Application of Raman spectroscopy in relative blue ballpoint pen ink dating for forensic document analysis – a case report

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Abstract

In this case report, blue ballpoint ink on a questioned document was investigated using a newly developed Raman model devoted for dating of documents via writing inks. The majority of blue ballpoint pen inks contain crystal violet - a triarylmethane dye which displays a typical "molecular fingerprint" type of Raman spectrum, of which most intense peaks at 749 cm^{-1} and 1542 cm^{-1} (under 785 nm laser excitation) represents the least and the most stable bonds of crystal violet molecules, respectively. The ratios of peak intensities at above mentioned Raman shifts are utilized to estimate the relative dating of the questioned blue ballpoint pen ink in practice, results of which agreed with estimations using other traditional relative dating methods.

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1 Introduction

Recent advances in Raman spectroscopy technology and research have enabled a wide range of practical applications for this rapid nondestructive method, especially in forensic examinations. Despite the early discovery of inelastic scattering effect of light in 1928, which was name after one of the discoverers – Indian scientist Chandrasekhar Raman (who later received the Nobel prize for physics in 1930 for such discovery), the practical applications of Raman spectroscopy only bloomed in the 1990s as a result of technology and instrumentation revolution. In the early days, weak light sources and poor-sensitivity detectors made the acquisition of Raman spectra very time-consuming with low resolution. Nowadays, the development of laser sources, spectrometry instruments, detectors, automated control components, miniaturization and efficient data processing software made Raman highly versatile. The versatility of this method can be demonstrated in terms of sample preparation (minimal to none, can even penetrate clear plastic cover avoiding contamination), shortened processing time (few seconds for each measurement), and wide application ranges (food, paints, drugs, currency, inks, explosives, gems, jewelry, ceramics, and glasses) [1].

Raman has recently been very popular for forensic analysis, due to its rapid sample-identification ability and nondestructive nature, along with the development on handheld equipment which enables the in-situ sample analysis at crime scenes. On top of such critical qualities, Raman offers high flexibility of material choices, high spatial resolution, and good specificity. However, a major drawback of Raman spectroscopy was the overwhelming fluorescence effect that usually hinder the revelation of weaker Raman signal. This disadvantage rendered Raman far less useful compared to other vibrational spectroscopy such as infrared, limiting its forensic applications until the breakthrough of adjustable laser excitation source, charge-coupled device (CCD) detector and computerized data processing in the 1990s [2].

The principle of Raman spectroscopy is described when a monochromatic radiation (wavelength λ, usually a laser source) strikes a sample and scatters in all direction, most of which are in the same original wavelength (elastic/Rayleigh scattering), while a very small portion scatters out in a different wavelength (inelastic/Raman scattering), which can be higher ($\lambda + \Delta\lambda$, Stokes shift) or lower ($\lambda - \Delta\lambda$, anti-Stokes shift) than the original radiation wavelength. This difference in wavelength ($\Delta\lambda$) is called the Raman shift, measured on spectrum in cm^{-1} (simplified from the correct unit of Δcm^{-1}). In conventional Raman spectroscopy, only Stoke-shifted Raman bands are of interest since these bands have much higher intensity than the anti-Stoke counterparts. Raman active modes of organic molecules are measurable in the range of 4000 cm^{-1} to 400 cm^{-1}, yet in regular practice, Raman scales of interest are normally in smaller ranges [3].

Sampling techniques required for Raman spectroscopy are also very simple, there is almost minimal to none sample handling and preparation needed since. In addition, another major advantage of Raman is that glass and water are relatively weak Raman scatterers, thus, samples can be investigated in glass containers or solution, which cannot be done with the other vibrational technique - infrared spectroscopy [3].

In the last 2 decades, Raman applications have expanded rapidly in all disciplines, especially forensic science. Possessing all the specific requirements for an excellent forensic analytic method as mentioned above, Raman has proved to be effective tool for writing ink examination. As a small sub-category of forensic document examination, writing ink analysis plays an important role in dating of questioned documents, which often involved backdated or additional contents that usually require destructive analytical methods to determine the authenticity. In the early years of forensic investigations, nondestructive traditional methods were based on basic observations such as photography, magnification, light filtering, or utilization of different light sources [4]. These simple methods of course cannot distinguish the chemical differences of similar colored and textured inks, therefore destructive methods were used to remove parts of the questioned ink for further in-depth analysis. Hole punchers or needle tips were used to extract milimeter-size pieces of ink-containing paper, these microsamples were then examined by chemical spot tests, chromatography (paper, thin-layered or liquid), electrophoresis, and densitometry [4].

Regarding ink analysis using Raman spectroscopy, the fluorescence effect is significant due to the colored pigments and dyes within inks, which in turn can reduce quality of spectra. To overcome this effect, several options were proposed. One of these options is Surfaced-enhanced Raman spectroscopy (SERS), which enhances signals using rough metal surfaces or nanostructures. The magnification effect of SERS can be as high as ~1,010 times [5]. Another method to negate the effect of fluorescent is spectral pre-processing, for example using derivatized spectra. Using longer-wavelength laser also reduce fluorescent effects, although this option suffers a small drawback which is the reduced Raman signal intensity. This option was demonstrated by an early study in 2000 [6] when examining several black inks in 514 nm and 782 nm laser excitation wavelength, the fluorescence was present in spectra generated by 514 nm-laser, but not under 782 nm-laser radiation.

Ink dating is a specialized area within many subcategories of forensic document examination. The ink dating experts can solve some of the most challenging questions such as when and in which time order that different parts of a questioned document were written. Ink dating research started from the 1980s by pioneers in forensic science such as Richard L. Brunelle, Antonio A. Cantu and Larry F. Stewart [7,8]. These early studies focused on extractability of ink (as a whole) by different solvents or change in volatile components of inks over time. It is not until 1993 when changes in dye components of ink were analyzed for the ink dating purpose [9].

The majorities of ink dye studies since then focus on crystal violet - the most popular dye in blue, black and violet inks, found in 80 % of blue and black inks [10,11]. Crystal violet (also called methyl violet 10B or hexamethyl pararosaniline) possesses 6 methyl groups attached to 3 outer amine groups. Once being written down, crystal violet (CV) in ink is subjected to the process of N-demethylation (replacing a methyl group attached with peripheral amine groups by a hydrogen atom, initiated by UV radiation in the sunlight and oxygen in the atmosphere. The demethylated products of CV are methyl violet 2B (pentamethyl pararosaniline), methyl violet 6B (tetramethyl pararosaniline) and other polymethylated pararosanilines.

A variety of methods have been employed to detect changes in CV following time, yet Raman spectroscopy only started to be utilized recently [12-14]. Using Raman spectra, blue writing inks were divided by Gorshkova [12] into 3 groups, based on the type of colorants – triarylmethane group of dyes, phthalocyanine blue pigment, and alcohol-soluble phthalocyanine blue mixed with triarylmethane dyes. This study suggested using the ratio of Raman peak intensities at specified wavenumbers to determine ink dating, which can be demonstrated on a time-dependent polynomial curve with a high-accuracy estimation of up to 15 years of ink age. This case report aims to demonstrate practical applications of this method in evaluating relative dating of questioned documents.

2 Materials and methods

2.1 Sample preparation

A questioned document dated July, 2011 written in blue ballpoint ink was submitted for analysis (named questioned sample A1), along with 3 known-date documents (named comparison samples A2, A3 and A4, dated March 2016, January 2016 and May 2016, respectively) written by CV-containing blue ballpoint pen inks. Samples were subjected to direct laser radiation for Raman analysis without further preparation.

2.2 Spectral acquisition

Raman spectra were acquired by Raman spectrometer (LabRAM HR Evolution, HORIBA Scientific Ltd., UK). Raman shift range was measured from 200 to 2200 cm^{-1}, with distance between 2 adjacent points on the spectrum was approximately 0.55 cm^{-1}. Spectra were obtained under low laser power to avoid burning the samples. The laser power was tested between 0.05 mW and 5 mW, of which 1 mW laser power produced the highest quality spectra. Other experimental settings are listed in Table 1 below.

Table 1 Raman settings for experiments on LabRAM HR Evolution, HORIBA

Parameters	**Value**
Acquisition time	30 seconds
Date of spectral acquisition	February, 2021
Accumulations	2
Laser excitation wavelength	785 nm_Edge
Hole	100.021
Grating	600 (500 nm)
Objective	× 50
ICS correction	Off

Spectral data of 4 samples were collected and processed before analysis. Each spectrum was smooth twice without any baseline subtraction, then stacked and offset on the same graph for clarity. Raman peak intensities at 749 cm^{-1} and 1542 cm^{-1} were recorded following Gorshkova's recent model of temporal dye degradation [12].

3 Results and discussion

Raman spectra of questioned sample and 3 comparison samples displayed similar "fingerprint", confirming that they are written by the same type of ink (Figure 1 & 2). While peak shift wavenumbers can provide information on certain chemical functional groups, analysts often pay attention to the "fingerprint" region of a particular spectrum. In general, Raman spectra display a "molecular skeleton" type of vibrations, which are seen at wavenumbers under 1500 cm^{-1} and possess a substance-specific pattern. These "molecular skeletal" vibrations are unique for each substance since the vibrational frequencies depends on atomic masses, geometric arrangement of the molecule, and chemical bonds' strength, making this feature a valuable tool for substance identification. [15]

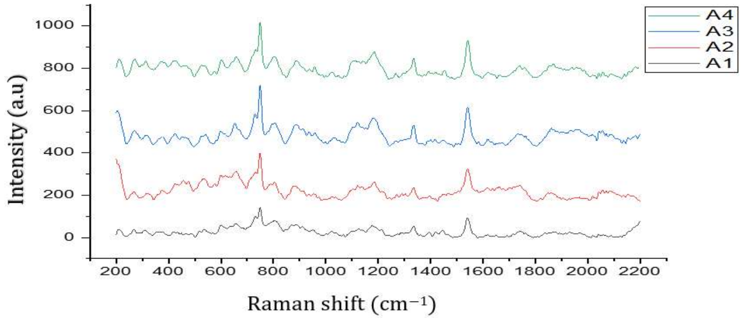

Fig. 1 Stacked Raman spectra of 4 samples showing similar "molecular skeleton"

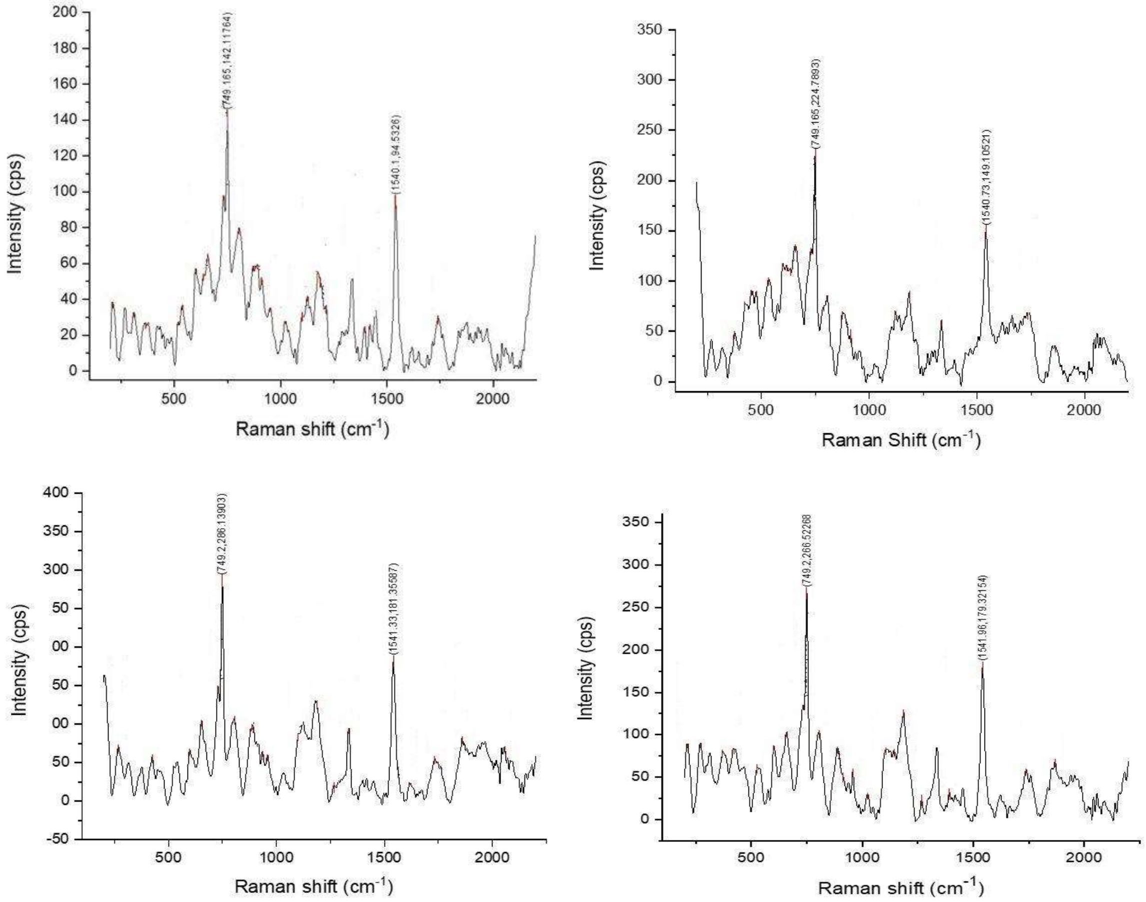

Fig. 2 Individual Raman spectrum of sample A1, A2, A3 and A4 (order from left to right, top to bottom)

The individual spectrum was baseline-substracted and peak intensities were measured accordingly. The intensity of peaks centered at 749 cm^{-1} and 1542 cm^{-1} and their ratios were recorded for each sample (Table 2). The absolute peak intensities are dependent on the concentration of samples on the studied focal area, which cannot be controlled in many cases, thus the ratios of peak intensities were used to negate such concentration influence [12]. According to Gorshkova [12], the most intense peaks of CV-based ink spectra are peaks centered at 729 cm^{-1}, representing vibrations of the (C-N) pi-conjugated systems formed by outer nitrogen atom and phenolic carbon atom in the inner rings, while the peaks centered at 1587 cm^{-1} represent $(C\text{-}C)_{ring}$ vibrations between phenolic carbon atoms in the inner rings themselves (Figure 3). These most prominent vibrations represented the least stable bonds (outer C-N) and the most stable bonds (inner $C\text{-}C_{ring}$) of the CV molecule via its N-demethylation degradation pathway, thus they are highly relevant when assessing the time dependency of CV based using Raman spectroscopy.

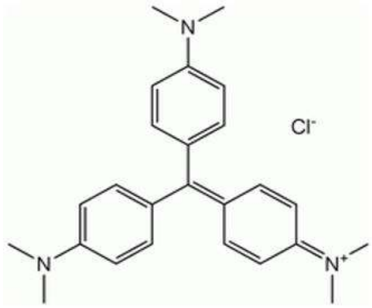

Fig. 3 The chemical formula of crystal violet

Table 2 Peak intensities at 1542 cm^{-1} and 749 cm^{-1} of 4 samples and their ratios.

Sample	I_{1542} (au)	I_{749} (au)	$R_{749/1542}$
A1	94.532	142.1176	1.504
A2 (Mar, 2016)	149.105	224.7893	1.508
A3 (Jan, 2016)	181.356	286.1390	1.580
A4 (May, 2016)	179.322	266.5227	1.486

The main difference in our case is that we are able to generate spectra for CV-containing type of ink under 785 nm laser excitation wavelength without high luminescence contribution. This may be attributed to either low laser power, different ink formula/paper substrate, or a combination of aforementioned factors. As a result, the peak shift values of interest are slightly different, most intense peaks centered at 729 cm^{-1} and 1587 cm^{-1} in the Raman spectra at 532 nm are now shifted to 749 cm^{-1} and 1542 cm^{-1} under the 785 nm laser radiation. However, with limited number of real case samples we were unable to form a time-dependent curve and only able to make comments on the relative dating of such samples.

$R_{749/1542}$ of the questioned sample A1 was similar to that of A2, and at a ~5% RSD from A3 and A4, which suggests that these 4 samples have the same relative dating, or they were written at around the same time. Although the peak ratio scaling value (X axis) of the degradation curve suggested by Gorshkova [12] are not applicable (our case used 785 nm laser excitation), the main graphical features are still relevant (time periods, Y value of peaks) since they are defined by the natural degradation process of CV and unaffected by the choice of laser wavelength. Period 3 of the curve (Figure 4) is monotone after around 40 months, thus the ratio $R_{749/1542}$ represent only 1 point on the curve. This feature enables the relative dating of A1 to be similar to that of A2 (written in March, 2016), with the ± 5 % RSD equaling to ± 2 months.

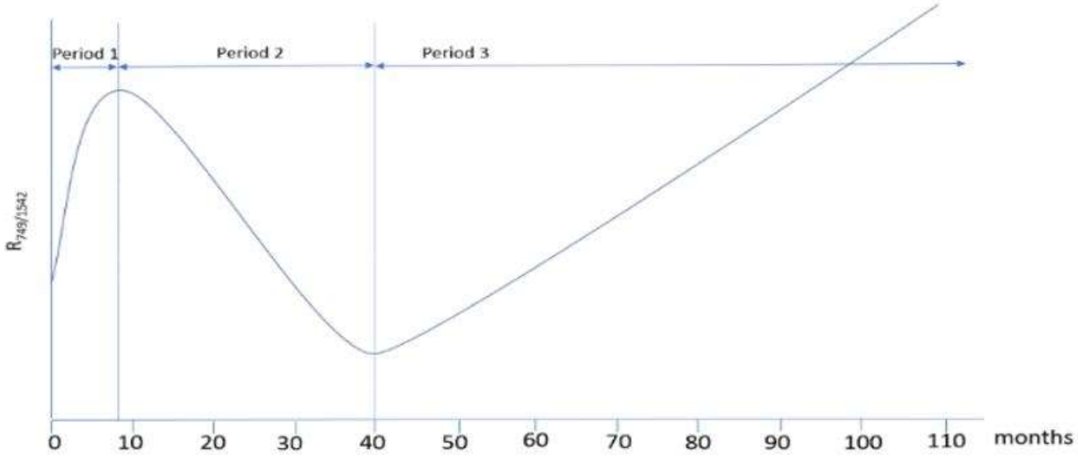

Fig. 4 Raman degradation curve of CV under 532 nm laser-wavelength excitation according to Gorshkova et al. (2016)

This dating estimation can also be tested by other traditional relative dating methods such as high performance thin-layered chromatography to validate the result. HPTLC results showed similar color intensity of CV spots (meaning similar extractability of dye, i.e similar relative dating) between A1 and A2 (Figure 5).

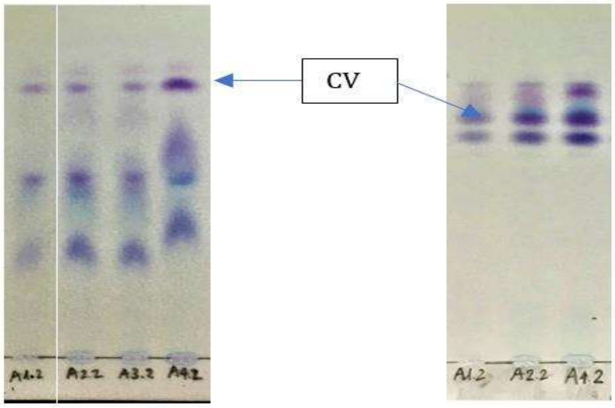

Fig. 5 HPTLC (developed in 2 different solvent systems) showing similarities between A1 and A2 (suffix .2 indicated the position of signatures on respective samples)

4 Conclusions

This case report has shown that Raman spectroscopy can be effectively used to estimate relative dating of the questioned documents with limited amount of comparison samples. In combination with other traditional methods, absolute ink dating can be estimated with sufficient accuracy for practical application without the need of a large comparison database.

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Ứng dụng phổ Raman trong xác định tuổi mực tương đối phục vụ cho giám định tài liệu trong khoa học hình sự

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Tóm tắt Trong nghiên cứu này, một mô hình Raman mới phát triển gần đây được sử dụng để nghiên cứu mực bút bi xanh trên tài liệu nghi vấn, tiến tới xác định tuổi của tài liệu thông qua tuổi mực viết. Phần lớn các loại mực bút bi màu xanh có chứa phẩm màu tím tinh thể - một loại thuốc nhuộm triarylmethan, hiển thị dạng phổ Raman điển hình gọi là “dấu vân tay của phân tử”, trong đó các cực đại mạnh nhất ở 749 cm^{-1} và 1542 cm^{-1} (dưới kích thích bằng tia laser 785 nm) đại diện cho các liên kết kém bền và bền nhất của phân tử tím tinh thể. Tỉ lệ cường độ cực đại ở các số sóng Raman nói trên được sử dụng để xác định tuổi mực tương đối của mực bút bi màu xanh trong nghiên cứu này và cho kết quả phù hợp với ước lượng bằng các phương pháp xác định tuổi mực tương đối truyền thống khác.

Từ khóa quang phổ tán xạ Raman, mực bút bi xanh, tài liệu giám định, tuổi mực tương đối, khoa học hình sự.