter and 50 cm length) (Princeton Instrument Acton SP2500, Trenton, NJ, USA). A total of 2400 lines/mm in the dispersion grating are used, covering wavelengths from 200 to 900. With an ICCD camera, the monochromator (1KRB-FG-43, gating time 2 ns). WinSpec/32, LIBS++, and the required database (open tools for analyzing the LIBS) are used for data acquisition and analysis. Three successive spectra were accumulated at the same position and measured in ambient air for each sample.

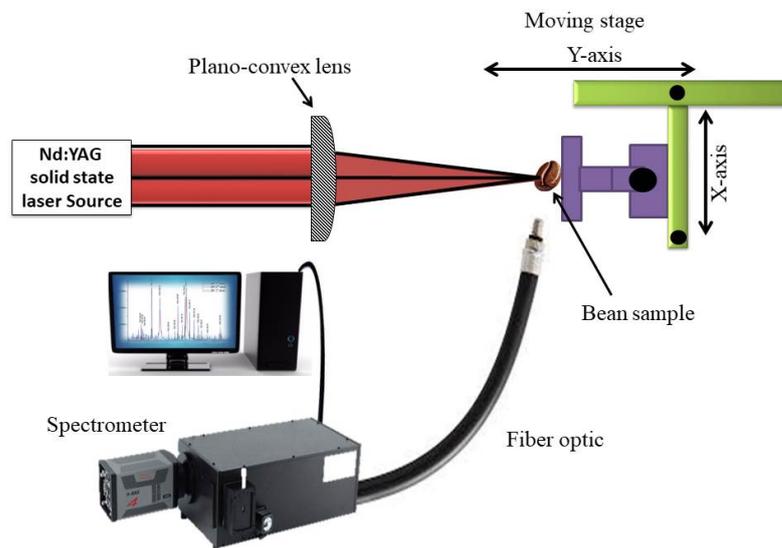


Figure 2. Schematic diagram of the LIBS experimental setup used for the analysis of the coffee samples.

For the atmospheric measurement condition, in the context of elemental measurement, Laser-Induced Breakdown Spectroscopy (LIBS) has shown that the laser-generated plasma ablation plume could alter its morphology in response to variations in the surrounding air pressure. Furthermore, the plasma is influenced by the specific composition of the ambient gas. Hence, the plasma formation processes, development, and emission, as well as the emission lines' atmospheric factors, such as pressure and the composition of the surrounding gas, have an impact on the LIBS spectra. Nevertheless, the utilization of the signal-to-background ratio (SBR) presents itself as a viable approach for quantifying the

measurement of Laser-Induced Breakdown Spectroscopy (LIBS) in atmospheric conditions. The utilization of SBR exhibits significant advantages in terms of enhanced performance at ideal pressure compared to atmospheric pressure, with the former being greater if it was measured just before sample measurement to reduce the effect of moisture.

2.4. Principle Component Analysis (PCA)

The analysis of spectral data is frequently made by PCA, a qualitative technique, in which one's original set of variables is transformed into a set of new variables that are linear combinations of the original set. Principal components are orthogonal variables that are ranked according to those differences which have explanations. Most of the variances could be accounted for by the first principal component (PC1), which was then followed by the second PC2, the third PC3, and so on. The first few PCs typically accounted for a large percentage of the total variance. Distributions of samples are typically shown in a score space using the score biplots, which are based on three PCs [27]. The spectroscopic data were analyzed statistically via PCA introduced by the commercial software OriginPro 2022 (version 9.5.0 SR1). The LIBS spectra of the eight types of roasted coffee samples were obtained after ten LIBS pulses to be confirmed theoretically by means of PCA analysis.

3. Result and Discussion

3.1. Main Elements Identified by LIBS

LIBS technique is used to analyze the elemental composition of the studied samples by focusing a laser beam individually on them and measuring the light emitted by the generated plasma. This technique is non-destructive and requires minimal sample preparation. The focused laser beam on the surface of the sample causes a small amount of material to vaporize and form plasma. This plasma emits radiation at specific wavelengths, which can be analyzed to determine the elemental composition of the sample. The typical LIBS spectra of the roasted coffee beans are shown in Figure 3, where ionic and molecular bands along with a neutral atomic emission line of hydrogen can be observed. The observed atomic emission lines and molecular lines were identified using the standard spectral lines collected from the National Institute of Standard Technology (NIST).

Emission lines of roasted coffee beans in the spectra showed that the spectrum mainly consisted of various elements such as C, H, O, N, K, Ca, Mg, Fe, and CN groups. These elements of C, N, O, and H reflect the organic structure, while the elements of Ca, Mg, K, and Fe represent the inorganic part. The elemental composition of coffee beans can vary depending on factors such as the origin of the beans, the roasting process used, and storage conditions. Additionally, the profile of the mineral content in coffee varies depending on soil composition, geographical origin, field practice, climate conditions, and fertilizers. This information can be useful in determining the quality and authenticity of coffee beans as well as identifying any potential contaminants or adulterants as shown in Figure 3. Table 1 summarizes the relative wavelengths and intensity spectra from each element identified from different roasted coffee. Moreover, according to the literature, K represents the highest mineral content of coffee beans, with the minor remaining elemental content typically consisting of Mg and Ca, as well as the presence of other trace elements such as Fe. The presence of the addition elements as a trace element or the varying ratio between elements has a significant impact on the taste of coffee. These spectral lines were chosen because they are stable emission lines for the elements being investigated. Furthermore, there is no interference or overlap between the selected lines and any other element's spectral lines.

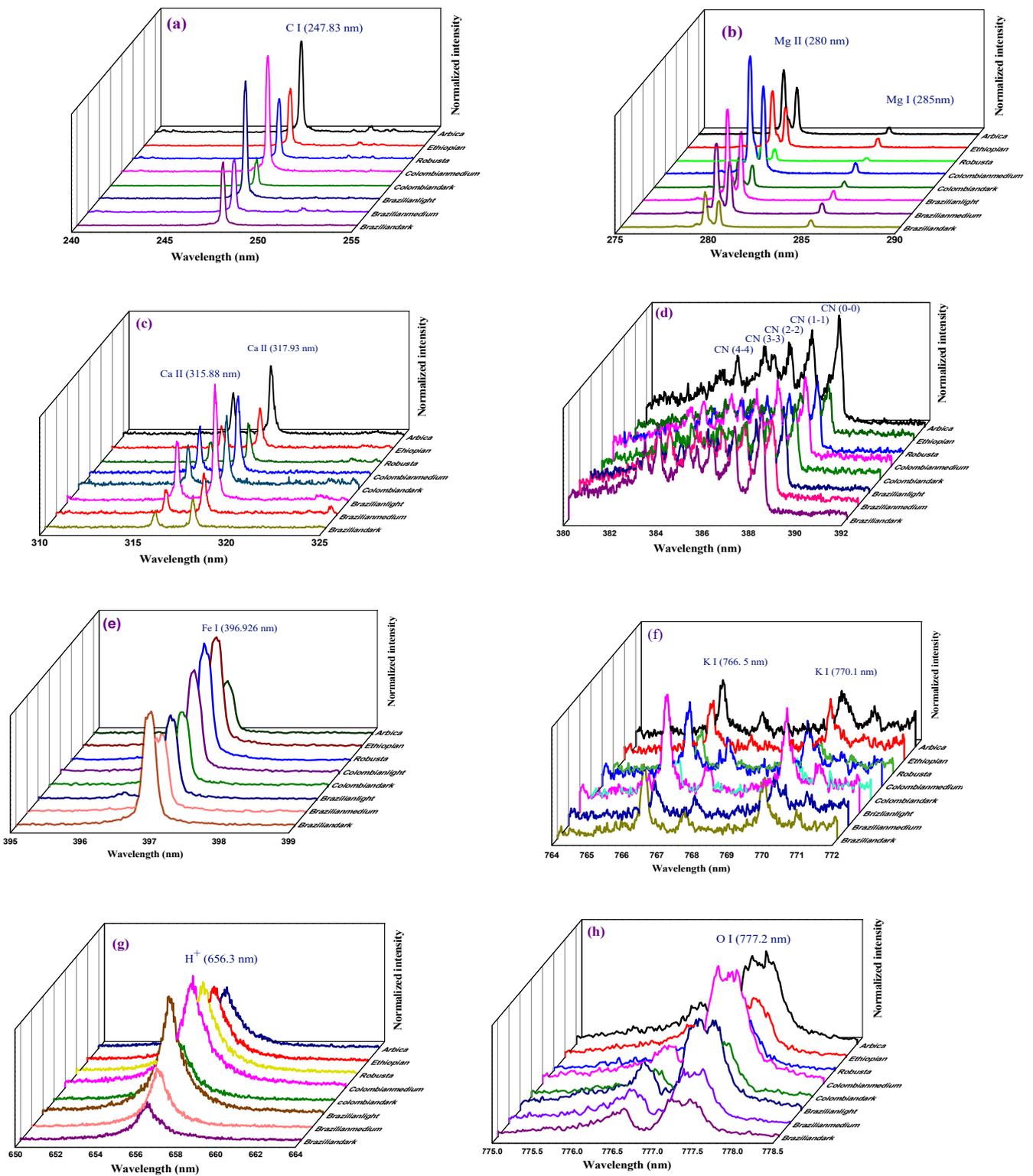


Figure 3. LIBS spectra of (a) C, (b) Mg, (c) Ca, (d) CN groups, and (e) Fe, (f) K, (g) H, and (h) O for eight different roasted coffee samples.

Table 1. Variation of integral emission intensity corresponds to the elements C(I), Mg (I, II), Ca(II), Fe(I), K(I), H(I), O(I), and CN group for different eight roasted coffee samples.

Element	Wave-length (nm)	Integral Emission Intensity (a. u.)								
		Brazilian Dark	Brazilian Medium	Brazilian Light	Colombian Dark	Colombian Medium	Robusta Medium	Ethiopian Dark	Arabica Medium	
Carbon	C (I)	247.856	53,712	45,535	99,489	22,258	98,867	51,561	49,009	77,518
	Mg (II)	279.553	49,538	98,348	127,475	60,735	64,427	20,808	79,253	90,062
Magnesium	Mg (II)	280.27	37,304	73,225	96,480	31,061	122,858	17,375	56,375	65,576
	Mg (I)	285.2	10,398	14,865	14,022	9194	16,275	4783	12,870	10,003
Calcium	Ca (II)	315.887	7882	9798	23,481	17,728	20,330	8685	9999	18,051
	Ca (II)	317.933	13,413	17,547	48,387	30,345	32,907	16,094	17,217	28,991
CN group	CN	388.342	10,922	15,692	25,404	15,895	31,965	14,470	17,030	26,202
	Fe (I)	396.926	67,296	47,085	49,795	43,785	60,683	68,531	63,619	31,481
Hydrogen	H (I)	656.3	18,434	27,690	54,355	29,294	48,918	42,241	34,613	28,428
	K (I)	766.4	12,624	8141	7216	19,012	14,024	8084	9732	10,984
Potassium	K (I)	769.897	10,601	8692	17,108	7519	11,195	5786	10,508	9727
	O (I)	777.194	10,922	15,692	25,404	15,895	31,965	14,470	17,030	26,202

3.2. Evaluation of LIBS Spectra

The LIBS spectra shown in Figure 3a–h were acquired from eight roasted coffee bean samples. Ten laser shots are taken at three different locations on each sample to generate an average LIBS spectrum. All of the samples were found to be composed of C, Mg, Ca, Fe, K, and CN groups, among other elements. The figure demonstrates how widely roasted coffees can vary in quality. Variations in the concentration of the individual elements can be seen in the LIBS spectra of the coffee beans as the changes in the normalized intensity values of the atomic emissions.

The sample spectra in Figure 3a show carbon recognition at wavelengths ranging from 235–259 nm. The C intensity of the most prominent C I lines differs almost imperceptibly between the dark Colombian sample, the light Brazilian sample, and the medium Colombian sample. Colombian dark coffee contains approximately 88% as much C as Brazilian light coffee. Furthermore, when comparing the Arabica medium sample to the Colombian dark, the amount of C increases by approximately 66%. Other Colombian dark samples showed carbon intensity increases ranging from 45.7% to 53.9%.

Additionally, three prominent Mg lines are visible between 279 and 286 nm, as shown in Figure 3b. Mg line intensities (279.668, 280.35, and 285.313 nm) are provided. The Mg line intensity was the highest in the Colombian medium coffee sample, while the convergent value of the Brazilian light coffee sample was very close to that of the C sample. In contrast, the Robusta medium contains 85.8% less Mg than the Colombian medium or Brazilian light.

Moreover, the level of Ca emission from the roasted coffee beans is depicted in Figure 3c. Ca emission intensity is reduced during roasting [28,29]. Coffee beans lose some of their Ca emission intensity during roasting because H and O are released from their hydrocarbon bonds. This is true; however, the coffee beans also lose weight, grow in volume, and shrink in density throughout the roasting process, making it a complex heat transfer process. Ca in coffee will be measured at 315.88 nm and 317.93 nm in this investigation. Light coffee from Brazil has the highest Ca emission intensity, while dark coffee from Brazil has the lowest Ca contribution, dropping by about 72.28% from the highest concentration.

Furthermore, to explain its high-fat content, the LIBS spectrum of Colombian medium coffee shows a much stronger CN band than the spectra of the other samples (Figure 3d).

Moreover, the spectra of the Fe lines between 394 and 400 nm are displayed in Figure 3e for all samples. The sample's Fe concentration was determined using the strong Fe line at 396.9 nm. Elevated Fe concentrations were found in all four samples (Brazilian dark, Colombian medium, Robusta medium, and Ethiopian dark), though to varying degrees. The remaining four samples are all very similar in intensity, dropping by only 36% from the strongest sample.

In addition, the K spectral lines between 764 and 772 nm are shown in Figure 3f. These lines have wavelengths of 766.4 and 769.897 nm, respectively. The findings show that the K intensities of Brazilian light, Colombian dark, and Robusta medium coffees all differ significantly. Except for the Brazilian medium, where the two K spectral lines have identical intensities, the difference in all other samples is negligible. This could be due to the roasting technique.

Additionally, the H line at 656.3 has the highest emission intensity and is, therefore, the most noticeable in both the Brazilian light and the Colombian medium coffee samples. From the highest concentration in the Brazilian light coffee sample to the lowest concentration in the remaining samples, as shown in Figure 3g, the H concentration gradually decreases.

Moreover, Figure 3h illustrates the O emission lines of eight coffee samples of varying concentrations. In Colombia type, the intensity ranges from medium to low, with the latter having a reduction of 65.8%.

3.3. PCA with LIBS Spectra

PCA can be used to dissect laser-pulsed element composition spectra to analyze large datasets for eight different types of roasted coffee with multiple variables while retaining as much information as possible. It can also determine which wavelengths or spectral bands best define each type of coffee. PCA would first normalize the data to remove any outliers caused by changes in laser pulse intensity or other factors that could affect the spectra. PCA can determine which factors are most and least dependent on one another after data normalization [30]. Highly correlated elements may have originated in the same location or been roasted under similar conditions. Separate components, on the other hand, may reveal unusual roasting or sourcing conditions. This is achieved by extracting patterns from the data and generating new variables (principal components) that account for the majority of the variance in the source data. PCA revealed that three major components accounted for 99% of the variance in the data in this study. Using these variables, a score plot depicting the relationships between the samples based on their elemental makeup was created. Each PC is a linear combination of element concentrations that explains the observed variation in the sample. The initial PC, followed by the smaller PCs, explains the greatest amount of variation. Some samples are grouped together based on their elemental composition, indicating that common factors influence their chemistry, whereas those with different compositions will branch off. This explains the significance of coffee quality and how these factors influence the coffee roasting process.

In Figure 4, 3D PCA is used to display the data in a geographical context as a useful tool. When dealing with massive, intricate datasets that resist easy two-dimensional display. It prioritizes various spectral elements that influence the overall variation in spectral LIBS data from roasted coffee samples. As a result, spectral differences between coffee varieties could be a useful grading metric. The PCA plot generated from the LIBS data in Figure 4a–h convincingly validated the coffee sample discrimination. The PCA model was constructed using three PCs and revealed significant variability among the various matrices. The first two PCs explain the vast majority of the variance. The first PC explained 74.60% of the total variance for C, 99.5% of the total variance for Mg and Fe, 97.5% of the total variance for Ca and O, 96.88% the total variance for the CN group, and 89% of the total variance for K. The second PC variance contains 24.31% C, 3.26% K, and 1.85% O, with the remaining elements ranging from 0.18 to 0.75%. Finally, the LIBS method allows for analysis in seconds with high accuracy and precision, with no need for chemicals or sample preparation steps.

It's worth noting that PCA can also be used to determine whether or not a given coffee sample is authentic by analyzing its chemical composition makeup. Principal component analysis can be used to zero in on the precise variables or chemical substances that have the greatest impact on the observed differentiation. The coffee samples can be analyzed with PCA to find connections between the many variables or chemical information. Knowing the effects of various adulterants on the composition and quality of roasted coffee is aided by these data. The PCA findings can be shown graphically in the form of scatter plots or biplots, which show the connections between the samples and the variables. The findings are easier to understand and relay thanks to the three-dimensional visualizations displayed. Therefore, PCA in the context of adulteration of roasted coffee offers a thorough analysis that aids in detecting trends, identifying outliers, discriminating between genuine and contaminated samples, understanding correlations, and visualizing results for better interpretation. Since principal component analysis (PCA) is a mathematical model used to explain the unseen reality, evaluating its veracity necessitates a convincing model in which the truth is not open to interpretation. The results of principal component analysis (PCA) are used to uncover patterns and form conclusions about the genesis, development, distribution, and relatedness of phenomena. Our results provide more evidence that PCA outputs and the insights gleaned from them are reliable and can be relied upon by LIBS.

Even though the first two principal components do a good job for explaining the total variance, the third principal component may still be useful. The third principal component may reveal new insights into the data that the first two principal components have missed. It can help shed light on previously unseen connections and trends. The addition of a PC3 can increase the analysis's interpretability, leading to a more satisfying result. It could focus on additional variables or factors that contribute to the total variance in ways that were not obvious from looking at the first two components. Therefore, the analysis will be more stable and reliable when using a larger number of principal components. Generally, adding more principal components provides more availability for working with different kinds of data. Therefore, while the first two principal components may explain a substantial amount of variance, taking into account additional components may yield insightful new information, improve the quality of interpretation, increase the robustness of the analysis, and make it more resistant to change.

Table 2 displays the loadings or the extent to which each variable is related to each factor in a factor analysis. It shows the strength and direction of the relationship between each variable and each factor as each cell in the table represents the loading value for the corresponding variable and factor. The loading value is a standardized estimate that ranges from -1 to 1 , where values closer to 1 indicate a strong positive relationship, values closer to -1 indicate a strong negative relationship and values closer to 0 indicate little to no relationship. The factor loadings table is used to interpret which variables are most strongly associated with each factor. By examining these loadings, they can identify the underlying factors that explain the correlations obtained in Table 3 among the studied variables. This information is crucial for understanding the structure or dimensions of the data and can guide further analysis or decision-making. Additionally, the variance percentage of factor score coefficients for all studied elements has been provided in Table 3. A factor analysis must be first performed to obtain the factor score coefficients (factor loadings). The variance percentage for each element may be calculated by squaring the coefficient and multiplying it by 100 . This estimation gives the percentage of variance explained by each factor for each element. Moreover, the correlation matrix is a statistical method for analyzing the connection between three or more variables (eight coffee samples). Therefore, Table 4 is built by summing up the correlation coefficients between every possible pair of variables in the dataset for each studied element. This matrix is usually square with the same number of rows and columns as the number of principal components variables. The diagonal elements are always 1 because each sample is perfectly correlated with itself. The generated matrix quantifies how strongly and in what direction the variables are related. A value of -1 in the matrix represents an absolutely negative correlation, a value of 0 indicates no correlation

at all, and a value of 1 represents an absolutely positive correlation. Consequently, in Table 4, the generated set of matrices corresponding to all elements under consideration is a powerful tool for exploring multivariate data for structure and relationships.

Table 2. Unrotated loading values correspond to each variable and the underlying factor.

Sample	Factor 1								Factor 2							
	C	Mg	Ca	CN Group	Fe	K	H	O	C	Mg	Ca	CN Group	Fe	K	H	O
Arabica	0.029	0.998	0.994	0.986	0.996	0.963	0.996	0.994	0.970	-0.006	-0.019	0.072	0.039	0.033	0.004	0.046
Ethiopian	0.998	0.999	0.989	0.976	0.998	0.951	0.997	0.994	-0.016	6.2×10^{-5}	0.003	0.038	0.019	-0.076	0.001	-0.028
Robusta	0.997	0.994	0.987	0.982	0.998	0.933	0.997	0.992	-0.017	0.007	-0.012	0.072	0.001	-0.126	-0.001	0.049
Colombian light	0.998	0.997	0.988	0.987	0.998	0.932	0.996	0.979	-0.013	-0.008	-0.006	0.018	0.019	-0.160	-0.006	0.116
Colombian dark	0.996	0.998	0.989	0.980	0.997	0.931	0.996	0.991	-0.005	0.002	0.0208	0.052	0.0304	0.086	-7.7×10^{-4}	0.027
Brazilian light	0.030	0.998	0.988	0.985	0.997	0.961	0.997	0.995	0.942	-0.007	-0.043	0.054	0.018	-0.160	0.002	0.007
Brazilian medium	0.995	0.997	0.98	0.984	0.993	0.909	0.994	0.979	-0.018	-0.001	0.003	0.006	0.020	0.222	-0.002	-0.104
Brazilian dark	0.997	0.997	0.980	0.983	0.998	0.963	0.994	0.972	-0.004	0.004	-0.035	0.057	0.028	-0.126	-0.008	-0.11

Table 3. Variance percentage of factor score coefficients for all studied elements.

Element	Variance	Percentage of Variance (%)	Cumulative (%)	Variance	Percentage of Variance (%)	Cumulative (%)
	Factor 1			Factor 2		
C	5.9686	66.31782	66.31782	2.12802	23.64466	89.96248
Mg	7.96531	88.50349	88.50349	1.00017	11.11297	99.61647
Ca	7.80191	86.68784	86.68784	0.99642	11.07136	97.7592
CN group	7.89182	87.68686	87.68686	0.86198	9.57751	97.26437
Fe	7.99277	88.80855	88.80855	0.97216	10.80183	99.61038
K	7.22654	80.29486	80.29486	1.02551	11.3945	91.68936
H	7.94608	88.28975	88.28975	1.00002	11.11132	99.40107
O	7.80127	86.68072	86.68072	1.04036	11.55961	98.24033

Table 4. Correlation matrices between all variables (eight roasted coffee samples) correspond to each element.

C	Arabica	Ethiopian	Robusta	Colombian Medium	Colombian Dark	Brazilian Light	Brazilian Medium	Brazilian Dark
Arabica medium	1	0.013	0.01362	0.01765	0.02325	0.9458	0.01129	0.02543
Ethiopian Robusta	0.013	1	0.9962	0.99552	0.99223	0.01368	0.994	0.99409
Colombian medium	0.0136	0.9962	1	0.99554	0.99125	0.01397	0.99241	0.99258
Colombian dark	0.0177	0.99552	0.99554	1	0.9942	0.02219	0.99033	0.99745
Brazilian light	0.0233	0.99223	0.99125	0.9942	1	0.02738	0.98964	0.99563
Brazilian medium	0.9458	0.01368	0.01397	0.02219	0.02738	1	0.01049	0.02879
Brazilian dark	0.0113	0.994	0.99241	0.99033	0.98964	0.01049	1	0.98892
	0.0254	0.99409	0.99258	0.99745	0.99563	0.02879	0.98892	1
Mg	Arabica	Ethiopian	Robusta	Colombian Medium	Colombian Dark	Brazilian Light	Brazilian Medium	Brazilian Dark
Arabica	1	0.998	0.99	0.99876	0.99589	0.99777	0.99549	0.99382
Ethiopian	0.998	1	0.99304	0.99685	0.99775	0.99644	0.9962	0.99681

Table 4. Cont.

Robusta	0.99	0.99304	1	0.98864	0.99336	0.99055	0.99039	0.99617
Colombian medium	0.9988	0.99685	0.98864	1	0.99508	0.9986	0.99582	0.99222
Colombian dark	0.9959	0.99775	0.99336	0.99508	1	0.99595	0.99602	0.99708
Brazilian light	0.9978	0.99644	0.99055	0.9986	0.99595	1	0.99618	0.99368
Brazilian medium	0.9955	0.9962	0.99039	0.99582	0.99602	0.99618	1	0.99437
Brazilian dark	0.9938	0.99681	0.99617	0.99222	0.99708	0.99368	0.99437	1
Ca	Arabica	Ethiopian	Robusta	Colombian Medium	Colombian Dark	Brazilian Light	Brazilian Medium	Brazilian Dark
Arabica	1	0.98054	0.98135	0.98364	0.97923	0.98498	0.96881	0.97213
Ethiopian	0.9805	1	0.97497	0.97284	0.97767	0.97784	0.96338	0.96193
Robusta	0.9814	0.97497	1	0.96769	0.97142	0.98274	0.9617	0.95603
Colombian medium	0.9836	0.97284	0.96769	1	0.97783	0.96815	0.95869	0.97648
Colombian dark	0.9792	0.97767	0.97142	0.97783	1	0.96879	0.96546	0.96789
Brazilian light	0.985	0.97784	0.98274	0.96815	0.96879	1	0.96678	0.95775
Brazilian medium	0.9688	0.96338	0.9617	0.95869	0.96546	0.96678	1	0.95368
Brazilian dark	0.9721	0.96193	0.95603	0.97648	0.96789	0.95775	0.95368	1
CN group	Arabic	Ethiopian	Robusta	Colombian Medium	Colombian Dark	Brazilian Light	Brazilian Medium	Brazilian Dark
Arabica	1	0.96045	0.97398	0.97432	0.96211	0.97489	0.97019	0.96796
Ethiopian	0.9605	1	0.9545	0.95723	0.95663	0.96093	0.951	0.95353
Robusta	0.974	0.9545	1	0.96796	0.95948	0.97405	0.95875	0.96142
Colombian medium	0.9743	0.95723	0.96796	1	0.963	0.97016	0.97239	0.96941
Colombian dark	0.9621	0.95663	0.95948	0.963	1	0.96375	0.96005	0.96725
Brazilian light	0.9749	0.96093	0.97405	0.97016	0.96375	1	0.95996	0.96374
Brazilian medium	0.9702	0.951	0.95875	0.97239	0.96005	0.95996	1	0.97059
Brazilian dark	0.968	0.95353	0.96142	0.96941	0.96725	0.96374	0.97059	1
Fe	Arabica	Ethiopian	Robusta	Colombian Light	Colombian Dark	Brazilian Light	Brazilian Medium	Brazilian Dark
Arabica	1	0.99428	0.99344	0.99692	0.9973	0.994	0.98747	0.99613
Ethiopian	0.9943	1	0.99762	0.997	0.99648	0.99798	0.99302	0.99815
Robusta	0.9934	0.99762	1	0.99538	0.99471	0.9968	0.99098	0.99551
Colombian light	0.9969	0.997	0.99538	1	0.99742	0.99547	0.99179	0.9977
Colombian dark	0.9973	0.99648	0.99471	0.99742	1	0.99555	0.98848	0.99739
Brazilian light	0.994	0.99798	0.9968	0.99547	0.99555	1	0.98984	0.99694
Brazilian medium	0.9875	0.99302	0.99098	0.99179	0.98848	0.98984	1	0.99252
Brazilian dark	0.9961	0.99815	0.99551	0.9977	0.99739	0.99694	0.99252	1

Table 4. Cont.

K	Arabica	Ethiopian	Robusta	Colombian Medium	Colombian Dark	Brazilian Light	Brazilian Medium	Brazilian Dark
Arabic	1	0.89863	0.88376	0.88735	0.88628	0.91759	0.86988	0.91524
Ethiopian	0.8986	1	0.88019	0.87758	0.87884	0.91863	0.83538	0.91461
Robusta	0.8838	0.88019	1	0.86027	0.84111	0.906	0.80031	0.90858
Colombian medium	0.8874	0.87758	0.86027	1	0.82393	0.91906	0.80515	0.91179
Colombian dark	0.8863	0.87884	0.84111	0.82393	1	0.86242	0.84596	0.87211
Brazilian light	0.9176	0.91863	0.906	0.91906	0.86242	1	0.82649	0.95212
Brazilian medium	0.8699	0.83538	0.80031	0.80515	0.84596	0.82649	1	0.82992
Brazilian dark	0.9152	0.91461	0.90858	0.91179	0.87211	0.95212	0.82992	1
H	Arabica	Ethiopian	Robusta	Colombian Medium	Colombian Dark	Brazilian Light	Brazilian Medium	Brazilian Dark
Arabic	1	0.99321	0.99411	0.99419	0.9927	0.99393	0.98926	0.98968
Ethiopian	0.9932	1	0.99493	0.99375	0.993	0.99553	0.99236	0.99179
Robusta	0.9941	0.99493	1	0.99495	0.99386	0.99448	0.989	0.9919
Colombian medium	0.9942	0.99375	0.99495	1	0.99314	0.99391	0.98783	0.99024
Colombian dark	0.9927	0.993	0.99386	0.99314	1	0.99333	0.99071	0.98939
Brazilian light	0.9939	0.99553	0.99448	0.99391	0.99333	1	0.99354	0.99109
Brazilian medium	0.9893	0.99236	0.989	0.98783	0.99071	0.99354	1	0.98804
Brazilian dark	0.9897	0.99179	0.9919	0.99024	0.98939	0.99109	0.98804	1
O	Arabica	Ethiopian	Robusta	Colombian Medium	Colombian Dark	Brazilian Light	Brazilian Medium	Brazilian Dark
Arabica	1	0.98397	0.99092	0.98566	0.9879	0.99044	0.96143	0.95367
Ethiopian	0.984	1	0.98518	0.96651	0.9844	0.98619	0.97827	0.97326
Robusta	0.9909	0.98518	1	0.98664	0.98406	0.98805	0.95919	0.94433
Colombian medium	0.9857	0.96651	0.98664	1	0.97602	0.97633	0.93038	0.91309
Colombian dark	0.9879	0.9844	0.98406	0.97602	1	0.98779	0.95954	0.95399
Brazilian light	0.9904	0.98619	0.98805	0.97633	0.98779	1	0.97195	0.96265
Brazilian medium	0.9614	0.97827	0.95919	0.93038	0.95954	0.97195	1	0.981
Brazilian dark	0.9537	0.97326	0.94433	0.91309	0.95399	0.96265	0.981	1

4. Conclusions

A detection system based on Laser-induced breakdown spectroscopy was used as a rapid, low-cost and residue free technique to perform multi-elemental analysis and investigating the composition makeup of eight coffee samples. In this study, LIBS was created and used to detect qualitative elemental composition in eight coffee samples from Egypt's local market. LIBS emission lines from the C(I), Mg(II, I), Ca(II), Fe(I), K(I), H(I), O(I), and CN groups demonstrated high discrimination power between roasted coffee beans. LIBS, in conjunction with Multivariate Analysis, plays an important role in the classification and contribution of spectral lines in various roasted coffee beans. Principal Component Analysis (PCA) was used to validate results and differentiate between eight samples due to their origin-producing area. The results demonstrate the potential relevance

of the methodology utilized in the accurate elemental identification and classification of coffee samples. The overall results revealed that using LIBS in addition to PCA to identify coffee types was viable.

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