Use of Raman spectroscopy and chemometrics to distinguish blue ballpoint pen inks

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ABSTRACT

The objective of this work is assessing whether the combination of Raman spectroscopy and chemometric tools is appropriate to differentiate blue ballpoint pen inks. Fourteen commercial blue ballpoint pen inks from different brands and models were studied and Raman spectra were obtained on ink lines written on A4 sulfite paper. First, a study of the best Raman configurations, in terms of laser intensity used and acquisition mode, was carried out to ensure sufficient spectroscopic quality without damaging the sample. Chemometric methods were applied first to improve the definition of spectral bands and to suppress fluorescence contributions from the signal. Once the spectra were suitably preprocessed, principal component analysis (PCA) and hierarchical cluster analysis (HCA) were applied to explore whether the different inks could be distinguished from their Raman spectra. Almost all inks could be gradually differentiated, through successive PCA analyses or looking at the different levels of the dendrogram structure provided by HCA. From these exploratory results, a tree structure was constructed based on PCA and HCA results in order to reflect the degree of similarity among ink classes. This tree structure was used as the basis to develop hierarchical classification models based on partial least squares-discriminant analysis (PLS-DA). Correct classification of inks was achieved by these PLS-DA models built and the most important regions to identify the ink classes were detected using the variable importance in projection plots (VIPs). The combination of Raman spectroscopy and chemometrics has been proven to be a promising fast non-destructive tool to differentiate among very similar ink types in documents.

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1. Introduction

When the pen is the writing material of questioned documents, evidences of the existence of two or more inks in the document can be valuable information for the court because this can indicate that the document was modified by addition or replacement of elements [1,2]. Distinct pens are commonly used to change the context of different kind of handwriting documents, for example, values of bank checks; data and medicines on medical prescriptions, rights on powers of attorney or beneficiaries in wills [1,2]. Therefore, ink differentiation is a subject of great importance in forensic science. Distinguishing inks present in a document is a complex scientific work, since techniques applicable to small amounts of ink on paper should be found and the analysis should be non-destructive because the physical integrity of the document

should not be compromised. Besides, pen inks are multicomponent chemical systems formed by a wide variety of chemical compounds and the detailed composition of the ink is often unknown [3–10].

Because of the complexity of the problem, semi-destructive methodologies have been employed for document analysis. Most semi-destructive methodologies initially involve ink extraction from small zones of the paper with suitable solvents for a subsequent analysis by techniques such as thin layer chromatography (TLC) [11], high performance liquid chromatography (HPLC) [5,6], infrared [7] and ultraviolet–visible spectroscopy [8,12]. Brazilian police commonly employ techniques based on reflectance spectrophotometry in the visible range or images generated in the visible range by application of sources in ultraviolet or infrared region. Simpler instruments, such as video spectral comparator (VSC), manufactured by Foster & Freeman, are used for documents examination [4,13]. These equipments are based on the sequential use of viewing filters or multiple illumination sources from UV to visible to IR wavelengths. The comparison of
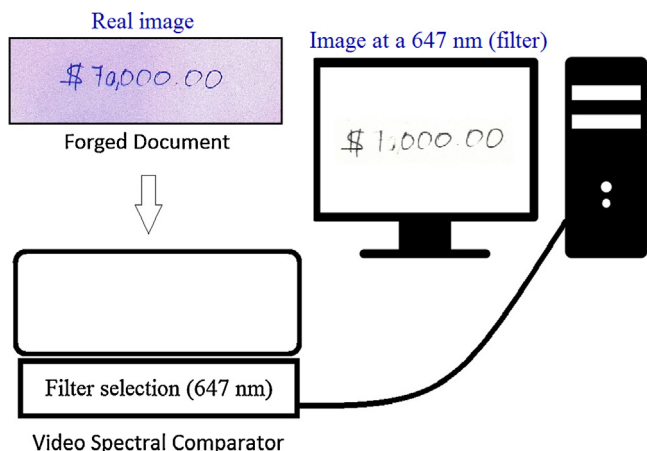
Fig. 1. Analysis by video spectral comparator by visual inspection. Identification of numerical value alteration, (from $1000.00 to $70,000.00), using a 647 nm bandpass filter.

inks is performed by visual inspection or by reflectance spectral registers, based differential visible/infrared absorption and fluorescence (see Fig. 1). This methodology is useful because is non-destructive, but Drexler and Smith have shown that the sole visual inspection is unable to differentiate many similar pen inks [13]. Only very few recent examples have shown the capability of this instrument coupled with chemometrics to differentiate among certain kinds of inks [14].

Techniques based on mass spectrometry have been widely applied to detect synthetic dyes on pen inks. In this context, easy ambient sonic-spray ionization mass spectrometry (EASI-MS) [9] is preferred because it generates minimal damage on samples in comparison with matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) [15], the laser energy of which can compromise the physical integrity of the document. Trejos, Flores and Almirall reported the use of laser induced breakdown spectroscopy (LIBS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [10] for elementary analysis of pen inks. According to the authors, both laser-based methods are appropriate for ink differentiation of many inks and the analyses just remove an approximate mass of 9–15 μg from the document.

Raman spectroscopy can be an advantageous technique for document analysis because it does not compromise the physical integrity of the document and can be employed to analyze micro-regions. Furthermore, it provides organic and inorganic information of the sample through fine spectroscopic features. An often commented disadvantage of employing Raman spectroscopy is the fluorescence contribution that can affect the definition of bands and, consequently, the spectra quality [3,16–18]. Therefore, more sophisticated variants, such as surface-enhanced Raman spectroscopy (SERS) have been tested to solve fluorescence problems and more informative spectra have been obtained for most pen inks [3,16–18]. Another alternative to cope with the fluorescence contribution is correcting this effect with spectral pre-processing, such as using derivative spectra. This alternative is preferable to SERS because it does not require sample treatment for spectra acquisition and can work with conventional Raman spectra obtained on the unaltered sample. Claybourn and Ansell reported that baseline corrections can be used to increase the spectra quality by removing fluorescence effect from Raman spectra of pen ink samples [19].

Literature reports the use of different laser excitation wavelengths (488, 514, 633, 685, 782, 785, 786 and 830 nm) in studies in which the Raman spectroscopy was employed alone or combined with other techniques to discriminate pen inks [3,16–23]. More

correct classifications were achieved when different laser excitation wavelengths or different techniques were combined. In the majority of works, the procedure followed to differentiate ink spectra is based on visual inspection, where the presence or absence of spectral bands [16–21,23] is examined. In this context, pen inks formed by mixtures slightly different from the same dyes cannot be distinguished because the spectra are too similar. In this work, we will show that the use of Raman spectra coming from a single laser source and suitably processed by chemometric tools would be sufficient to provide a very good approach to distinguish among ink samples.

The use of chemometric tools is extremely useful to investigate complex and very similar spectra. It is useful to extract the relevant chemical information from the raw spectra and is essential when the spectra have a large number of variables and significant overlap of analytical signals. Another advantage is that chemometric tools are statistical methods and provide an objective way to examine spectra, as opposed to pure visual inspection. Principal component analysis (PCA) [24,25], soft independent modeling of class analogy (SIMCA) [25,26] and linear discriminant analysis (LDA) [27] have shown very promising results in the field of ink pen analysis [5,28–31]. Kher et al. analyzed blue ballpoint pen inks by HPLC and infrared spectroscopy coupled with PCA, SIMCA and LDA [5]. The best results were obtained with HPLC data, where 97.9% of correct classification by LDA was obtained. Thanasoulias, Parisis and Evmiridis achieved a correct prediction rate of 100% in ink solution samples collected directly from the plastic ink reservoir of the pen and after dissolving it in ethanol before the analysis by UV–Vis spectrophotometry [28]. This methodology, however, cannot be applied in real cases of document analysis because the ink should not be removed from the document as far as possible. Silva and collaborators provided 100% of correct classification employing attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy to acquire ink spectra from circular areas with a 1 cm radius painted on paper [31]. Although the ink spectra were acquired in a non-destructive way, the described methodology may not be suitable for many real cases, where ink analysis in sample micro-regions is required. Considering the above, this work proposes the combined use of Raman spectroscopy and chemometric tools to discriminate among ink pens. Raman spectroscopy is proposed because this technique does not compromise the physical integrity of the document, may be employed in small regions, of the order of a few micrometers, has very informative fine spectral features and has potential to discriminate pen inks in document analysis. Several chemometric tools are used with three different objectives: (1) Signal preprocessing techniques, to enhance the relevant spectral features in Raman spectra and remove the fluorescence contribution; (2) exploratory analysis methods, such as PCA and hierarchical cluster analysis (HCA) to observe the presence of natural grouping structures among the different inks (3) classification methods, such as partial least squares-discriminant analysis (PLS-DA) to model the different ink classes, test the predictions capacity of each model to assign unknown ink samples to the right class and to detect the most important spectral regions to distinguish among ink classes.

2. Materials and methods

2.1. Samples

Commercial blue ballpoint pens were acquired to form a dataset with 14 pen ink classes. A class is formed by all Raman spectra collected from lines performed with pens of the same brand and the same model. In this study, the classes were from 14 pen models of different brands, namely, five pen models from Bic brand, four from Pilot brand, two from Noguera & Vintró brand and one from