Scholarly Research Exchange

Volume 2008 • Article ID 152607 • doi:10.3814/2008/152607

Research Article

Aromatic Herbal Products Analysis by Laser-Induced Breakdown Spectroscopy

Jesús Anzano,[1] Beatriz Bonilla,[1] Beatriz Montull-Ibor,[1] and Justiniano Casas[2]

[1] *Laser Laboratory & Environment Group, Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, Pedro Cerbuna #12, 50009 Zaragoza, Spain*
[2] *Department of Condensed Matter Physics, Faculty of Sciences, University of Zaragoza, Pedro Cerbuna #12, 50009 Zaragoza, Spain*

Correspondence should be addressed to Jesús Anzano, janzano@unizar.es

Received 23 May 2008; Revised 7 August 2008; Accepted 19 September 2008

Quick online classification allows the installation of the equipment in the line of work. In this sense, the laser-induced breakdown spectroscopy (LIBS) technique offers all the possible advantages: speed, possibility of online analysis, nondestructive, and so on. For the present work, a 350 mJ laser and Mechelle spectrograph were used. Analysis of the data with principal component analysis (PCA) allows an automatic classification of the aromatic herbal products like tea and camomile in a nondestructive and fast way.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy which utilises a highly energetic laser pulse as the excitation source. LIBS operates by focusing the laser onto a small area at the surface of the specimen; when the laser is discharged it ablates a very small amount of material, in the range of nanograms to picograms, which instantaneously generates a plasma plume with temperatures of about 10 000–20 000 K. At these temperatures, the ablated material dissociates (breaks down) into excited ionic and atomic species. During this time, the plasma emits a continuum of radiation which does not contain any useful information about the species present, but within a very small timeframe the plasma expands at supersonic velocities and cools. At this point, the characteristic atomic emission lines of the elements can be observed. It has been successfully applied before in qualitative analysis and to sort different kinds of materials like paper [1], plastics [2], glasses [3], cinematographics films [4], and so on. This technique has been used because it is powerful, has online possibilities, performs quick classification, and so on.

The application of multivariant techniques in LIBS has been previously studied. In this way, principal component analysis (PCA) and cluster analysis (CA) were used by Amador-Hernández et al. [5] to classify the spectral information provided by all the components in order to obtain two-dimensional plots of the sample composition. Multivariate statistical analysis (MVA) techniques are coupled with laser-induced breakdown spectroscopy (LIBS) to identify preservative types and to predict elemental content in preservative-treated wood where principal component analysis (PCA) was used to differentiate the samples treated with different preservative formulations by Martin et al. [6]. PLSR (partial least-squares regression) was also used in [7] to predict the composition of the samples. Partial least-squares (PLS) regression was used with LIBS technique to quantify samples in the jewellery industry [8] and for their characterization [9]. Also, PLS was used to study the matrix effects in steel samples [10]. In LIBS, PCA was also applied in forensic and environmental fields [11], in soil samples [12], and for detection of biological contaminants on surfaces [13].

In this work, we present a new, fast, and easy method for aromatic herbal products classification with LIBS using a multivariant technique called principal component analysis (PCA).

2. Theoretical

PCA is a useful statistical technique that has found application in fields such as face recognition and image compression, and is a common technique for finding patterns in data of high dimension. So it is a way of identifying patterns in data, and expressing the data in such a way as to highlight their similarities and differences. Here we will present a little explanation for the technique but more details for this analysis can be found anywhere [14, 15].

The mathematics for this model are based on the consideration of a data matrix X with $N \times K$ dimensions, where N are the samples and K the variables, expressed as product of two matrices with their more significant characteristics: $X = t \cdot p' + E$ where **t** are the *scores* ($N \times q$), p the *loadings* ($K \times q$), and q the number of principal components (PC) ($q \leq \min(N, K)$). In PCA model, the importance of a variable is indicated by its variance, and E are the residuals. The variance explained by every PC is the algebraic concept of the associated eigenvalue.

It is important to point out that the PCs are a new set of new variables with several important properties [16]: (i) the information explained by a PC is not present in the other PCs; (ii) the first PC contributes with most of the information, the second less, and so forth; (iii) a very reduced number of PCs carry almost all the information that was in the original set of atomic peaks. It derives from the stems out property that noise and unrelevant spectral data are left out for the last PCs, which is very advantageous.

3. Experimental

3.1. Instrumental Setup. The instrumentation used consisted of an Nd:YAG laser, an *xyz* stage carrying the sample (Standa 011957), a spectrograph, and an intensified charged coupled device (ICCD) detector. An Nd:YAG laser (Brilliant Quantel, Q-Switched) with a 115 mJ laser pulse energy at the second harmonic of 532 nm, a 4.4 nanoseconds pulse duration, and 0.7 Hz repetition frequency was used. The crater diameter was 0.4 mm. The plasma light was collected and transported to the spectrograph by lens and optical fiber. The lens position was adjusted by a diode laser (Andor, HE-OPI-0009). An Echelle spectrograph (Andor Mechelle ME5000, focal length 195 mm, F/7, $\lambda/\Delta\lambda$ 5000, spectral range from 200 to 975 nm) was coupled to an ICCD detector (Andor iStar DH734, 1024 × 1024 pixels, 13.6 × 13.6 μm^2/pixel, 18 mm intesificator diameter). This system was calibrated by an Hg:Ar lamp (Ocean Optics, HG-1, Hg-Ar lines 253–922 nm). A measurement gate delay time of 1 microsecond and an integration time of 500 nanoseconds were optimized.

3.2. Samples and Sample Preparation. No sample preparation was necessary preventing sample contamination. This makes the analysis faster and easier. This kind of analysis makes this technique perfect for fast analysis and its application online.

Different kinds of samples of commercial aromatic herbal products (dry pulverized leaves) were analyzed: camomile, anise camomile, large-leaved lime 1, large-leaved lime 2, tea 1, tea 2, tea 3, tea 4, and tea 5. An average of ten shots in one point for each sample (the samples did not break through the leaves) was used for the analysis. A spectrum of one sample to show the data obtained is shown in Figure 1.

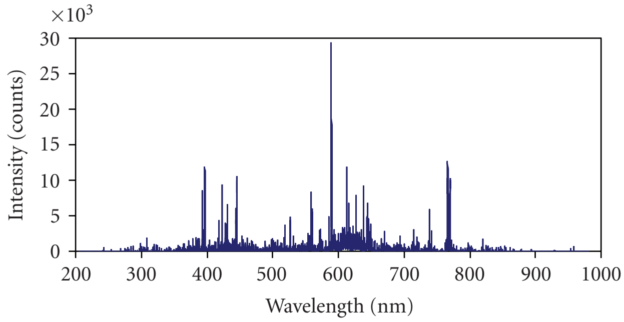

Figure 1: Camomile sample spectrum.

4. Results and Discussion

4.1. Data Preprocesssing. The preprocessing of data is a usual practice prior to the application of PCA because the results are based on the variance patterns of the original data. There are four preprocessing strategies: mean centering, autoscaling, range scaling, and variance scaling. In this work, the preprocesssing strategy used by the software was mean centering. Mean centering is almost always applied when calculating any multivariate calibration model. This involves calculating the average spectrum of all the spectra in the training set and then subtracting the result from each spectrum. In addition, the mean concentration value for each constituent is calculated and subtracted from the concentrations of every sample.

4.2. Principal Components Analysis (PCA). The Unscrambler v.9.1, chemometrics software package by Camo, allows a bigger depth in the study by PCA, and was used for this study mainly because it allows the introduction of the complete spectrum (27000 pixels) for its direct study by PCA, without carrying out a previous selection by visual inspection of wavelength ranges. The graphs can also be obtained in 3 dimensions, representing the first 3 PCs together that improve the interpretation and visualization of the data clouds. Another difference with other programs is that it is possible to carry out the PCA by covariance method. It also allows graphics between PC1 and PC2, PC2 and PC3, and so on.

Three principal components were used to perform the classification. The first PC explains the 42% of the variance, the second PC the 28%, and the third one the 10% (80% variance total explained).

In Figure 2, the three-dimension score plot obtained after performing PCA analysis to the samples is presented. Looking at this graphic, it can be deduced that with PC1 tea can be differentiated from camomile and large-leaved lime; also, with PC2 camomile can be differentiated from camomile large-leaved lime. So, with just one quick analysis these three kinds of aromatic herbal products can be easily sorted.

It is also convenient to search what range of wavelengths made this classification. These ranges are obtained with the loadings plot, and they are presented in Table 1. Loadings

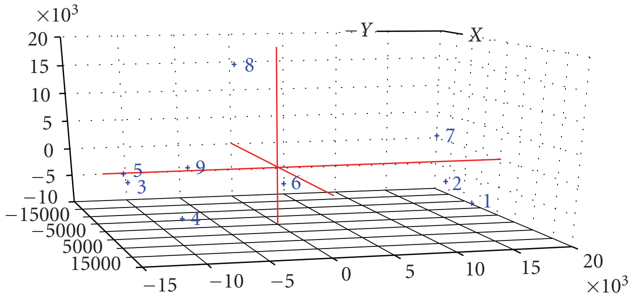

FIGURE 2: 3D scores plot. 1: camomile; 2: anise camomile; 3: large-leaved lime sample 1; 4: large-leaved lime sample 2; 5: tea sample 1; 6: tea sample 2; 7: tea sample 3; 8: tea sample 4; 9: tea sample 5.

TABLE 1: Range wavelengths that produce the classification.

Tea (nm)	Large-leaved lime (nm)	Camomile (nm)
764 to 768	442 to 445	588 to 591
768 to 773	610 to 614	
570 to 573	614 to 618	
737 to 741		

plot shows the variables (wavelengths in this case) that produce the separation. This plot is similar to the scores one, and the wavelength corresponding to one sample is in the same position than the score point for that sample. In posterior analysis, it is enough to study these ranges for an optimal classification of new samples. With this model, it is easy to sort new samples introducing them in the PCA.

5. Conclusions

PCA reduces the dimensionality of a group of data, offers transformation with a reduced number of variables, but describes the data in most part. The analysis of PCs can be used as classifier and detector of "outliers," since the representation of the first scores vectors or components offers an image with the classes of the separate cases. Its application to the spectra of LIBS that offer a high quantity of information guarantees a correct and reliable simplification, classification of aromatic herbal products and potentially of other natural commonly used products.

Acknowledgment

This work was supported by Spanish Environmental Government 2.7.241/2005/2-B; 634/2006/2-2.7; A344/2007/3-02.7.

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