Laser Induced Breakdown Spectroscopy (LIBS) Coupled with Multivariate Chemometric Method for Characterization and Quality Control of Coffee

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Abstract

Authentication of coffee is important for ensuring reasonable competition and as a means of protecting consumers against deception of mislabeling. Due to this there is a demand to have a fast and reliable means of measurement allowing the characterization and discrimination of coffee samples. We believe that Laser Induced Breakdown Spectroscopy (LIBS) coupled with multivariate chemometric methods is a solution for inspecting quality and adulterations of coffee. In this work seven Ethiopian export quality coffee and their ten mixtures are analyzed by using LIBS technique. Using the most relevant emission signals attempt was made to discriminate the samples and their mixtures using Principal Component Analysis (PCA). Moreover by taking each sample with its mixtures at a time we have shown the discriminating power of PCA using LIBS spectra for the detection of adulteration. We have also shown that the spectral markers for discrimination of coffee samples are Mg and Ca lines.

Keywords: Coffee, spectral marker, multivariate chemometric methods, Laser Induced Breakdown Spectroscopy (LIBS)

1. Introduction

The content of elements in coffee is only about 5 %, but it is a good indicator of the coffee authenticity. It can also bring the useful information about individual elemental patterns that are distinctive to the origin of growing soils for coffee plants in addition to cultivation and environmental conditions used (Pohl *et al*., 2013; Anderson and Smith 2002; Gonzalvez. A 2009; Dos Santos *et al*. 2010).For the evaluation of the quality of coffee infusions, the flavor of prepared beverages is commonly described under standardized conditions (Sanz *et al*. 2002). All individual notes of each sample are collected and its unique profile is assessed, however, it should be noted that opinions of qualified coffee testers on coffee taste and aroma are subjective (Krivan *et al.* 1993; Anderson and Smith 2002).The quality of Ethiopian coffee is determined by two main factors namely the geographic origin and the post harvest processing (Nicholas, 2007).

A reliable and independent method enabling to differentiate the geographic growing origin of coffee has to be focused on compounds that are stable during all coffee production stages and a subsequent storage. Elements and their concentrations fulfill this requirement and for that reason the elemental analysis of coffee, aimed at determining its elemental composition, is so important for the purpose of its quality control and bromatological value evaluation (Krivan *et al*. 1993; Anderson and Smith 2002).

Currently for determinations of different elements of coffee, several spectroscopic techniques are available, such as Flame Atomic Absorption Spectrometry (Filho *et al*. 2007) (FAAS) is quite often used for selective determinations of different major (Ca, K, Mg, Na), minor (Cu, Fe, Mn, Zn) and trace (Cd, Co, Cr, Ni, Pb) elements of coffee (Krivan *et al*. 1993; Onianwa *et al*. 1999; Anthemidis and Pliatsika 2005; Filho et al. 2007; Grembecka et al. 2007; Dos Santos *et al.* 2009 ; Ashu and Chandravanshi 2011). High Resolution Continuum Source - FAAS (HRCS-FAAS) can also be used for this purpose (Oliveira *et al.* 2012).Some important trace elements are preferred to be determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP - OES), e.g., Cd, Cr, Ni, and Pb, (Dos Santos *et al.* 2010) or Differential Pulse - Anodic Stripping Voltammetry (DP - ASV), e.g., Pb, Cd, and Cu (Suseela *et al.* 2001).Other spectrometric methods, including ICP - Mass Spectrometry (ICP - MS), Direct Current Plasma - Optical Emission Spectrometry (DCP - OES) or Total Reflection X-ray Fluorescence Spectrometry (TXRFS) are much rarely used for the analysis of coffee (Santos *et al.* 2004;Rajwanshi et al. 1997; Haswell and Walmsley 1998). In the most of the above mentioned analytical methods green, roasted, or instant coffee samples require being appropriately prepared before measurements by the digestion and the mineralization of their organic matrix.

Laser induced breakdown spectroscopy (LIBS) is an emerging spectroscopic technique that operates with high-power laser pulses focused onto a small spot of the sample material. The interaction of the pulsed laser beam with the target sample produces high temperature ionized plasma, containing excited elements that radiate the characteristic emission lines of the corresponding elements. LIBS has the capability of multi-elemental

analysis of any type of material present in any phase (solid, liquid and gas) with minimal sample preparation, real-time, in situ, remote detection, and with the capability of non-destructive determination of elemental composition (De Lucia2003; Pandhija.S 2009).

Principal Component Analysis (PCA) has been called one of the most valuable results from applied linear algebra. It is a useful statistical technique that has found application in fields such as face recognition, image compression, neuroscience, computer graphics and is also a common technique for finding patterns in data of high dimension. It is a way of expressing the data in such a way as to highlight their similarities and differences. Since patterns in data can be hard to find in data of high dimension, where the luxury of graphical representation is not available, PCA is a powerful tool for analyzing data (I.T. Jolliffe 2002 22).

In PCA we arrange data in a matrix, for example, with samples arranged as a row and the spectra of the elements arranged as columns from which we will find the covariance matrix. Covariance provides a measure of the strength of the correlation between two or more sets of random variables. A large (small) value indicates high (low) redundancy. It captures the correlations between all possible pairs of measurements. The correlation values reflect the noise and redundancy in our measurements. The diagonal terms, by assumption, large (small) values correspond to interesting dynamics (or noise).The off-diagonal terms large (small) values correspond to high (low) redundancy. The eigenvectors and eigenvalues of the covariance matrix provide us with information about the patterns in the data. By this process of taking the eigenvectors of the covariance matrix, we have been able to extract the most important lines that characterize the sample. The eigenvector with the highest eigenvalue is the first principal component of the data set. We can decide to ignore the components of lesser significance, without losing much information of the original data. Here is where the notion of data compression and reduced dimensionality comes into PCA. Finally we project the input data onto the main principal components, which forms the representation of our data (Parinya Sanguansat 2012).

2. Experimental methods

2.1 LIBS set up

In the experimental configuration (shown in figure 1) we use a standard Nd:YAG laser (Brilliant, Quantel) to generate the plasma. It was running in its second harmonic at 532 nm, at a repetition rate of 2 Hz. Individual laser pulses had a pulse length of approximately 4 ns.The pulse energy used was 30 mJ. A mirror is used to direct the laser beam onto the target surface.It is inclined at an angle of 45° to the direction of incident laser beam. The laser light was focused by a lens of 10 cm focal length. The distance between the plasma plume and the entrance slit of the monochromator was 40 cm. Light from the plasma was collected by a lens of 10 cm focal length placed at the same distance from the plasma plume and the entrance slit of the monochromator, under this condition the image magnification was 1:1. The system used for spectral analysis consisted of a JobinYvon THR 1500 monochromator equipped with a 1200 grooves mm^{-1} grating. An ICCD (Intensified Charge Coupled Device) detector (Andor Technology, model DH520- 25F-03) was employed for spectral acquisition.Synchronization between the laser and the ICCD detector was ensured by microcomputer via a pulse delay generator (Model DG 535, Stanford Research Systems, Inc). The microcomputer was equipped with software for data acquisition and plotting spectra. The selected spectrum was processed by averaging the signal over twenty successive laser shots.Due to this, we had a good signal-to noise ratio. Then it was verified that the plasma was reproducible by recording the same average spectrum several times. Our spectra are recorded with a delay of 1 μs after the laser pulse and a gate width of 10 μs.
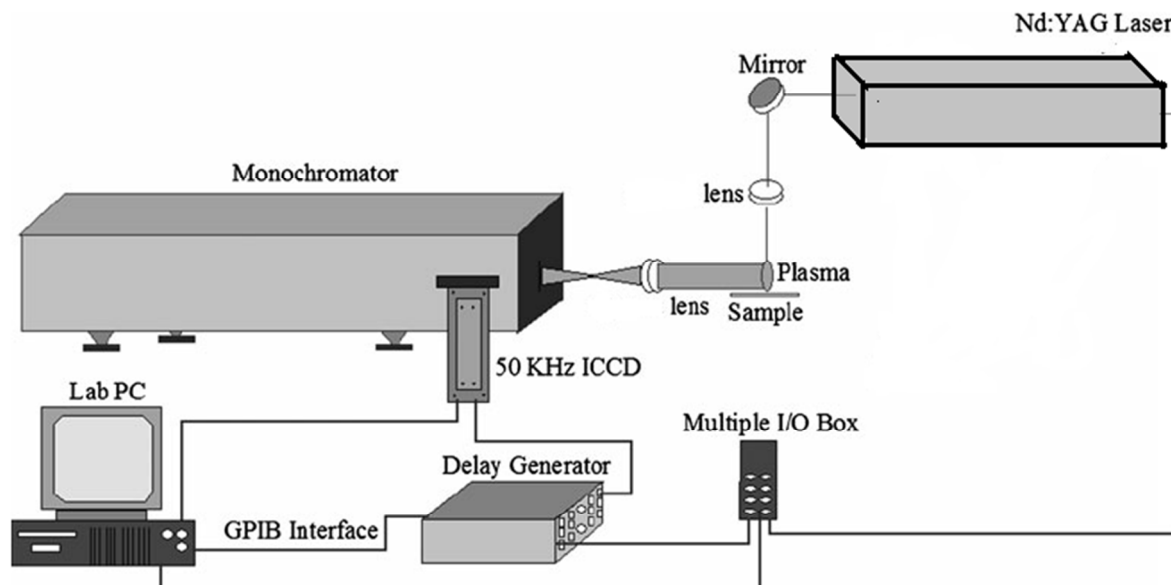
Figure 1: LIBS set up used at the LSAMA laboratory

2.2 Sample preparations and analysis

The roasted coffee samples found from Ethiopian coffee authority grounded by using grinding machine. About 300 mg of each sample were pelletized using a hydraulic press with a pressure around 2 tons/cm^2 to produce an intermediate thick pellet samples. Ten mixtures of samples were also prepared by mixing 150mg of each sample. For each sample three pellets were prepared to check the repeatability of the experiments. The preparation of the powders into pellets was necessary to have better ablation efficiency and higher repeatability of LIBS measurements. The names of the samples are shown in the table below.

No	Nomenclature	Types of Coffee
Sample 1	(1S1, 1S2, 1S3)	UNWASHED HARAR
Sample 2	(2S1, 2S2, 2S3)	WASHED LEKEMTE
Sample 3	(3S1, 3S2, 3S3)	UNWASHED LIMU
Sample 4	(4S1, 4S2, 4S3)	HARAR BLEND
Sample 5	(5S1, 5S2, 5S3)	WASHED SIDAMA
Sample 6	(6S1, 6S2, 6S3)	UNWASHED SIDAMA
Sample 7	(7S1, 7S2, 7S3)	WASHED YIRGACHEFE
Example of mixtures	(75S1, 75S2, 75S3)	Mixture of sample 5 and sample 7

Table 1: The different samples studied with the chosen nomenclature

3. Results and discussions

3.1 Characterizations of non-mixed coffee samples

The LIBS spectrum of coffee samples were collected in wavelength range 200-800 nm in air atmosphere. Spectra acquired by LIBS are processed using Igor software. We have displayed part of the spectrum in the range of 424-436 nm as shown in figure 2
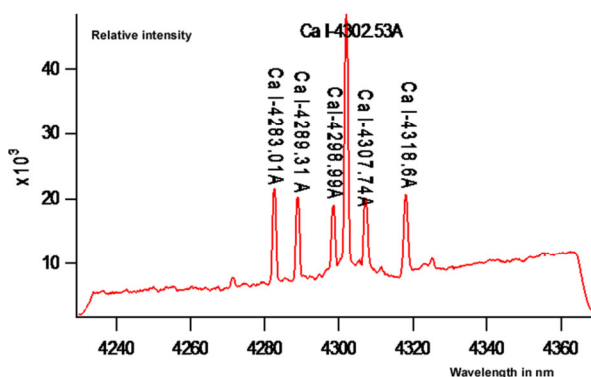
Figure 2: LIBS spectra of coffee in the spectral range of 424-436 nm.

The variations in term of relative intensity of the emission lines of some elements in our coffee samples are gathered and shown in figure 3 using histogram. From the histogram we can observe that in our coffee samples the amount of magnesium, calcium and potassium is relatively higher than the amount of copper, aluminum and sodium. Moreover in our coffee samples we have identified zinc, manganese and iron but in small amount.
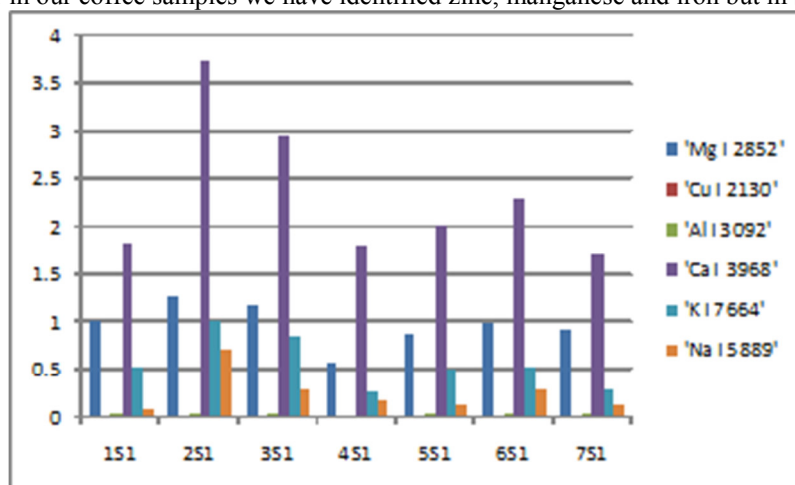

Figure 3: Elemental variations in terms of relative intensity of emission lines.

A couple of researches has done on elemental analysis of Ethiopian coffee. The first was done by Frezer Kassa and A.V.Gholap (Frezer Kassa 2013).On their work they analyzed four Ethiopian coffee samples (Washed Lekempti, Washed Yirgacheffe, Washed Sidamu and Unwashed Harar) to find the concentrations of five elements (K, Mg, Ca, P and S). The second was done by Abera Gure, B. S. Chandravanshi and Taddese Wondimu (AberaGure 138 2006). On their work they analyzed five Ethiopian coffee samples from Wollega, Sidamo, Bench Maji, Harar and Kafa to find the Concentrations of metals; (Ca, Cd, Cr, Co, Cu, Fe,K, Mg, Mn, Ni, Pb and Zn) by flame atomic absorption spectrometer FAAS technique. In both cases the results they have got in terms of the variation of the amounts of elements are similar to what we have found in our researches.

The preprocessed data matrix was subjected to PCA in R package in order to have an overview of existing trends and discover the main property variations in the data. First we tried to characterizes our samples by using forty nine atomic and ionic lines of Zn,Cu,Mg,Al,Ca, K, Mn and Na as shown in the figure 4(left). Then by observing the variable factor map we have selected four lines (Ca I-4226Å, Ca I-3158Å,Mg I-2797Å and Mg I-3832Å) to characterize our samples as in the figure 4(right).Finally we have optimized our characterization of coffee samples by choosing only two lines(Ca I- 4226Å and Mg I-2797Å) as indicated in figure 5.
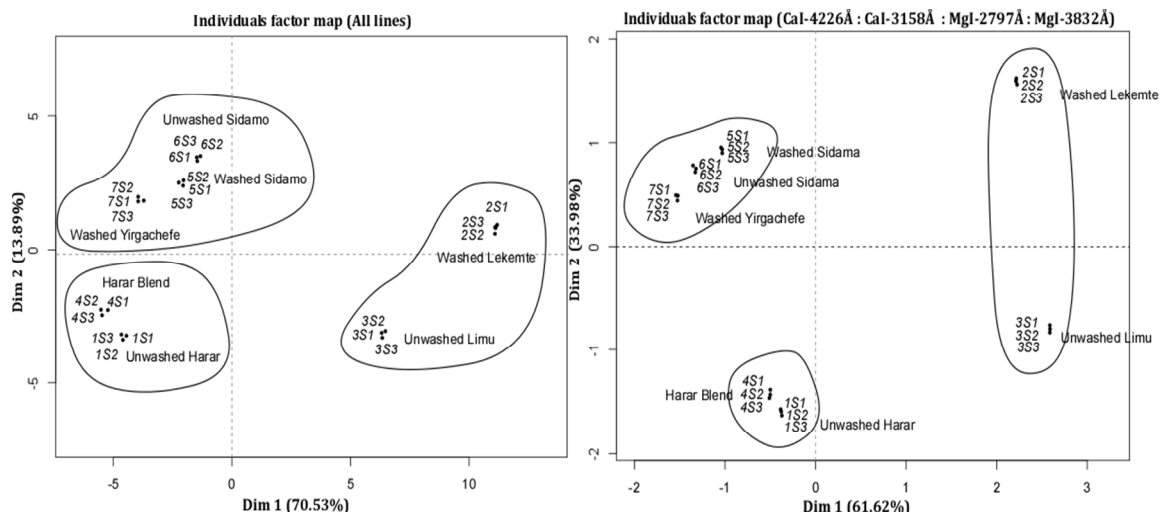
Figure 4: Characterization of non mixed coffee samples by 49lines (left) and by using 4 lines (right).
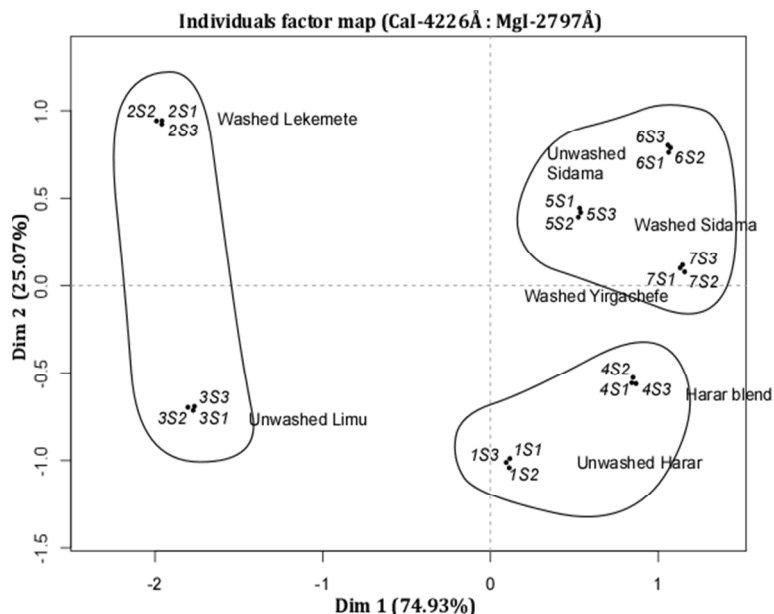

Figure 5: Characterizations of non mixed coffee samples by using two lines only

The scores plots show the coordinates of the spectra in the plane of the two first principal components (PCs), i.e. PC1 (70.53%) and PC 2 (13.89%) which contains 84.42% of the total variance spectral information. The samples belonging to the same geographical origins tend to cluster together and in almost all cases are separated from the other classes.Moreover the clustering of the result of the three pellets for each sample at the same point shows the repeatability of our experiments.

3.2 Inspection of adulteration of coffee.

Discrimination of coffee samples from their mixtures is important for ensuring reasonable competition and as a means of protecting consumers against deception due to mislabeling. Due to this there is a demand to have a fast and reliable means of measurement allowing discrimination of coffee samples. In our researches we have pointed out that LIBS with appropriate multivariate chemometric method serve the desired purpose. In the figure 6 we have displayed the PCA results of sample 3(left) and sample 6(right) with their mixtures respectively.
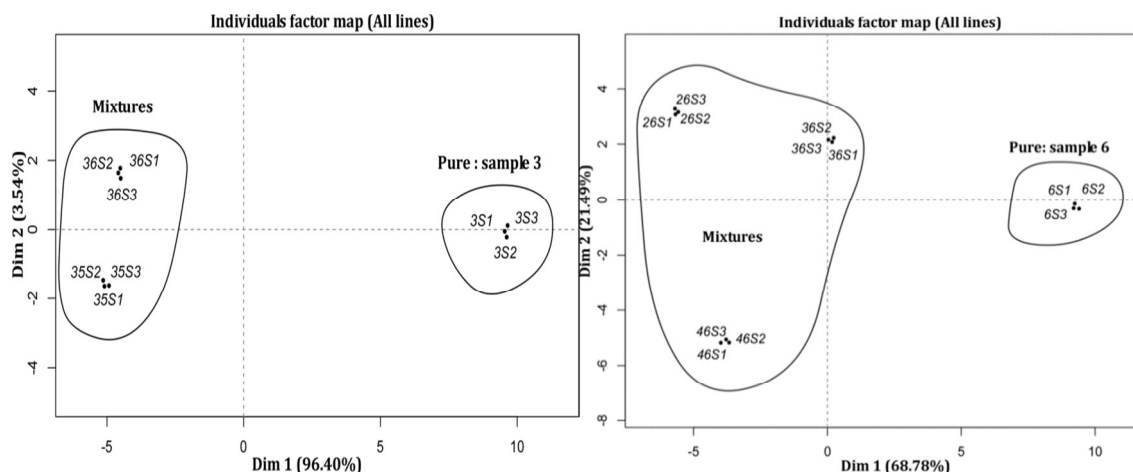
Figure6: Discrimination of sample from their mixtures for sample 3 (left) and sample 6(right).

As we see from PCA score plots in almost all cases the pure samples are separated from the mixtures. According to these results, we can build, based on the two markers Ca and Mg lines, a fast and efficient technique to detect adulteration.

4. Conclusions

In our researches we have demonstrated the potential of LIBS in analysis and characterization of coffee utilizing multivariate chemometric method. We have also pointed out that elements in coffee are a good indicator of the coffee authenticity. It can also bring the useful information about individual elemental patterns that are distinctive to the origin of growing soils for coffee plants in addition to cultivation and environmental conditions used.In our researches we have clearly shown that Ca and Mg lines are the spectral markers for discrimination of coffee samples. Finally we have shown that LIBS coupled with the appropriate multivariate chemometric method is a solution for inspecting quality and adulterations of coffee

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