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Non-Destructive Discrimination of Blue Inks on Suspected Documents through the Combination of Raman Spectroscopy and Chemometric Analysis

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Abstract: Increasingly sophisticated techniques for falsifying and forging legal documents demand non-destructive and accurate analysis methods. Researchers have extensively investigated ink discrimination through an interdisciplinary analysis involving Raman spectroscopy and chemometrics, which is now regarded as a leading forensic document analysis approach. In this study, a ground-breaking method was developed to identify the specific origin of blue-ink pens used in written documents. By employing Raman spectroscopy in conjunction with principal component analysis (PCA), we successfully differentiated between 45 different blue-ink pens used on various documents. The Raman spectroscopy analysis provided a visual examination of each blue ink's unique Raman signature, and PCA was then applied to the processed spectral data. Moreover, we successfully distinguished highly similar ink types in documents through the combined use of Raman spectroscopy, Pearson's correlation analysis, and a statistical approach (PCA).

Keywords: blue ink; Raman spectroscopy; PCA; Pearson's correlation; non-destructive analysis; forensic investigation

1. Introduction

Forensic authorities face a critical task in identifying the true origin of ink pens used in fraudulent alterations of legal documents and forged written letters found at crime scenes [1]. With the ease of producing counterfeit documents using computers and manual expertise, these fabricated documents have become significant evidence in forensic cases. However, a common challenge arises as most counterfeit legal documents and letters are written using the same color pens (blue) [2–5]. Suspected documents may suffer damage during forensic examinations, making it essential to employ non-destructive and reusable investigative techniques. In this regard, Raman spectroscopy analysis emerges as a secure approach, as it leaves no lasting marks on the documents [6–8]. The combined use of Raman spectroscopy and chemometric analysis ensures high precision and negligible experimental risks [9–12]. Successfully employing forensic document analysis hinges on meticulous sample collection, analytical accuracy, and the ability to determine the document's authenticity. These robust findings can then be presented as compelling evidence in a court of law [13].

Inks can be effectively categorized based on their RS (Raman spectroscopy) spectrum signatures, as these signatures are derived from the fundamental components that impart color to the inks. For instance, a study by W. D Mazzella et al. from Switzerland highlighted the identification of 2 crucial pigments, blue and violet, among 36 pigments through Raman spectroscopy [14]. Similarly, I Geiman et al. demonstrated the distinction of ballpoint pen inks by combining surface-enhanced Raman spectroscopy (SERS) with thin-layer chromatography (TLC) plate analysis, focusing on the dyes present in inks [15]. Furthermore, Y. C. Ho et al. successfully differentiated ink sources based on the chemical composition of dyes, using surface-enhanced resonance Raman spectroscopy (SERS) with slight differences [16]. In another study, A. Alyami et al. utilized various laser extractions of Raman spectroscopy to examine unknown dyes in all types of pens through SERS [17]. Moreover, the analysis of inkjet and laser-printed papers was carried out by M. N. M. Asri et al. through a combined approach involving Raman spectroscopy and principal component analysis (PCA). This chemometric analysis enables accurate discrimination [18]. Recent publications have emphasized the significance of Raman spectroscopy analysis in tandem with chemometric methods for enhancing forensic examinations in cases involving forged and illicit documents [19–22]. As a result, the application of Raman spectroscopy and chemometric techniques has proven to be invaluable in investigating crimes related to falsified and illegal documents.

In this study, we present a multidisciplinary approach involving Raman spectroscopy and principal component analysis (PCA) to effectively distinguish between three distinct brands of blue ballpoint pen ink. Each pen brand exhibits a similar Raman spectrum signature, as they contain either the same dyes or pigments, and it is challenging to visually differentiate the inks due to variations in dye concentration. To address this challenge, we employ chemometric techniques, such as PCA and Pearson's correlation analysis, as statistical methods to successfully discriminate between the ink pens. These non-destructive Raman spectroscopy techniques, combined with the statistical chemometric model, offer an efficient means for forensic scientists to determine whether suspected documents were produced using a specific source of blue pen ink. By utilizing these techniques, we can expedite the investigation process and uncover the truth behind potentially fraudulent or illegal documents. The ability to accurately identify the source of blue pen inks plays a crucial role in enhancing the overall effectiveness of forensic examinations.

2. Materials and Methods

2.1. Sample Collection

In this study, we selected three widely recognized blue ballpoint pen brands, which were obtained from a nearby stationery store. For each brand, we collected multiple blue pens manufactured by the same company. As part of our measurements and subsequent analysis, we engaged a volunteer designated as "unknown" (UK) to randomly choose one of the pens and write a few phrases on an A4 sheet of white paper. The main objective of the entire project was to identify the specific brand of pen the volunteer had used based on the writing samples provided.

2.2. Raman Spectroscopy

The Raman spectrum of each blue ink was analyzed using the ACRON model for Micro-Raman Spectrum. The Raman spectroscopy system from UniNanoTech Co., Ltd. was utilized for this purpose, featuring a 532 nm excitation laser and a resolution of approximately 1 um at 633 nm. No sample preparation was necessary, as all samples were placed on the sample holder of the Raman instrument. For each sample, ten measurements of the spectrum were taken to ensure robust data collection. The entire spectrum was calibrated using a silicon chip, and normalization was applied in the original software to minimize any disturbances. This approach resulted in superior visual inspection-based discrimination, facilitating a more accurate analysis of the Raman spectra, and enabling better differentiation between the various blue inks.

2.3. Principal Component Analysis (PCA)

In this research, principal component analysis (PCA) was utilized as a statistical method to convert numerical data into multiple variables in matrices and to reduce the dimension of the Raman dataset into a set of orthogonal features known as principal components (PCs). PCA is particularly beneficial when analyzing Raman spectra for intentional classification purposes. The PCA analysis was conducted using the trial version of the "UNSCRAMBLER" 11.0 software.

2.4. Pearson's Correlation

Pearson's correlation serves as a standard statistic tool employed in linear regression analysis. It facilitates the examination of the relationship between two variables, while the correlation coefficients quantitatively express the strength of the association between these variables. To conduct Pearson's correlation analysis, the trial version of the XLstate 2021 software was utilized.

3. Results and Discussion

The primary objective of this study was to determine the origin of the blue-ink pens utilized in writing the suspected fraudulent documents. A comprehensive analysis was conducted on the collection of blue ballpoint pens listed in Table 1. Raman spectroscopy measurements were performed on all the gathered pens, and based on their distinct Raman spectrum patterns, they were categorized into three sets of pens. The Raman spectroscopy data for each group are presented in Figure 1. Additionally, the Raman spectra of unknown blue ballpoint pens, confidentially provided by volunteers, were also measured for further investigation.

Table 1. List of blue ballpoint pens analyzed.

Group A		Group B		Group C	
Sample Name	**Sample Code**	**Sample Name**	**Sample Code**	**Sample Name**	**Sample Code**
FAXION BS	BS	FAXION B	FB	PIOLET	PT
FAXION BL	BL	SIGNO	SN	DISNEY	DY
PENROTE	PE	UNI ONE	UN	SARASA	SA
UNI BALL	US	JETSTREAM	JM	ENERG	EG
SANDER	SR	CLASSIC	CL		
		TEMPO	TO		

Based on the Raman signature of each sample, all blue pens were categorized into three groups. An unknown ink sample was linked to the corresponding Raman signature for further investigation of its source. However, visual examination of each classified sample, including the unknown ink sample, did not lead to its identification, as it closely replicated the Raman signature of known sources. Therefore, distinguishing the unknown-source blue pens was challenging. As a result, the utilization of advanced statistical tools such as PCA and Pearson's correlation techniques became necessary for a comprehensive analysis.

These sophisticated methods were expected to provide deeper insights and aid in resolving the identification of the unknown ink source.

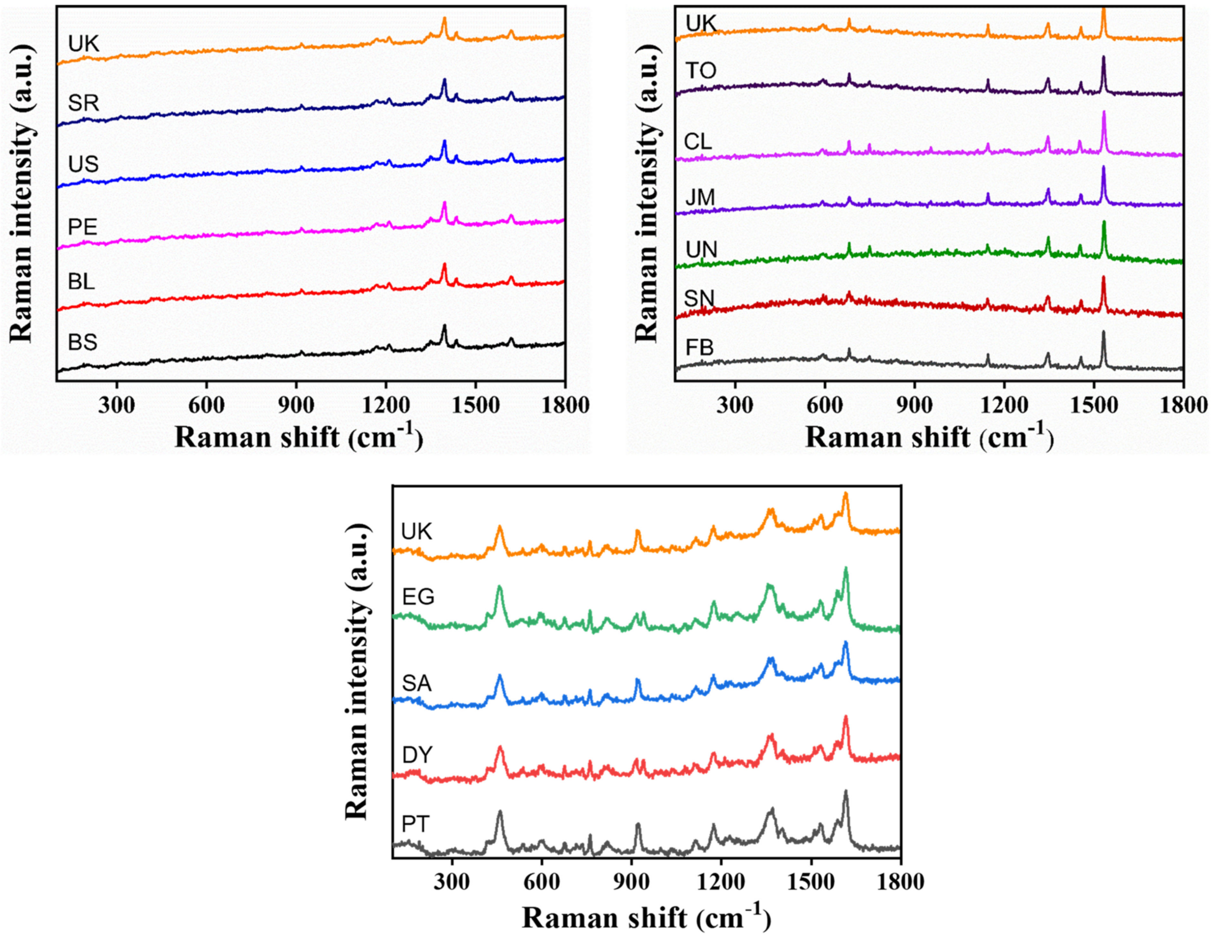

Figure 1. Raman spectrum of collected blue ballpoint pens classified into three groups with unknown-source pens.

3.1. Principal Component Analysis

To ensure accuracy and minimize instrumentation error, all Raman spectra underwent data pre-processing through standardization [23]. A PCA analysis was conducted using the trial version of the UNSCRAMBLER statistical software on the pre-processed data of the blue ballpoint pens. This analysis aimed to distinguish the unknown-source blue-ink pen from other categorized Raman signatures. The statistical analysis involved the Raman spectra of each pen. Covering wavelengths from 0 to 1800 cm^{-1}, these data were input into the PCA software for further examination. The PCA results were graphically represented as a score plot, as depicted in Figure 2. This score plot effectively visualizes and summarizes the numerical dataset of all examined ballpoint pen samples, illustrating how the ink from unknown sources compares to samples from known sources and how it differs from them. A precise interpretation was obtained by considering the first component (PCA 1) and the second component (PCA 2) in the score plot. This analysis facilitated a comprehensive understanding of the variations and relationships between the different pen samples.

Figure 1 displays the PCA score plot for the group of samples. The plot reveals distinct and separate clustering of blue ink samples into five groups. Despite having similar Raman signatures, PCA effectively distinguished each brand of blue-ink pens based on the score plot corresponding to each group. This observation prompted further examination of the PCA score plots for Groups A, B, and C, as depicted in Figure 2a, Figure 2b and Figure 2c, respectively. Each score plot reflects various brands of blue-ink pens. As expected, a blue pen of unknown origin was utilized to write the text on the A4 sheet of paper, and this unknown pen was successfully identified by analyzing its PCA score plot in comparison to the score plots of the known original blue pens. Notably, Figure 2 illustrates how PCA score plots were instrumental in pinpointing the origin of the blue pen. The pairs for each group examined are UK and TO (Group A), UK and EG (Group B), and UK and SR (Group C).

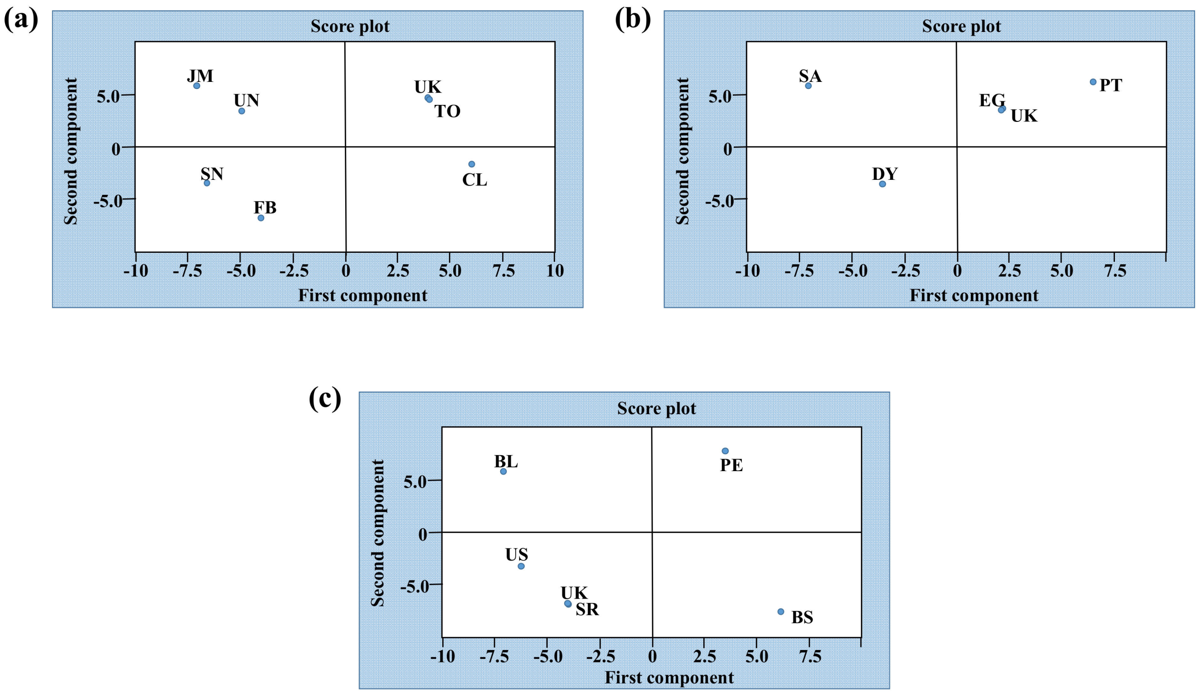

Figure 2. PCA score plot of blue ballpoint pen samples analyzed by using XLSTAE showing a successful classification of Group A (**a**), Group B (**b**), and Group C (**c**).

3.2. Pearson's Correlation Coefficient

One of the commonly employed statistical techniques for assessing linear correlations is Pearson's correlation. This method provides a correlation coefficient of 1 when comparing data from identical spectra or perfectly matched variables that share similarities or dissimilarities [19,24–28]. To perform statistical analyses like PCA and Pearson's correlation, the Raman signatures of the measured samples from all three groups of blue ballpoint pens were transformed into a numerical dataset. Below are the tables displaying the Pearson's correlation values for each pair.

This outcome is achieved by clustering Raman signals based on the average value of the coefficient related to blue-ink pen analysis. The symmetry of the coefficient values, as evident in the table's arrangement, is noteworthy and holds significance in the analysis.

It is evident that the spectral similarities across different spectral regions will not be identical. This is demonstrated by the correlations in Tables 2–4, where maximum correlation coefficient values of 1.000 are observed for each group's samples. These coefficient values indicate the extent of similarities between known- and unknown-source blue pens. Analyzing how a blue ink's Raman spectrum corresponds with the spectrum of an unknown source becomes relatively straightforward when writing a text on an A4 sheet of paper. To effectively differentiate and demonstrate similar spectrum signatures, an integrated analysis of Raman spectroscopy and statistical tools is employed. By utilizing Raman spectroscopy and chemometric approaches, the source of the blue pen was successfully identified for each group: UK and TO (Group A), UK and EG (Group B), and UK and SR (Group C). We assert that this investigation strategy allows for a swift assessment of the distinctness of the investigated spectrum from others, providing valuable insights for forensic document analysis.

Table 2. Pearson's correlation matrix table of Group A samples.

Variables	FB	SN	UN	JM	CL	TO	UK
FB	1	0.907	0.542	0.463	0.340	0.729	0.617
SN	0.907	1	0.711	0.563	0.461	0.907	0.907
UN	0.542	0.711	1	0.830	0.805	0.542	0.542
JM	0.463	0.563	0.830	1	0.837	0.463	0.463
CL	0.340	0.461	0.805	0.837	1	0.340	0.340
TO	0.729	0.907	0.542	0.463	0.340	1	1.000
UK	0.617	0.907	0.542	0.463	0.340	1.000	1

Table 3. Pearson's correlation matrix table of Group B samples.

Variables	PT	DY	SA	EG	UK
PT	1	0.777	0.778	0.934	0.778
DY	0.777	1	0.832	0.529	0.914
SA	0.778	0.954	1	0.619	0.731
EG	0.934	0.631	0.148	1	1.000
UK	0.778	0.954	0.609	1.000	1

Table 4. Pearson's correlation matrix table of Group C samples.

Variables	Var1	BL	BS	PE	US	SR	UK
Var1	1	0.542	0.631	0.721	0.911	0.973	0.157
BL	0.542	1	0.814	0.316	0.892	0.715	0.681
BS	0.631	0.659	1	0.701	0.502	0.691	0.606
PE	0.721	0.532	0.911	1	0.722	0.472	0.192
US	0.911	0.695	0.853	0.621	1	0.481	0.265
SR	0.973	0.490	0.195	0.819	0.501	1	1.000
UK	0.157	0.780	0.184	0.519	0.744	1.000	1

4. Conclusions

In this study, Raman spectroscopy, PCA, and Pearson's correlation were employed to identify an unknown-source blue ballpoint ink pen. The Raman signature of the analyzed samples displayed a consistent pattern, making it visually impossible to differentiate between them. However, PCA proved to be more objective than visual judgment. The PCA score plots indicated the similarity between the unknown blue pen samples and the known ones. Additionally, Pearson's correlation technique was utilized to identify the pen used in the unknown sample, and its results agreed with those obtained through PCA. Undoubtedly, these statistical techniques hold great potential to evolve into effective, discrimination-focused methodologies for forensic document inspections. By combining Raman spectroscopy, PCA, and Pearson's correlation, forensic experts can accurately determine the origin of an unknown blue pen, enhancing the overall accuracy and reliability of such investigations.

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Data Availability Statement: The data that support the finding of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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