

Proceeding Paper

Raman Spectroscopy Applied to Blue and Green Ink Discrimination—A Pilot Study †

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Abstract: The requirement for the preservation of evidence in court continues to pose a challenge to forensic document analysis, where the answer to the discrimination of writing utensils is recurrent in requested questions. This study aims to contribute to the identification of the blue and green inks of handwriting instruments using Raman spectroscopy. Based on the Raman spectra obtained and after processing with Spectragryph software, a predictive model was built using KNIME software, where a discriminative power of 72.7% was obtained.

Keywords: questioned document; inks; Raman spectroscopy; handwriting instruments

1. Introduction

The analysis of the ink of common writing instruments is one of the most relevant areas of modern criminalistics in document fraud since the specific characteristics of inks can answer identification, comparison, and/or dating questions in requested forensic examinations [1–3]. This work aims to contribute to the discrimination of blue and green inks from common writing instruments through a non-destructive technique in which the full analysis of Raman spectra is exploited with Knime software in order to build a predictive model.

2. Materials and Methods

Eleven pens (five blue and six green) were selected from a collection of pens purchased on commercial surfaces. After signal Raman screening: pen 8: Unilakubo—SG100 Rubber Grip 0.7 mm; pen 10: Bic Crystal; pen 14: Bic—unidentifiable model; pen 32: Uni-ball Eye micro 0.5 mm; pen 39: Stabilo Sensor F 0.3 mm; pen 3: Papermate—Inkjoy 1.0 mm; pen 9: Bic Crystal; pen 51: Bic Crystal Soft Medium; pen 53: Papermate Inkjoy 1.0 mm; pen 54: Staples Stick Pens; pen 55: FlairZing—Color Flair 0.7 mm. The ink of each pen has been deposited in notebooks, created with current paper (Navigator) in circular areas with different stroke overlaps in each quadrant, in order to optimize the acquisition conditions. Raman spectra of the ink circular area deposits were acquired using a Raman Mira DS spectrometer equipped with a laser with an excitation wavelength of 785 nm (100 mW) and a spectral range of 200–2300 nm. The equipment provides a spectral resolution of 8–10 cm⁻¹ and a measuring spot of 0.042–2.5 mm. The detection technique used is Orbital Raster Scan (ORS), where a tightly focused beam (0.04 mm) scans a relatively larger area compared to



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the conventional Raman scanning, averaging the information. It has a universal fixture with three positions that allow the surface of objects to be analysed at three different distances: in contact and at 3 mm and 5 mm.

After acquiring 3 replicates of the Raman spectra for the pen inks, the respective baseline was adjusted using Spectragryph software version 1.2.15 [4]. The baseline of the spectra was adjusted 2 times. The Raman spectra files of each ink were split into 2 databases to create a predictive model using KNIME Analytics Platform software version 4.6.0 [5]: (a) the training database (which contained the data from 2 replicates for each of the dyes, the averages of the triplicates and the average between each two replicates) and the (b) validation database (which contained 1 of the replicates that were not present in the training database).

3. Results

The visual analysis of the Raman spectra of the pen inks studied revealed differentiating bands that could contribute to the construction of a predictive model, Figure 1.

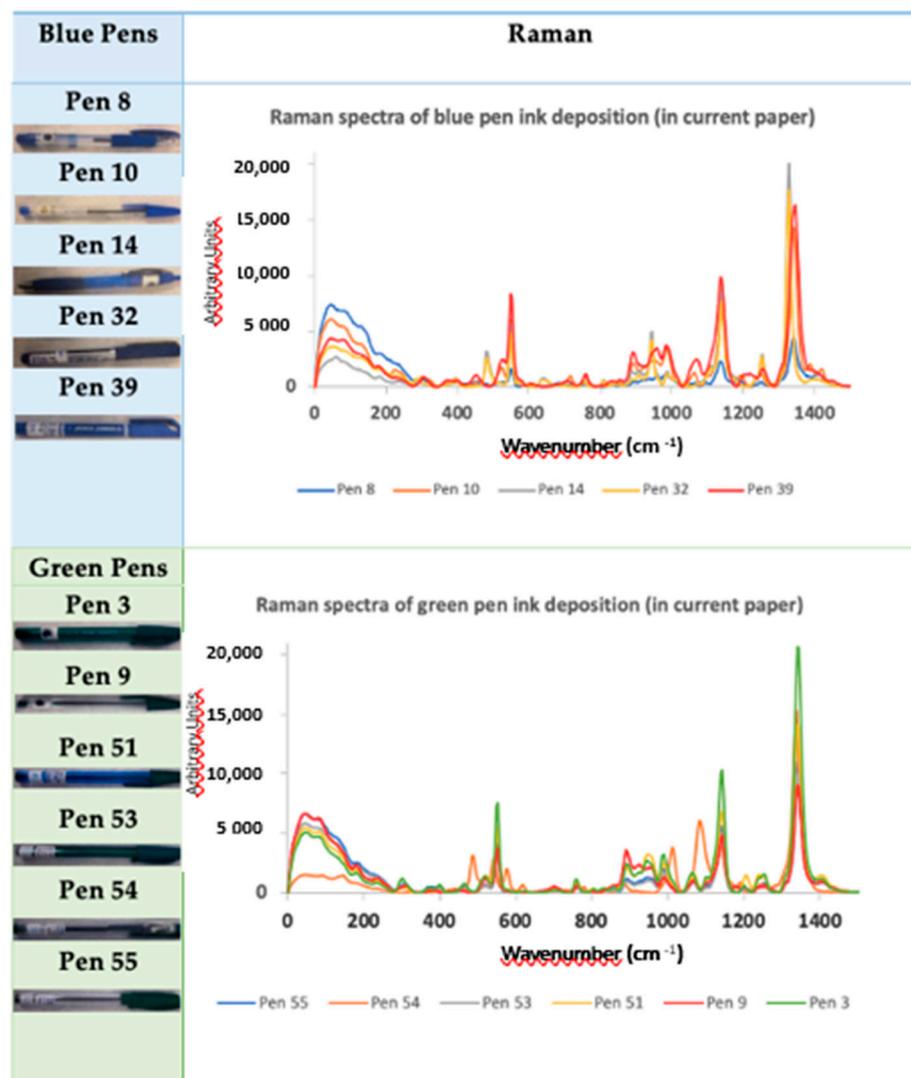


Figure 1. Raman spectra of blue and green ink pens.

After obtaining the Raman spectra on the handwriting instrument inks, the predictive model was built using Knime software to evaluate the discriminative ability of the model, Figure 2.

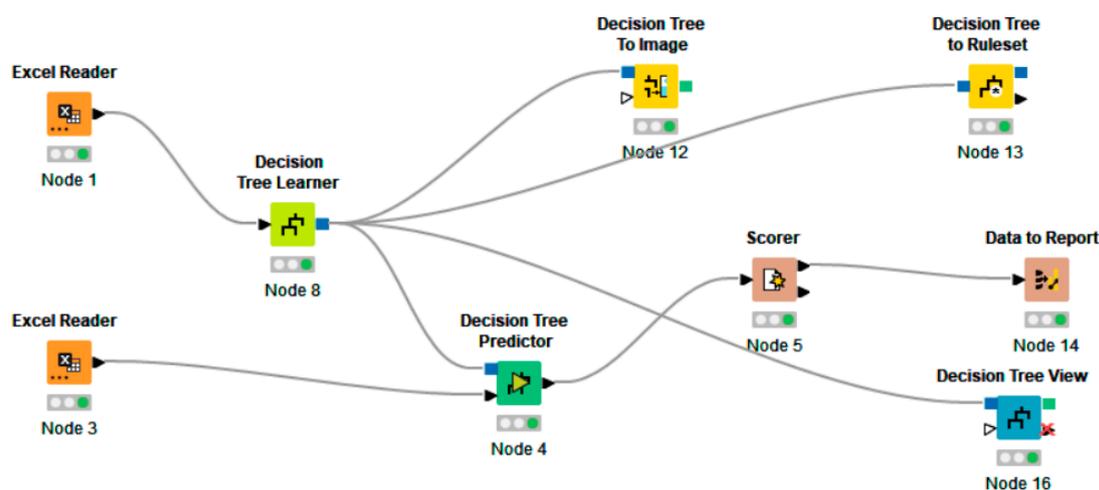


Figure 2. Predictive model performed in KNIME Analytics Platform software version 4.6.0 for the analysis of ink samples from handwriting instruments.

The following nodes were used in the model: Decision Tree Learner, Decision Tree Predictor, Scorer, Decision Tree View, Decision Tree To Image, Decision Tree To Ruleset, and Data to Report.

According to Berthold's instructions [5], in the nodes called Excel Reader (Nodes 1 and 3), the files intended to be processed by the predictive model were inserted: in node 1, the document of the training database, and in node 3, the test database. Decision Tree Learner (node 8) parameters were set, and a decision tree was generated from the training file (node 1). The Decision Tree Predictor (node 4) draws on the tree of node 8 to predict the class value for new patterns, in this case, for the "test" file. The Scorer, node 5, analyses the test and training files inserted in the previous nodes and provides the accuracy and error of the analysis. The following nodes (12, 13, 14, and 16) serve only to visualize the decision trees on an image.

After creating the Decision Tree Learner, a second tree was generated with the same nodes, but with the objective of validation in real context. In node 1, the same training file was inserted (for each technique), and in node 3, the validation file containing the data of the one replicate that was not present in the training file was inserted.

The predictive model created achieved a discriminatory power of 72.7% and an error of 27.3%.

4. Discussion

Despite the reduced number of replicates in each database, the present technique achieved values not much lower than those obtained in other studies with other techniques such as Micro-ATR-FTIR combined with chemometrics in which the discrimination power did not exceed 86.67% [6] and 89.99% [7], or in studies where multispectral imaging coupled with FCM was used and achieved discrimination percentages of 76% [8] and 85.7% [9].

5. Conclusions

The present pilot study allowed the development of a predictive model based on pen ink Raman spectra with a high discriminatory power of 72.7%.

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