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Review article

Raman spectroscopy for forensic analysis of inks in questioned documents

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ABSTRACT

The methods for perpetrating forgery and alteration of documents are becoming increasingly more sophisticated. Forensic examinations of questioned documents routinely involve physical and chemical analysis of inks. Raman spectroscopy is a very attractive technique for ink analysis because it combines chemical selectivity with ease and fast analysis and it does not require sample preparation nor leads to destruction of the evidence. However, some limitations of this technique include low sensitivity and the overwhelming phenomenon of fluorescence, which can be solved by resonance Raman spectroscopy and surface-enhanced Raman spectroscopy.

This article aims to demonstrate the great potential of the Raman-based techniques by providing an overview of their application to forensic examinations of ink evidence from pens and printers. Moreover, it is also addressed the chemistry of ink-paper interactions and the problematic of intersecting lines.

Contents

1. Introduction

A "questioned" document can be any written document whose source or authenticity is doubtful. Forensic document examiners (FDE) handle different types of questioned documents, e.g. letters, checks, identity documents, contracts, wills, insurance claims, petitions, threatening letters, suicide notes, lottery tickets, which can be found in a variety of criminal investigations. Document examinations usually start with predicting the type of device used to produce the document (pens, pencils, photocopiers, printers, seals, stamps, etc.) [1], followed by physical and chemical analysis of inks, where FDE are asked to (i) test whether any written entries might have been added or altered, (ii) compare two or more ink contributions and determine whether these exhibit similar composition, (iii) determine the possible source of the ink, (iv) determine the chronological sequence of two or more ink contributions that intersect each other, and (v) backdating of inks.

Non-destructive examinations are preferred since they are simpler to perform, involve little or no manipulation of the

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document and can provide sufficient information without lost of the documents evidential value [2]. These involve visual examinations using the microscope, filters that enhance different contrast between inks and optic excitation under various light wavelengths [3]. However, such examinations are merely qualitative and depend on the judgment of the FDE. Additionally, although these techniques are very sensitive to small quantities of ink, the discriminating power obtained with inks that show similar luminescence is limited.

Consequently, developing more informative and effective tools for question document examinations become necessary and simultaneously, a challenge, as the methods for falsification and document alteration grow more sophisticated. In this sense, the analytical sciences have played an important role. For example, techniques such as UV–vis spectrophotometry [4] thin layer chromatography (TLC) [5–7], high performance liquid chromatography [8], capillary electrophoresis [9,10], gas chromatography [11] and even mass spectrometry (MS) using various ionization methods [12–19] have shown in the literature their great potential for ink analysis. However, ink extractions and sample preparations are required, thus compromising the integrity of the document.

Vibrational techniques such as Fourier transform infrared (FTIR) spectroscopy have also been reported for ink analysis [20–22], but also here, ink extractions and sample preparations are usually necessary. Notwithstanding, Dirwono et al. [23] has recently reported the successful use of attenuated total reflectance (ATR)-FTIR microspectroscopy for ink analysis of red seals without destruction of the document. The only problem associated with this technique is that often, the strong absorption bands of the paper overlap with the inks signal. Alternatively, Raman spectroscopy (RS) has rapidly gained interest for ink analysis of questioned documents because it also provides relevant chemical information about the ink composition with little or no contributions from the paper. Additionally, this vibrational technique performs the analyses directly on the document, it only requires small amount of ink, analysis times are fast and most importantly it is non-destructive. The recent technologic advances with instrumentation have also allowed this technique to provide robust and reproducible results.

1.1. Raman spectroscopy technique

RS consists of irradiating samples with a monochromatic laser beam which interacts with the molecules originating a scattered light. The light that is scattered with a different frequency than the incident photons (inelastic scattering) is registered to construct a Raman spectrum that is characteristic to the molecular structure, allowing its identification. Given the fact that inks are complex mixtures of unknown components, molecular identification of all specific ink components using RS can sometimes be a hard task. Instead, spectral fingerprinting comparison is preferably used to differentiate inks in forensic contexts. Comparison involves examining the overall pattern of the spectra, as well as differences in band positions (presence or absence at specific shift values), band intensities (broad or sharp) and relative intensities of adjacent bands. The absolute intensities of the bands are not used because it depends on a number of factors such as orientation, laser power and other instrumental effects which cannot be reliably reproduced [24].

There are two main drawbacks associated with this technique: (i) low sensitivity due to the naturally weak Raman scattering and (ii) intense fluorescence signals exhibited by many inks, or paper, which covers the desired chemical information [25]. Increasing the sensitivity of the instruments can be achieved by performing resonance Raman spectroscopy (RRS). RRS consists of using a laser wavelength similar to the maximum absorption of the ink chromophore to induce an electronic resonance effect. Another technique that enhances the scattering signal and also quenches fluorescence is surface-enhanced Raman spectroscopy (SERS). SERS require an intrusive sample pre-treatment, using either a nanoscale roughened metal surface or metal colloids of gold or silver, which prevents the documents from being examined naturally. There are chemical and electromagnetic effects causing the enhancement. Depending on the excitation wavelength, one or the other may dominate the spectrum [26]. Ultimately, the combination of RRS and SERS techniques (i.e. surface-enhanced resonance Raman spectroscopy (SERRS)) can increase the sensitivity up to ten orders of magnitude compared to RS [27].

The technologic advances of this technique over the last two decades have put RS in a vanguard position in the analysis of various evidential materials within the forensic sciences [28]. The contribution of RS to ink examinations of questioned documents can be of great value, particularly over destructive analytical techniques. Hence, so that new barriers keep on improving, this article reviews the scientific developments that marked the last decade regarding the RS techniques mentioned above for ink analysis. Although most studies focused mainly in discriminating pens and printers, some studies introduced interesting approaches to determine the chronological sequence of two or more ink contributions that intersect each other.

2. Discussion

2.1. Pen inks

Forensic laboratories routinely encounter ink evidence originated from pens during their investigations. Pen inks are viscous liquids made of a mixture of several dyes and pigments that provide color, organic solvents that serve as a vehicle, resins that sustain the right viscosity and adhering properties, and also other agents like antioxidants, preservatives and trace elements. The detailed composition of pen inks is proprietary for each brand and manufacturer and it is usually kept secret. This complicates investigations since researchers have to analyze a sample of the ink in question and determine the compositions using their own resources. Ballpoint and gel pens are the most commonly type of pens commercially available, thus it is not surprising that most of the studies on ink analysis by RS referred to discrimination between different brands of ballpoint and gel pens written on white paper. Claybourn & Ansell [29] compared and discriminated several black inks using 514 and 782 nm laser excitation wavelengths. They observed that black inks were easily burned unless very low laser powers were used and fluorescence was also encountered with the 514 nm laser but not with the 782 nm. Four forensic cases were also described to exemplify the RS potential for proving document alterations but also its limitations, particularly when more corroborating data is needed to reach conclusive results. Mazzella & Buzzini [30] focused on the discrimination of blue gel pen inks manufactured in different geographical regions, as a sequence of their previous work [31]. The Raman spectra of pens from the same brand and model obtained in different geographical origin showed no differences. Additionally, combining the discriminating performance obtained by the two laser excitation wavelengths (514 and 830 nm) allowed for better differentiation of gel pen inks than if they were considered separately. Savioli et al. [32] were also able to univocally discriminate black and other different colored ballpoint pen inks using the 633 and 785 nm laser excitation wavelengths. The authors further used SERRS to reduce fluorescence problems and reported that the bands definition was improved as well as the quality of entire spectra. Kalantzis [33] however, focused on possible paper contributions to ink analysis in documents. The author analyzed blue and black ballpoint and gel pen inks in different white, colored and lined papers by RS and SERRS. Results