Forensic Science International 245 (2014) 38–44

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Studying the variability in the Raman signature of writing pen inks

André Braz [a,b], María López-López [a,b], Carmen García-Ruiz [a,b,1,*]

[a] University Institute of Research in Police Sciences, University of Alcalá, Ctra. Madrid-Barcelona Km. 33.600, 28871 Alcalá de Henares (Madrid), Spain
[b] Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Multipurpose Building of Chemistry, University of Alcalá, Ctra. Madrid-Barcelona Km. 33.600, 28871 Alcalá de Henares (Madrid), Spain

ARTICLE INFO

Article history:
Received 2 July 2014
Received in revised form 15 September 2014
Accepted 1 October 2014
Available online 14 October 2014

Keywords:
Writing ink
Questioned document
Raman spectroscopy
Signature
Variability

ABSTRACT

This manuscript aims to study the inter and intra brand, model and batch variability in the Raman spectral signature among modern pen inks that will help forensic document examiners during the interpretation process. Results showed that most oil-based samples have similar Raman signatures that are characteristic of the Crystal Violet dye, independently of the brand. Exception was the Pilot samples that use Victoria Pure Blue BO instead. This small inter-brand variability makes oil-based pens difficult to discriminate by brand. On the contrary, gel and liquid-based samples use different colorants such as Rhodamine B, Copper Phthalocyanine, Ethyl Violet and Victoria Blue B. No particular pattern was observed regarding the colorants used by each brand, except the Pilot samples that were the only brand using the Victoria Blue B dye, which is a clear distinct feature. Additionally, the intra-brand variability was also large among gel-based Pilot samples. The small spectral differences observed among several batches of Bic Crystal Medium samples demonstrated that changes were introduced in their chemical formula over the years. The intra-batch variability was small and no spectral differences were observed within batches. This manuscript demonstrates the potential of Raman spectroscopy for discriminating pens inks from different brands and models and even, batches. Additionally, the main colorants used in modern pens were also identified.

1. Introduction

Questioned document examinations are highly demanded in civil and criminal cases related to the manipulation and falsification of documents. When a certain ink entry is in question, examiners must perform physical and chemical analyses and comparisons with other entries in the same document as well as with ink libraries [1]. Their main interest is the verification that the components in the questioned ink are the same as a control ink sample, which is representative of a certain brand/model of pens [2]. However, this simplistic approach does not consider the current ink market, which has become far more complicated. These complications derive from the mass production of pens that originates batches with thousands of pens with similar ink formula, and also from the constant variations inserted in the global market by ink producers and pen manufacturers that, in compliance to market and economic demands, originate pens from different brands to have similar ink formula, and also pens from the same brand/model to have different ink formula [3]. Moreover, some companies are starting to recycle writing instruments so it will become more frequent to have mixtures of chemical compositions. The techniques on non-destructive ink examinations that are mostly published in the literature are useful to distinguish among different types of inks but do not provide individualization information to characterize the varied ink formulations. Other techniques, based on chromatography (e.g., high-performance liquid chromatography or gas chromatography), offer great discrimination performance in the identification process of the source of a questioned ink, but they are destructive, time consuming and require cost-intensive sample preparations [4]. Even so, none of the studies published to date considered the different sources of variations present in pen inks: variation between groups and variation within a group (i.e. differences between individual pens of a single group). A study describes the statistical variations in the infrared spectra between brands and models of black pen inks [5]. The authors showed that the inter-brand/model variability was overall larger than the intra-brand/model variability but within groups varied, depending on the

* Corresponding author at: Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Multipurpose Building of Chemistry, University of Alcalá, Ctra. Madrid-Barcelona Km. 33.600, 28871 Alcalá de Henares (Madrid), Spain. Tel.: +34 91 8856431.
E-mail address: carmen.gruiz@uah.es (C. García-Ruiz).
1 http://www inquifor com/.

http://dx.doi.org/10.1016/j.forsciint.2014.10.014
0379-0738/

manufacturer. However, only three brands of pens were studied and the authors failed to report more detailed information about the pens studied. They also found that the paper substrate greatly interfered in the inks infrared spectra.

For forensic purposes, it is important to follow the market tendencies to know when and what sort of variations mostly occur and whether they are systematically or arbitrary, in order to have an indication on how common or characteristic the chemical composition of a questioned ink is, and thus its evidential value. Therefore, considering the lack of information regarding the variability in the Raman chemical signatures of modern inks, this manuscript aims to study if the Raman spectra of ink lines produced by a group of representative pen samples from various brands, models and batches allow to establish patterns and identify particular spectral differences and similarities among them for a better assessment of the evidential value of ink examinations in questioned document cases. More specifically, the variability was investigated among pens with different ink formula types (oil, liquid, gel-based and other combinations), between brands of the same ink formula type (inter-brand), between models of the same brand (intra-brand) and between and within batches of the same model (inter and intra-batches variability, respectively). Raman spectroscopy was chosen for this study because it is becoming an invaluable and increasingly frequent technique in many forensic laboratories that is non-destructive and has the ability for detecting the inks major chemical components, such as dyes, pigments and resins as well as other minor organic and inorganic components used in their manufacture. Additionally, Raman technique was preferred over infrared because paper has scarce influence in measurements [6,7].

2. Materials and methods

2.1. Raman spectroscopy

Raman measurements were performed using a Thermo Scientific DXR Raman microscope controlled by the Omnic for dispersive Raman 8.3 software (Thermo Fisher Scientific Inc., Madison, USA). A diode-pumped solid state laser of 532 nm wavelength was used, with an intensity below 1.0 mW to avoid sample burning. The microscope objective was set to 50× magnification, which resulted in an estimated spot size of 1.1 μm. Spectra were measured in the 300–2000 cm^{-1} range and a spectral resolution of 2.7–4.2 cm^{-1} was obtained. Spectral acquisitions were 1 s × 10 scans for all samples. Each sample was measured five times at different points of the same line. Cosmic spikes filter was systematically applied for all measurements as well as automatic fluorescence corrections (polynomial of order 6) to scale-remove the slowly variations of background.

2.2. Data treatment

The Raman spectra were imported into Unscrambler X 10.2 (CAMO, Norway) for preprocessing and statistical analysis. Baseline correction of each spectrum was used to remove the gradual curvature from both the sample and background that is not due to the Raman effect, followed by smoothing with the Savitzky–Golay algorithm (polynomial order 2, section size nine points) in order to reduce spectral noise and unit vector normalization. The spectral range was reduced to 400–1700 cm^{-1} in order to eliminate the non-informative parts of the spectra as well as to reduce the initial number of variables. In Principal Component Analysis (PCA), the data was organized in a 3D scores plot using the first three Principal Components (PCs) according to spectral similarities and differences among samples. From the PCs used, a value of explained variance is given that quantifies the variation in the data and expresses the proportion of structure found in the data by the model.

2.3. Samples

The initial sampling set consisted of 190 blue pens of 12 known brands and 38 models (Table 1) that were acquired from several sources (privately, on several local shops and directly from the manufacturer). Additionally to this set, 120 blue Bic Crystal pens (Societé Bic, France) of twelve different batches manufactured in 2007, 2008, 2010, 2011, 2012 and 2013 (two batches per year, ten pens per batch) were obtained for inter-batch variability studies. For each pen, one straight parallel line was drawn on the same sheet of common office paper (white, A4 80 g kg^{-1} density). The standard references Victoria Blue B, Solvent Blue 38, Rhodamine B, Victoria Pure Blue BO, Ethyl Violet, Victoria Blue R and Copper (II) Phthalocyanine were purchased by Sigma–Aldrich.

Table 1
Detailed information of the pen samples studied.

Brand and model		Sample ID	Ink type	#Pens
Bic	Crystal Medium	B_1	Oil	5
	Ecolutions	B_2	Oil	1
	Rondo Style	B_3	Oil	1
	Cristal Gel	B_4	Gel	1
	Atlantis Gel	B_5	Gel	1
	Atlantis	B_6	Other (Easyglide)	4
Pilot	SupergripM	P_1	Oil	5
	BPS-GP	P_2	Oil	5
	Rexgrip EF	P_3	Oil	1
	G1	P_4	Gel	3
	G2	P_5	Gel	5
	G-Tec	P_6	Gel	5
	Frixionball	P_7	Gel	2
	V5	P_8	Liq	4
	Vball	P_9	Liq	5
	Greenball	P_10	Liq	1
	Acroball	P_11	Other (Oil-Gel)	5
Papermate	Stick 2020	PM_1	Oil	2
	Gel 2020	PM_2	Gel	1
	Flexigripultra	PM_3	Other (Lubriglide)	1
	Flexgrip Elite 1.4	PM_4	Oil	1
Uniball	Jetstream	U_1	Gel	2
	Eye Fine	U_2	Liq	1
	Insight UB-211	U_3	Other (Liq-Gel-Unisuperior)	2
Inoxcrom	Medium	I_1	Oil	5
	Roller Smooth Writing	I_2	Liq	4
Staedtler	Stick 430	ST_1	Oil	5
	Ball 432	ST_2	Oil	5
	Triplus Fineliner	ST_3	Liq	1
Pelikan	Stick	PK	Oil	5
Pentel	BK 77	PE_1	Oil	1
	BK 77 C Superb	PE_2	Oil	5
	Energel	PE_3	Other (Liq-Gel)	1
Unipapel	Unipen	UP	Oil	1
Milan	P1 Touch	M	Oil	1
Faber-Castell	CX 7	FC	Oil	5
Stabilo	Pointvisco	S_1	Other (Liq-Gel)	1
	Cultdocusafe	S_2	Oil	1