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A Further Analysis of Laser-Induced Breakdown Spectroscopy Ink Pens' Spectra Using Principal Component Analysis (PCA) for Forensic Characterization

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Because characterization of ink pens on documents represents an important forensic discipline, the need of legal systems for faster, *in-situ* and more accurate technique that identify and differentiate questioned documents involved in criminal or legal matters is of great interest. Laser-induced breakdown spectroscopy (LIBS) was experimentally proved to be a promising technique emerging in the field of forensic applications, specifically, questioned documents despite being from the same source or different source. However, the call for newly improved data analysis is unlimited and the need to know if the used ink has the same principal components or not. In the present work, the application of PCA has been demonstrated as statistics-based spectral analysis of the output resultant LIBS spectra for the forensic questioned documents analysis. The LIBS spectra were acquired from IR laser induced plasmas of black ink on regular document paper of ten brands of black gel inks commercially available in the Egyptian market. The idea behind principal component analysis is based on the loadings for the first three principal components. The obtained results have been shown to characterize ink pens used in the analysis. However, the first principal component encompasses the dominant characterization for the used pens. The results of this study indicate that Laser Induced Breakdown Spectroscopy (LIBS) of ink pens aided with PCA technique can promote the LIBS capability to faster, error-free and automatic elemental identification and differentiation for *in-situ* forensic purposes, specifically, questioned documents.

Keywords: *Forensic sciences, questioned document, Ink pen characterization, Laser induced breakdown spectroscopy, Principal component analysis*

Background and Introduction

Forensic examination on questioned documents basically deals with document whose legitimacy is uncertain and can be a clue in any criminal scenes and/or legal investigations [1, 2]. Official or non-official questioned documents including ink writings have been the focus of several works in litreture which facilitate delivering useful information regarding their authenticity [3]. For such purpose, examinations are usually initiated with identifying which ink device was used to produce the document, then analyzing the ink's physical and chemical properties. A comparison of such properties of two or more inks can define if the inks were of the same characterizations, therefore the same manufacture. Other examinations may conclude if any written alteration might have been added or deleted, also decide if any consecutive sequence of any ink contributions overlap each other [4].

Precise separation and classification of inks is a complex process since ink constituents are not only dyes and pigments but they contain additives that specify their flowing and drying properties; solvents and oils. All these ink constituents contribute to its chemical pattern which is

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considered the basis for differentiation by chemical analysis for forensic and other purposes [5]. Spectroscopic techniques, specifically, LIBS offer a fast and direct measurement and examination with sample minimal preparation and destruction. Few research work has been previously published demonstrating the application of LIBS as an analytical technique in the analysis of contemporary writing inks for forensic examination [4]. However, in these researches, LIBS was coupled to another spectroscopic technique such as laser ablation inductively coupled plasma (LA-ICP) mass spectrometry (LA-ICP-MS) or Raman spectroscopy (RS) [6-9]. Their experimental results should that the application of LIBS successfully proved the elemental discrimination of different ink pens samples.

Different spectral data algorithms have been developed to classify and eliminate a lot of redundant information that many spectroscopic output spectrum contains, specifically, LIBS spectrum. Such algorithms need a large dataset and training time to provide accurate classifying and differentiating results. The so-called chemometrics provide powerful statistical signal-processing techniques which provide the automatic identification of chemical information in relation to their spectral fingerprints [7]**.** There are two different kinds of algorithms that discard redundant information. The first group is composed of algorithms which select the best features of the input dataset in order to improve the classification ratio (in LIBS, the best wavelengths). The second group includes algorithms which combine the features of the input dataset and generate new features, such as Principal Component Analysis (PCA) [8]. With the help of such influential algorithms, LIBS systems can go beyond a mere spectra-capturing device to an integrated and portable device that, not only automatically detects materials, but also discriminates among them as well.

In the present work, Principal Component Analysis (PCA) coupled with LIBS has been applied to examine its differentiating capabilitiy to output LIBS spectral data of writing inks of black gel pens in a way to visualize and determine patterns among samples under investigation. The principle component analysis (PCA) was used as a second step or way of discrimination to reduce the number of variables and to cluster samples into groups.

Methods

Samples and experiment

In the present study, detailed experimental data (spectra) analyzed in this work had been obtained from their previously measured spectra using the LIBS technique for ten different sources of black gel ink pens (different brand, manufacturer, and batch) [9]. In brief, the LIBS spectra represents a total of ten different sources of black gel ink pens (different brand, manufacturer and batch). Each ink collection consisted of three straight lines of ~30 mm length and ~5 mm width then they were placed directly in the respective ablation holder. Sheets of commercially available standard document paper of a specific brand are used in all measurements. The ink from ten pens was analyzed to determine the variation of the chemical composition of ink within a single pen, and between brands of black gel inks. Addionaly, the spectral data considered here is a result of single-pulse conventional LIBS setup that included an excitation source of a Q-switched Nd:YAG laser (BRIO, Quantel, France), operating at the fundamental wavelength; 1064 nm with a pulse duration of 5 ns (FWHM). The measurements were carried out using pulse energies of ~87 mJ. The pulse energy was adjusted using glass slides and monitored by a power meter (ScienTech AC5001-USA). A 10-cm focal length plano-convex fused silica lens was used to focus the laser beam onto the target. The samples were mounted on an X–Y translational stage for controlling the irradiated position and introducing a fresh spot in each acquisition. The emitted light from the laser-induced plasma is collected by a 1.5 m optical fiber (600 µm diameter) which is connected to an echelle spectrometer (Mechelle 7500, Multichannel instruments, Sweden) coupled with an ICCD camera, DiCAMPRO (PCO Computer Optics, Germany) for the detection of the produced plasma emission. The obtained atomic emission spectra are displayed on a PC where data analysis and processing are carried out using the commercial 2D- and 3D-Gram/32, software programs (National Instruments, USA). Peak identification is performed using LIBS++ software whose main task is to compare the measured center wavelengths and intensities to those of each element as listed in a large emission spectra database based on the National Institute of Standards and Technology (NIST).

Data analysis approach
Our goal is to apply Principal Component Analysis (PCA) when coupled with laser-induced breakdown spectroscopy (LIBS) output spectra and investigate its capability as a statistical tool in differentiating among inks on regular office documents. To this end, PCA was performed on the single covariance matrix of LIBS ink pens' spectra, conducted onto document papers [10]. Thus, all spectral data were first collected, normalized and tabulated to be analyzed. Different methods of data analysis were applied over the course of this study in order to investigate relative discrimination powers. The data analysis approach employed was first directed at comparing a set of elemental emission lines, depending on the applied analytical method and the sample ink type, and then constructing a set of elemental ratios. Principle component analysis (PCA) was then employed as a second layer of discrimination, in an attempt to reduce the number of variables and to cluster samples into groups. The comparison and differentiation of selected elemental ratios was performed by an analysis of variance (ANOVA). Tukey's highly significant difference (HSD) post hoc test at a 95% confidence limit was employed for the remaining indistinguishable pairs.

Results and Discussions
The laser wavelength is a significant influence for the launch of plasma and its choice is commonly dependent on the analytical task. The application of spectroscopy for forensic using LIBS for the analysis of printed documents, the characterization of ink pens by laser-based methods and using different statistical and comparison methods was also reported (i.e., ANOVA with Tukey's post hoc test and PCA) [11]. A number of ten spectra of pens were recorded, data acquisition and preliminary data analyses were performed using IBM (Statistical Package for the Social Sciences) SPSS Statistics v.23. The optimized LIBS spectra for ink pens were statistically analyzed to test if there are any significant changes or differences based on the ink pens type and constituent [6, 12]. ANOVA results of elments spectral profile means showed that the similar ink types showed non-significant results, only the distinguished ink type that showed the difference Table (1) and graph (1). All results showed very high significant differences between all ten pens p=0.0001, post hoc Tukey's test was done to determine which ink type that cause the difference or the unique effect. The obtained PCA results showed three ink pen types; pen7, pen3 and pen 10 respectively that significantly compromise the main ink types among the ten pens used.
The first three principal components have eigenvalues greater than 1.0 Table (2) and Figs. (3, 4 and 5). These three components explain 98.7% of the variation in the data. The scree plot shows that the eigenvalues start to form a straight line after the third principal component. If 98.7% is an adequate amount of variation explained in the data, then one should use the first three principal components. But the first component only showed a percentage of 88% of the ten components. This reflects its leadership and importance for its inclusion. The second component comprises 9.6% and the third one 1.0 % as shown in Table (3).
Results from principal component analysis of the LIBS data, show differentiation and grouping of the ink pens produced in different spectrum and their total variance scores. Principal component 1 (PC1), principal component 2 (PC2) and principal component 3 (PC3) represents 95.4%, 2.9% and 0.97% of the total variance of the data, respectively Table (3).

Table (1): Comparison of the mean elemental profiles obtained by LIBS analysis for the investigated 10 ink pen types

Pen no.#	Mean	Std. Error	P value
Pen1	725.9285	18.59555	
Pen2	1846.8396	37.18666	
Pen3	2365.3909	48.70531	
Pen4	1627.4711	31.62921	
Pen5	1627.4711	31.62921	
Pen6	631.4762	18.32922	
Pen7	2876.1007	72.15410	0.0001
Pen8	355.2556	7.37679	
Pen9	430.5300	9.18176	
Pen10	1812.5657	43.06764	

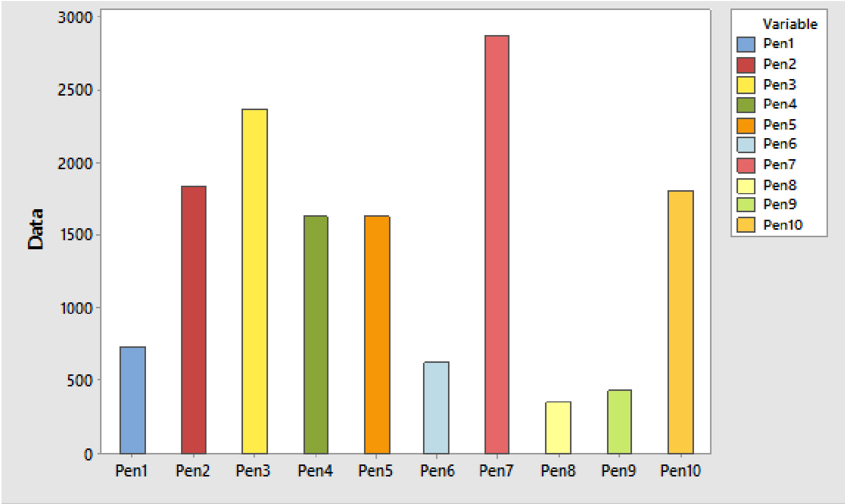

Fig. (1): The mean elemental profiles obtained by LIBS analysis of the investigated ten ink pen types

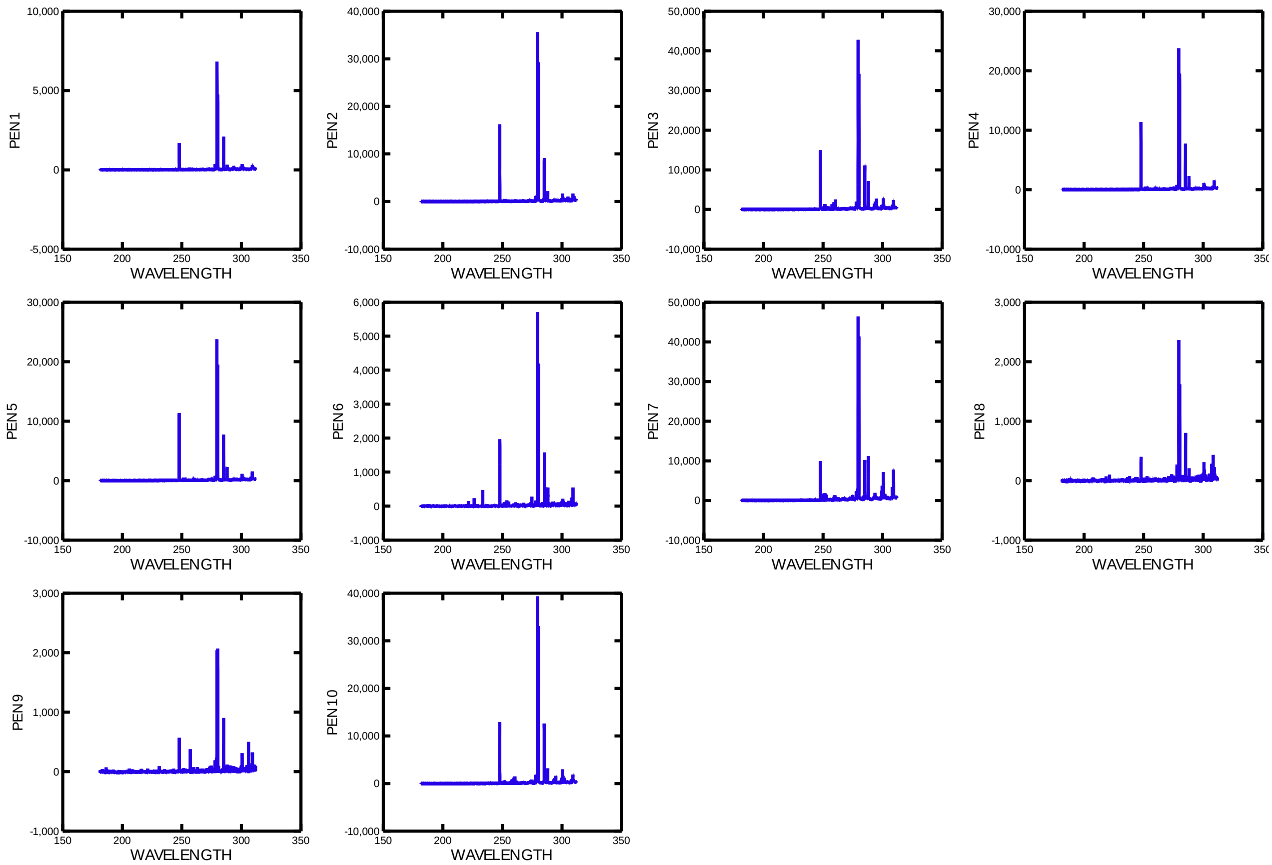

Fig. (2): LIBS elemental spectra of different ink pens at different spectral ranges obtained from the previous work [9]

Table (2): Principal component analysis eigenvector scores

	Component Loadings								
	1	2	3	4	5	6	7	8	9
PEN1	66.313	97.744	115.030	117.450	-0.568	-1.299	11.984	-11.759	4.942
PEN2	1,081.942	414.333	34.560	-74.577	32.540	-4.894	-1.144	-0.287	0.037
PEN3	1,410.345	22.789	-23.394	6.237	-82.455	57.260	0.412	0.286	0.092
PEN4	802.473	-33.449	-117.306	55.630	53.187	15.442	0.932	-0.028	0.026
PEN5	802.473	-33.449	-117.306	55.630	53.187	15.442	0.932	-0.028	0.026
PEN6	46.841	75.963	93.173	110.532	2.096	1.925	-22.236	5.477	-2.727
PEN7	1,581.409	-261.844	169.148	-49.166	34.696	-1.616	-0.618	-0.251	0.134
PEN8	29.175	33.700	41.694	32.673	1.147	0.061	13.036	4.124	-16.619
PEN9	30.958	36.742	42.058	34.522	1.648	-1.812	11.930	17.471	8.108
PEN10	1,326.066	-18.716	-74.001	34.216	-44.713	-73.629	-0.275	0.159	-0.294

Table (3): Percent of variance for each component

Percent of total variance explained								
1	2	3	4	5	6	7	8	9
95.389	2.858	0.972	0.478	0.183	0.101	0.010	0.005	0.004

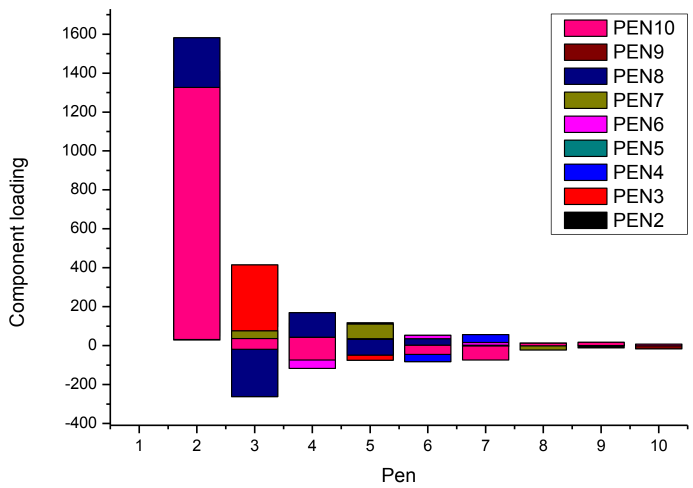

Fig. (3): The score plot graphs showed the component loading of the different pens

The eigenvectors, which comprises of coefficients corresponding to each variable are referred to by the principal component scores [13,14]. The coefficients indicate the relative weight of each variable in the component. Thus, first principal component has large positive associations with pen7, pen3 and pen10, respectively. These components considered as being primarily measurement of ink pens constituents Fig. (5).

The other two components have large negative associations with some ink pen types, small positive associations with other ink types, so both components have low relative weight among the ink types. The scree plot arranges the eigenvalues from largest to smallest. The eigenvalues of the correlation matrix equal the variances of the principal components [15]. The main components for ink pens has been illustrated. The present study revealed the benefit of using standard technique and instrumentation conjugated with statistical analysis technique; PCA calculations. However, the time-dependent measurements outcome needs further investigation as was also mentioned by Adam et al. [16].

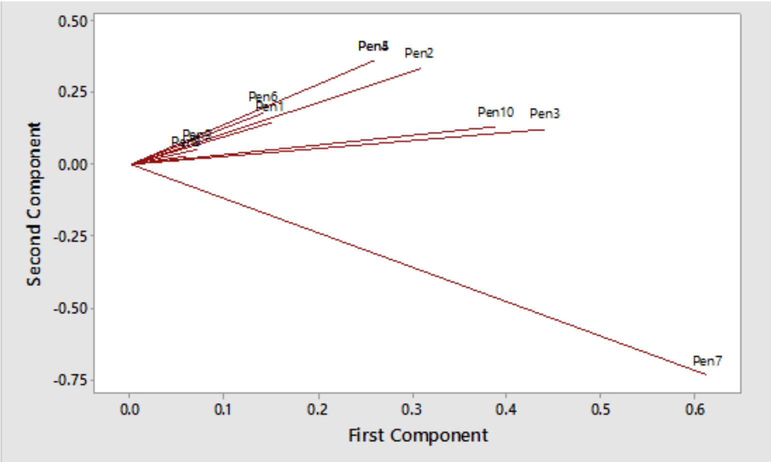

Fig. (4): The loading plot graphs the coefficients of each variable for the first component versus the coefficients for the second component

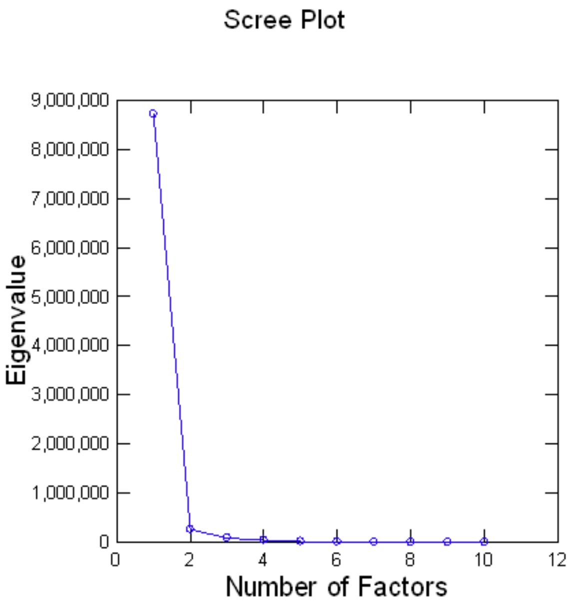

Fig. (5): The scree plot displays the number of the principal component versus its corresponding eigenvalue

Conclusion

The merge between Laser Induced Breakdown Spectroscopy; LIBS technique and statistically-based analysis has been studied in a way to broaden the scope of *in situ* characteristic of LIBS to forensic purposes specifically, questioned documents. In the present study, Principal Component Analysis (PCA)-aided LIBS were used to examine the discrimination capabilities of different elemental profiles of writing ink pens on questioned documents. The LIBS optical emission spectra is a result the interaction of an excitation laser source of wavelength of 1064 nm and pulse energy of 87 mJ with different black gel ink samples. The variation of the chemical composition and the discrimination of thirty black gel-ink pens comprising ten brands were analyzed considering minimum mass removal and minimum damage to the document's paper. Multivariant statistical analysis based on Principal Component Analysis (PCA) provided a model of comparison of LIBS resulted profiles, from inks on question of the considered samples. The results support the potential of LIBS technique assisted by PCA to be considered as a fast and automatic tool for in-situ characterization and differentiation capabilities of LIBS developed for forensic document examination.

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