

Forensic identification of pen ink pigments using dual-wavelength Raman spectroscopy combined with chemometrics

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In forensic document examination, ink analysis plays a crucial role in investigating forgery crimes. Raman spectroscopy is frequently preferred in ink analysis due to the absence of a sample preparation step, its non-destructive nature, and its rapid analysis process. In this study, pigment blue (PB 15:1, 15:3, 15:4, and PB 15:4 Mallak), which is commonly used as a colorant in ballpoint pen inks, methyl violet (MV), and crystal violet (CV) pigments, which are commonly used as colorants in ballpoint pen inks, were analyzed using confocal Raman spectroscopy at wavelengths of 532 nm and 785 nm. After applying data preprocessing to the obtained spectra, the spectral data were analyzed using principal component analysis (PCA). Upon examining the study results, it was determined that the spectral data were separated into two distinct clusters (triarylmethanes and phthalocyanines) that did not overlap. In conclusion, the use of two-wavelength Raman spectroscopy in conjunction with PCA provides a fast, reliable, and statistically validated non-destructive approach for the characterization and classification of pigments commonly used in inks.

Keywords: Pigment analysis, Raman spectroscopy, Forensic chemistry, Principal component analysis (PCA)

INTRODUCTION

Document examination in forensic science plays a critical role in solving forgery cases. In these examinations, ink analysis is one of the most fundamental methods used to detect forgery. Traditionally, the chemical profiling of inks has been performed using separation techniques such as thin-layer chromatography (TLC), gas chromatography-mass spectrometry (GC-MS), and high-performance liquid chromatography (HPLC) [1, 2]. However, chromatographic methods cannot fully meet the non-destructive analysis requirements of the judicial system today, as they require physical sample collection and compromise the integrity of the document.

For this reason, in recent years, experts have preferred fast and non-destructive spectroscopic techniques that do not require a sample preparation stage in forensic document examinations. In this context, Raman spectroscopy has become one of the most preferred analytical techniques in ink analysis due to its ability to characterize the chemical structure of inks on documents with high precision [3-5]. Raman spectroscopy has been used for the analysis and differentiation of a wide variety of ink formulations, including gel pens and stamp inks [6, 7]. Furthermore, the superiority of Raman spectroscopy over other methods in elucidating ink

aging processes, the photodegradation of dyes over time, and degradation dynamics on paper has been reported in numerous studies [8-10].

The identification and classification of inks is possible through the accurate identification of the dyes and pigments present in their formulations. In particular, triarylmethane dyes and phthalocyanine pigments, which are frequently found in the composition of blue and black ballpoint pen inks, constitute one of the main focuses of ink analysis [11-13]. In the literature, studies have been conducted on the vibrational characterization of triarylmethane-derived dyes (e.g., crystal violet), their analysis via surface-enhanced Raman scattering (SERS), and their degradation mechanisms under light exposure [14, 15]. Similarly, phthalocyanine-based pigment blue 15 (PB15) derivatives have been analyzed both as a dye pigment and as an ink component [16]. These studies are based on the complex chemical and structural variations inherent in these pigments. crystal violet and methyl violet, which stand out in ink formulations, are closely related triarylmethane dyes sharing a common molecular skeleton and possessing a carbocation structure with resonance stabilization. In both pigments, there is a central, positively charged carbon atom bonded to three phenyl rings, at least two of which contain nitrogen groups, and the main structural differences between

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the molecules stem from the number of methyl groups attached to the nitrogen atoms [17, 18]. The PB 15 pigments has a large, flat, and symmetrical macrocyclic ring. It consists of four isoindole units linked to each other via nitrogen atoms. A 16-membered inner ring containing a chelated copper ion is formed at its center. PB 15:1 (alpha form) has an unstable alpha crystal structure. PB 15:3 (beta form) has a stable beta crystal structure. It is a pure, unchlorinated copper phthalocyanine. PB 15:4 (beta form + derivatives) shares the same pure, unchlorinated beta-copper phthalocyanine chemical core as PB 15:3. However, it is physically/chemically modified with specific derivatives (such as sulfonated or aminomethyl-substituted phthalocyanines) to prevent agglomeration [19-21]. The chemical structures of the pigments are shown in Figure 1.

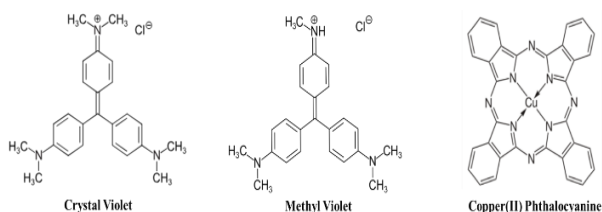


Figure 1. Chemical structures of the pigments

Upon reviewing studies on pigment analysis in the literature, it has been observed that due to the structural complexity of spectral data obtained via Raman spectroscopy and matrix effects, multivariate data analysis techniques must be used in conjunction with these analyses. The integration of chemometric methods, such as principal component analysis (PCA), with spectroscopic data enables the statistical clustering of chemical variations in inks and the creation of discrimination models [22, 23].

In this study, phthalocyanine pigment derivatives commonly encountered in ink structures during forensic document examination (PB 15:1, 15:3, 15:4, and PB 15:4 Mallak) and the pigments MV and CV, using wavelengths of 532 nm and 785 nm. The obtained data were examined using principal component analysis (PCA), revealing that the ink spectra could be classified into two main clusters: triarylmethane and phthalocyanine. In conclusion, the combination of two-wavelength Raman spectroscopy with chemometric approaches (PCA) was found to be a fast, reliable, and non-destructive analytical method for the characterization and classification of ink pigments in the investigation of forgery crimes.

EXPERIMENTAL

Chemicals and sample preparation

In this study, methyl violet (MV), crystal violet (CV), and phthalocyanine group derivatives (PB 15:1, 15:3, 15:4, PB 15:4 Mallak) which are commonly used as colorants in inks—were analyzed. Phenoxyethanol (TCI, Japan) was used as the solvent during the transfer of pigments onto paper. A 1 mg sample of each pigment was weighed and dissolved in 2 mL of phenoxyethanol to form a solution. The prepared solutions were dispensed onto a standard paper surface using a glass pipette and left to dry to allow the solvent to evaporate, thereby preparing the samples for spectroscopic analysis.

Raman spectroscopy analysis

Spectral analyses were performed using a confocal Raman spectrometer with two different wavelengths. The system utilized a 532 nm (green) diode laser with a power of 50 mW and a 1800 lines/mm grating, along with a 785 nm (red) air-cooled diode laser source with a power of 300 mW and a 1200 lines/mm grating. During measurements, parameters such as exposure time, laser power, and accumulation were optimized to maximize spectral quality.

A 785 nm laser source was used in the analysis of phthalocyanine group pigment blue (PB 15:1, 15:3, 15:4) derivatives, which are frequently encountered in gel pen formulations. The characteristic spectra of this group were successfully obtained in static mode at a central wavelength of 1100 cm^{-1} , with an exposure time of 25 seconds and a laser power of 0.0001%.

In contrast, during the analysis of triarylmethane based MV and CV pigments, severe fluorescence interference was observed at the 785 nm wavelength due to their specific chromophore structures, and spectral data could not be obtained. To overcome this issue, a laser source with a wavelength of 532 nm was used in the system. By re-optimizing the parameters (static mode, center: 1100 cm^{-1} , exposure time: 5 sec, Laser power: 0.5%), the fluorescence effect was successfully suppressed, and the characteristic Raman peaks of these pigments were clearly observed.

Data preprocessing and chemometric analysis

Data preprocessing steps were applied to reduce noise in the raw spectral data obtained from the Raman system and to improve the quality of the analysis. To this end, baseline subtraction was performed, and the data were smoothed using the

Savitzky–Golay algorithm (Window: 9, Polynomial Order: 2).

The chemometric analysis and graphical representations of the spectral data following preprocessing were performed using OriginPro 2025b (OriginLab Corporation, Northampton, MA, USA) software. PCA was applied to reduce the complexity and dimensionality of the multivariate dataset, explain the relationships among variables, and visualize the clustering tendencies of the samples. To prevent the variables included in the analysis from being affected by differences in scale, the PCA model was constructed based on the correlation matrix, and the principal components explaining the highest variance in the system were interpreted.

RESULTS AND DISCUSSION

CV and MV analysis

CV and MV, which belong to the triarylmethane class of dyes, constitute the primary coloring components of blue ballpoint pen inks. The Raman spectra of CV and MV, obtained experimentally, are shown in Figure 2.

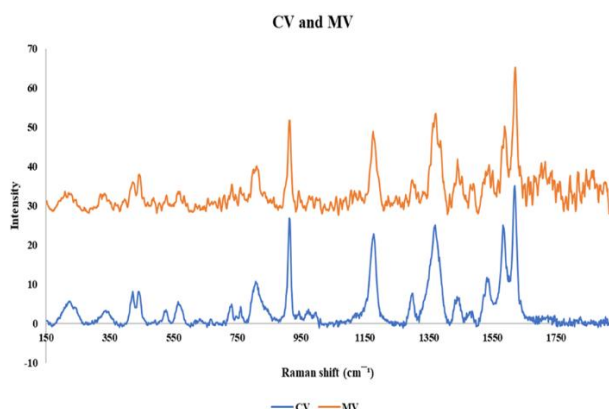


Figure 2. Raman spectra of CV and MV

Upon examination of the spectral data in Figure 2, the ~ 1619 – 1621 cm^{-1} band was identified as the most intense peak for both pigments. This peak corresponds to the C–C central stretching vibrations of the aromatic ring in the triarylmethane structure [11, 12]. The strong peaks observed in the ~ 1584 – 1588 cm^{-1} band represent the C=C stretching and asymmetric stretching vibrations of the aromatic ring [23]. The asymmetric stretching vibrations of the structure linking the central carbon atom to the phenyl rings, or the N-phenyl bond (C–N), appear as a very distinct peak in the ~ 1370 – 1371 cm^{-1} band range [15]. The in-plane bending vibrations of the C–H bonds in the aromatic structure produce a strong peak in the ~ 1175 – 1177 cm^{-1} range, consistent with the literature [13]. The ~ 912 – 914

cm^{-1} band is characterized by the ring skeleton vibrations of the triarylmethane molecule and is one of its characteristic peaks [9]. The peak around ~ 809 cm^{-1} reflects C–H out-of-plane bending and yields a signal of moderate intensity; while the signals in the ~ 422 – 443 cm^{-1} range form weak peaks representing deformations of the entire molecular skeleton [15].

PB15 analysis

PB15 pigment derivatives, commonly used as colorants in the formulation of blue gel pen inks, were analyzed by Raman spectroscopy.

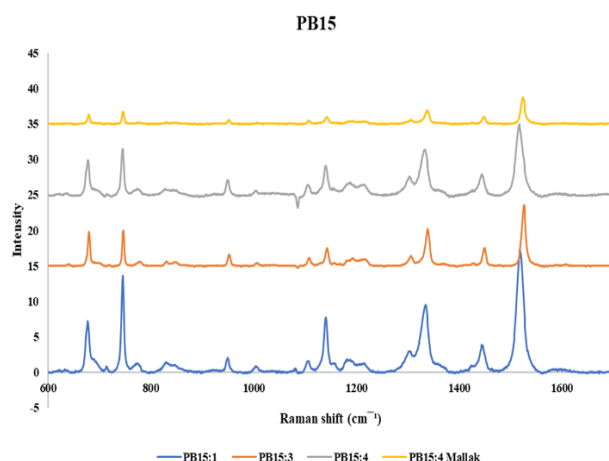


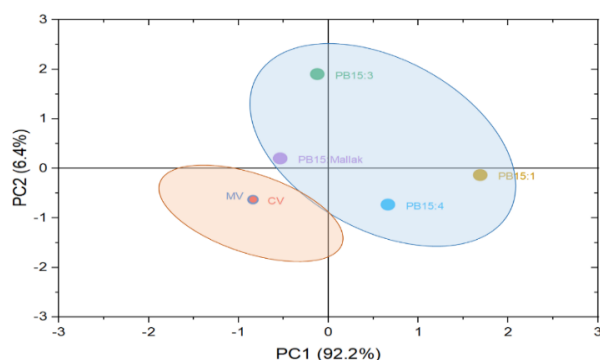
Figure 3. Raman spectra of pigment blue (PB 15:1, 15:3, 15:4) derivatives

Upon examination of the spectral data in Figure 3, characteristic and reproducible spectral profiles were identified due to the highly stable macrocyclic structure of the PB15 derivatives. The high Raman scattering of PB15 ensures that the pigment can be distinguished despite fluorescence or masking effects that may be caused by resins, solvents, and other additives in the ink mixture. In the obtained data, the intense peaks at 1530 cm^{-1} , 1342 cm^{-1} , and 748 cm^{-1} are considered distinctive peaks indicating the presence of PB15 in the ink formulation [6]. Furthermore, upon examination of the spectral data obtained in the study, the strong signal observed at the ~ 1530 cm^{-1} band was found to correspond to the asymmetric stretching of C=N and C=C bonds in the pyrrole rings; the peak at the ~ 1342 cm^{-1} band, on the other hand, corresponds to the symmetric stretching of C–N and C–C bonds in the isoindole skeleton. The peak detected in the low-wavenumber region at ~ 748 cm^{-1} originates from a vibration representing the overall stretching of the molecule [16]. The characteristic Raman vibrational modes, types, and signal intensities of triarylmethane (CV and MV) and macrocyclic phthalocyanine pigment derivatives (PB 15:1, 15:3, 15:4) are presented in a comparative manner in Table 1.

Table 1. Characteristic Raman vibration modes of CV, MV, and PB15

Raman shifts (cm ⁻¹)	Vibration type	Triaryl methane group (CV, MV)	Cu(II) phthalocyanine group (PB 15:1, 15:3, 15:4)
~1619 - 1621	Aromatic ring C-C stretching	S	-
~1584 - 1588	Aromatic ring C=C stretching	S	-
~1528 - 1530	Pyrrole ring C=N and C=C asymmetric stretching	-	S
~1450 - 1453	Isoindole ring stretching	-	M
~1370 - 1371	N-phenyl (C-N) stretching	S	-
~1340 - 1342	Isoindole ring C-N and C-C symmetric stretching	-	S
~1175 - 1177	Aromatic C-H in-plane bending	S	-
~1143 - 1145	C-H in-plane bending	-	M
~912 - 914	Ring skeletal vibration	S	-
~809 - 811	C-H out-of-plane bending	M	-
~746 - 748	Macrocycle breathing and C-H out-of-plane bending	-	S
~680 - 682	Skeletal deformation	-	W
~422 - 443	Skeletal deformation	W	-

S: strong, M: medium, W: weak

**Figure 4.** PCA plot of the analyzed pigments (CV, MV, PB 15:1, PB 15:3, and PB 15:4)

PCA analysis

The PCA plot created to statistically model the vibrational differences at the molecular level of the analyzed pigments (CV, PB 15:1, PB 15:3, and PB 15:4) is shown in Figure 4.

When examining the model based on the first two principal components (PC1 and PC2), which account for the vast majority of the system's total variance, the dataset is seen to be modeled quite successfully from a chemometric perspective. The distributions in the graph not only separate the pigment classes with different chemical skeletons but also distinguish derivatives that are structurally very close to one another.

The graph clearly shows that the triarylmethane group (CV and MV) and the phthalocyanine-based macrocyclic pigments (PB 15 series) are clustered in distinct planes. In the grouping of triarylmethane pigments, the C-C and C=C stretching vibrations of the aromatic ring skeleton (1621 cm⁻¹ and 1586 cm⁻¹), the N-phenyl C-N asymmetric stretch (1371 cm⁻¹), and the in-plane bending vibrations of the aromatic C-H bonds (1176 cm⁻¹). In contrast, the 1530 cm⁻¹ peak, representing the C=N and C=C stretches of the pyrrole ring, the 1342 cm⁻¹ peak indicating the C-N/C-C symmetric stretching specific to the isoindole ring, and the 748 cm⁻¹ peak corresponding to the molecule's macrocycle vibration were found to emerge as statistical discriminants distinguishing PB15 derivatives from triarylmethanes.

CONCLUSION

In this study, triarylmethanes (crystal violet and methyl violet) and phthalocyanines (pigment blue 15 derivatives), which are the coloring components of blue ballpoint and gel pen inks frequently encountered in forensic document examinations, were characterized and classified using dual-wavelength (532 nm and 785 nm) confocal Raman spectroscopy and chemometric analysis.

The spectroscopic analyses performed demonstrated that severe fluorescence interference caused by different chromophore structures in the ink matrices can be effectively overcome by selecting laser wavelengths appropriate for the target molecule (532 nm for triarylmethanes, 785 nm for phthalocyanines) and optimizing the analysis parameters. Thanks to this approach, characteristic molecular vibrations of both pigment classes were identified.

The obtained spectral data were statistically modeled using PCA. As a result, triarylmethane and phthalocyanine pigments were separated into two main clusters, and the more difficult-to-distinguish crystal polymorphs (PB 15:1, PB 15:3, PB 15:4) were also distinguished within their own groups. In conclusion, the use of multivariate chemometric analyses such as PCA in confocal Raman spectroscopy offers a fast and reliable approach for

the examination of suspect documents while preserving sample integrity.

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