Writing instruments inks: microspectrophotometry forensic analysis and characterisation

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Abstract

An important aspect in the analysis of written documents is the type of materials used in questionable documents. The present study aims to characterise and create a database of the absorption spectra in the visible region, obtained by microspectrophotometry (in reflectance mode), of inks from blue and black writing instruments, such as ballpoint pens and liquid ink pens (rollerball pens, gel pens, felt-tip pens and fountain pens). The study was performed with 167 ink samples of 36 different brands commonly used in national and international markets. To validate the possible use of the database a preliminary blind test with 22 samples yielding a consistent and accurate match of 13 samples revealed that this technique has a good potential to obtain a list of inks with the same spectral characteristics. To evaluate the differentiation level of this method the samples were grouped based on the overlap of the 1st derivative spectra. As this grouping systematisation was found to present some limitations when we have a large number of samples, a multivariate analysis of the data was made. For this, a hierarchical cluster analysis (HCA) was performed. The discrimination power was calculated and compared with another works.

Keywords

Document examination, ink analysis, blue and black writing instruments, microspectrophotometry, hierarchical cluster analysis (HCA)

Introduction

The technological development of the past 30 years has put us in a digital era, in which we increasingly resort to electronic means for identification and commercialisation purposes. However, documents continue to play a key role in different segments. They are used in the establishment of various relationships, whether personal, financial, commercial or institutional. In order to serve the most varied interests and conveniences, documents are in constant threat of being susceptible to imitations or changes. The forgery and counterfeiting of documents is associated with different types of crimes, particularly trafficking of drugs, weapons, vehicles and people, money laundering, organised illegal immigration, homicides, kidnapping, paedophilia, international terrorism, corruption, theft, swindling, economic and financial crimes (Hammond, 2013).

Scientific analysis of documents, as part of forensic science, aims to clarify the nature of a document for legal purposes (Ellen, 1997). In the Portuguese Scientific Police Laboratory different types of analysis to all kinds of questionable documents using appropriate methodologies and instrumentation are performed. One of the aspects of the document analysis is to detect evidence of tampering. This kind of alterations, where a different ink of a manual writing instrument, although of the same colour, has been used, is very common and involves overlap and adds features, obliteration and insertion of new entries and signatures for various types of documents such as bank checks, invoices and contracts.

Nowadays one can find more easily manual writing instruments since they are often used in the production/filling of a certain document or used to sign it. Writing instruments are divided into two major (and broad) categories: (1) ballpoint pens and (2) liquid ink pens. In the first category are the inks of the ballpoint pens which are unique in that their inks are viscous — oils or glycols are used as solvents and colourants, which are mostly dyes. In the second category the inks of the rollerball and gel pens, felt pens and fountain pens are included. In this category, inks are liquid or gel using solvents and aqueous solutions in their constitution, and whose colourants may be dyes, pigments or both. The colourants (dyes or pigments) are one of the main components used in the writing ink composition and are responsible for the colour of the writing instruments (Ezcurra et al. 2010; Brunelle et al., 2003; Andrasko, 2002).

Microspectrophotometry in the analysis of questionable documents

Colour is a feature with an important role in forensic comparative studies. A visual description of colour, particularly a comparison between two objects is difficult because the human eye sees only within a narrow range of the electromagnetic radiation (the visible region), and even in this range it is not uniformly sensitive to all wavelengths. Moreover, the lighting and observation conditions can compromise the visual result of the comparison made by the observer (Zięba-Palus, 2006; Martyna et al. 2013).

Microspectrophotometry is a technique that allows the comparison of colour between small samples from different materials, such as fibres, fabrics, paints or plastics (Zięba-Palus, 2006; Pfefferli, 1983).

The microspectrophotometer consists of an optical microscope coupled to a spectrophotometer connected to a computer via an analogue-digital converter (Zięba-Palus, 2006; Martin, 2014). It can be used for analysis in the visible and ultraviolet regions, and spectra in transmittance or reflectance mode can also be obtained (Martin, 2014).

When light interacts with the sample, several (physical) phenomena can occur. These are absorption, transmission and reflection (Figure 1.1) in addition to scattering and (fluorescence or phosphorescence) emission (not shown in Figure 1.1). In the analysis of the writing instrument inks, the diffuse reflection phenomenon is dominant relative to specular reflection; this happens because the ink is a non-homogeneous sample. Therefore, the reflected light is measured with respect to the diffuse reflectance (Seipp, 1997).

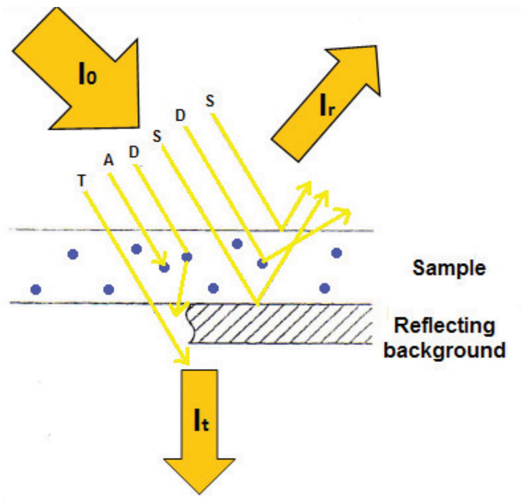


Figure 1.1 — The path of light involved in the interaction process with a sample. The phenomena that are presented are: absorption (A), transmission (T) (which only occurs when working in transmittance mode) and reflection. The reflection may be diffuse (D) or specular (S). I0 is the intensity of incident light, It the intensity of light leaving the substance and Ir intensity of light reflected into a specified direction. (Adapted from Seipp, 1997)

A study carried out at the Home Office Forensic Science Laboratory of UK in 1985 showed that the microspectrophotometry technique in the transmission mode was less discriminatory than the high performance thin layer chromathography (HPTLC) for the porous tip and roller ball pen (Totty, R. et al., 1985). More recently, inks have been studied by HPTLC to complete the International Ink Library chromatogram library, maintained by the United States Secret Service (Neumann C., 2011).

Microspectrophotometry does not reveal the identity of the individual components of an ink and many authors have shown in their investigations that this methodology alone may be inconclusive. The use of this technique is comprehensive in terms of its purpose, and has been used not only to respond to ink differentiation, but has also been used as a tool for classification and dating (Zięba-Palus J. et al., 2012). In 2013, the colour of 40 blue pen inks (36 ballpont and 4 gel) was studied in the three colour systems defined by the International Commission on Illumination (CIE) through the spectra in the visible region obtained by microspectrophotometry (Martyna, A. et al., 2013). More recently, this technique was also used in the study of the sequence of intersecting lines (Biao Li, 2016), showing positive results.

Reflectance microspectrophotometry showed less discriminatory power when compared to Thin Layer Chromatography (TLC) and filtered light examination (visible luminescence, infrared luminescence and infrared reflectance) (Roux, C. et al., 1999). UV-VIS spectrophotometry was also compared with TLC and Fourier Transform Infrared Spectrometry in the analysis of 21 black and 12 blue ballpoint inks, being verified the complementarity of the FTIR by detecting resins and solvents in addition to the colouring agents (Causin, V. et al.). In most of the studies performed with this technique no chemometric methods were used for sample differentiation.

Aim of the study

This study aims to characterise and to analyse writing instrument inks in order to create a database of the absorption spectra in the visible region with a non-destructive reflectance mode microspectrophotometry technique. In the present work, the objects of study are the inks from blue and black writing instruments, such as ballpoint pens and liquid ink pens (rollerball pens, gel pens, felt-tip pens and fountain pens). To facilitate these comparisons and evaluate the discrimination level of the technique, the data obtained from the writing instrument inks will be grouped according to the first derivative of the observed peaks in the visible region and with a hierarchical cluster analysis method (HCA).

Materials and Instrumentation

Sample characterisation and the ink database

80 blue inks [56 ballpoint pens (BBn), 17 rollerball and gel pens (LBn), 5 felt pens (FBn) and 2 fountain pens (FOBn)] and 87 black inks [55 ballpoint pens (BKn), 17 rollerball and gel pens (LKn), 5 felt-tip pens (FKn) and 10 fountain pens (FOKn)] were analysed. They came either from national (Portuguese) or international markets from 36 different brands (and some models) such as BIC, Pentel, Uni Mitsubishi Pencil, Paper Mate, Corvina, Reynolds, Molin, ACVILA, Lecce Pen, RTC, Office Cover, Pelikan, LINC, STABILO, A.G. SPALDING BROS, WATERMAN, mab, PLUS B-2, Unix, Epene, Fegol, Q-CONNECT, PARKER, MONTE LEMA, AURORA, Rotring, Fisher Space Pen, PILOT, STAEDTLER ZEBRA, Ergo marker, HERO, LAMY, CROSS, MONT BLANC and 'white label' — see tables 2.1 to 2.4.

Table 2.1
Samples of blue (BB) and black (BK) ballpoint pen ink

Code	Brand	Model/name
BB1	BIC	E-O-30
BB2	BIC	U-E-08
BB3	BIC	P-F-26
BB4	BIC	N-H-9
BB5	BIC	T-G-4
BB6	BIC	T-G-10
BB7	BIC	A-H-10
BB8	BIC	Cristal GRIP (Q-H-19)
BB9	BIC	ATLANTIS
BB21	Pentel	SUPERB (BK77)
BB22	Pentel	STAR V (BK66)
BB31	White label	Estetica Dental Lopez (Espanha)
BB32	White label	i RISO
BB33	White label	www.FCT.unl.pt
BB34	White label	Caixa Geral de Depósitos
BB35	White label	Caixa Geral de Depósitos-Banco da EXPO 98 Lisboa
BB36	White label	Caixa Geral de Depósitos-Banco da EXPO 98 Lisboa
BB37	White label	Caixa Geral de Depósitos-Banco da EXPO 98 Lisboa
BB38	White label	Caixa Geral de Depósitos-Banco da EXPO 98 Lisboa
BB39	White label	Caixa Geral de Depósitos-Banco da EXPO 98 Lisboa
BB40	White label	Grupo Banco Espirito Santo (BES)
BB41	White label	Note it
BB42	White label	Note it
BB43	White label	Note it
BB44	White label	Sagres-Companhia de Seguros. s.a.
BB45	White label	Estúdio Fotográfico, Lda
BB46	White label	STAPLES (traço de 0.7 mm)
BB47	White label	Note it
BB48	White label	USO
BB49	White label	IBEROSTAR,Hotels e Resorts (Tunisia)
BB50	White label	C A1
BB51	White label	STAPLES — REVU
BB52	White label	Santander Totta
BB53	White label	STAPLES-COMFORT STIC. 1.0
BB54	White label	KEESING Technologies

Code	Brand	Model/name
BB55	White label	LaborSpirit,Lda
BB56	White label	TECHNO SPEC
BB57	White label	---
BB81	Uni Mitsubishi Pencil	Lakubo (uni SG-100 (07) blue)
BB91	Paper Mate	Ink Joy 100 1.0M (Ponta:1.0 mm)
BB101	Corvina	WH-T (Ponta:1.0 mm)
BB102	Corvina	51 (Ponta:1.0 mm)
BB106	Reynolds	Medium 048
BB116	molin	twisty
BB121	ACVILA	FINE 309
BB126	Lecce Pen	---
BB127	Lecce Pen	---
BB128	Lecce Pen	---
BB131	RTC	---
BB132	RTC	---
BB136	Office Cover	ASTRO (Ponta: 1.0 mm)
BB141	Pelikan	---
BB151	LINC	Glycer fine
BB156	STABILO	galaxy 818 M
BB161	A.G. SPALDING BROS.	---
BB166	WATERMAN	STANDARD MAX. (MOYENNE/MEDIUM)
BK1	BIC	Z-E-17
BK2	BIC	E-O-32
BK3	BIC	H-E-5
BK4	BIC	I-H-30
BK5	BIC	I-H-6
BK6	BIC	SOFT Feel Med. USA
BK7	BIC	Cristal GRIP (Q-H-11)
BK8	BIC	ATLANTIS 1.2
BK9	BIC	Cristal STYLUS (T-L-03 Tunisia)
BK21	Pentel	SUPERB (BK77)
BK22	Pentel	STAR V
BK23	Pentel	SUPERB (BK77)
BK31	White label	STAPLES (Traço de 0.7 mm)
BK32	White label	Note it
BK33	White label	Note it
BK34	White label	USO
BK35	White label	Grupo Banco Espirito Santo (BES)

Code	Brand	Model/name
BK36	White label	IP ST-Instituto Português do Sangue e da Transplantação,IP
BK37	White label	---
BK38	White label	---
BK39	White label	CS — www.cs-hoteis.com
BK40	White label	Sapo.pt
BK41	White label	Note it (esferográfica cristal preta)
BK42	White label	CA Crédito Agrícola
BK43	White label	Novo Banco (Antigo Banco Espirito Santo — BES)
BK44	White label	BPI (Banco Português de Investimento)
BK45	White label	STAPLES — COMFORT STIC. 1.0
BK46	White label	STAPLES — COMFORT STIC. 1.0
BK47	White label	Nao tem
BK71	Pelikan	STICK
BK72	Pelikan	---
BK73	Pelikan	STICK
BK81	Paper Mate	Comfort Mate MED.
BK82	Paper Mate	Ink Joy 100 1.0M (Ponta: 1,0mm)
BK83	Paper Mate	Replay U.S.A
BK91	mab	---
BK92	mab	---
BK101	PLUS B-2	traço 0.7 mm
BK106	Office Cover	ASTRO (Ponta: 1.0 mm)
BK111	RTC	---
BK112	RTC	---
BK116	Unix	Unix 2001-TC POINT 0.7 — Italy
BK121	Epene	ball point pen EP01-0108
BK122	Epene	ball point pen EP01-0108
BK126	Fegol	Cristal Line 1
BK131	Q-CONNECT	Ponta 0.7 mm
BK136	Uni Mitsubishi Pencil	Lakubo (uni SG-100(07) black)
BK137	Uni Mitsubishi Pencil	Lakubo fine (uni Mitsubishi SA-G JAPAN 45)
BK146	PARKER	Ball Pen Refill (Fine)
BK151	WATERMAN	STANDARD MAX. (MOYENNE/MEDIUM)
BK156	A.G. SPALDING BROS.	---
BK161	MONTE LEMA	Ink Dokumental
BK166	AURORA	tungsten long-life refill
BK171	Rotring	---
BK176	Fisher Space Pen	Black Med. Refill Send

Table 2.2
Samples of blue (LB) and black (LK) rollerball and gel ink

Code	Brand	Model	Code	Brand	Model
LB1	BIC	Cristal Gel + Medium	**LK1**	BIC	Cristal Gel + Medium
LB11	Pentel	K108 Hybrid roller (K108-MC)	**LK11**	Pentel	K106 Hybrid roller
LB21	White label	Note it 0.7 (gel ink)	**LK21**	white label	Note it 0.7 (gel ink)
LB22	White label	Note it (gel ink)	**LK22**	white label	Note it (gel ink)
LB23	White label	30457	**LK23**	white label	30457
LB24	White label	30457	**LK24**	white label	30457
LB25	White label	30457	**LK25**	white label	UNITED OFFICE Roller-ball 0.7
LB26	White label	30457	**LK41**	STAEDTLER	Gel Roller 465 Fine Point 0,25
LB27	White label	UNITED OFFICE Rollerball 0.7	**LK51**	ZEBRA	J-ROLLER MEDIUM 0,7 (JAPAN E222)
LB41	Paper Mate	Gel - Roller XF (0,5mm) D8	**LK61**	PILOT	PILOT V BALL 05
LB51	PILOT	PILOT V BALL 05	**LK71**	Uni Mitsubishi Pencil	uni-ball fine DELUXE (UB-177)
LB61	Uni Mitsubishi Pencil	uni-ball fine DELUXE (UB-177)	**LK72**	Uni Mitsubishi Pencil	uni-ball Signo (UM-100 JAPAN 89)
LB62	Uni Mitsubishi Pencil	uni-ball Signo (UM-100 JAPAN 136 (UM-100 .64))	**LK73**	Uni Mitsubishi Pencil	uni-ball eYe fine (UB-157 BLACK)
LB63	Uni Mitsubishi Pencil	uni-ball Signo (UMN-207F BLUE)	**LK74**	Uni Mitsubishi Pencil	uni-ball Signo (UMN-207F BLACK)
LB64	Uni Mitsubishi Pencil	uni-ball eYe micro (UB-150 BLUE)	**LK75**	Uni Mitsubishi Pencil	uni-ball eYe micro (UB-150 BLACK)
LB65	Uni Mitsubishi Pencil	uni-ball Signo (UM-120 (0.5) BLUE JAPAN G29)	**LK76**	Uni Mitsubishi Pencil	uni-ball Signo (UM-120 (0.5) BLACK JAPAN G32)
LB71	PARKER	Roller ball Refill 0,8 mm Blue Medium	**LK81**	PARKER	Roller ball Refill 0,8mm Black Medium

Table 2.3
Samples of blue (FB) and black (FK) felt pen ink

Code	Brand	Model	Code	Brand	Model
FB1	Bic	metal point	**FK1**	Paper Mate	Flair Original M
FB6	Paper Mate	2000 ROLLER	**FK6**	White label	Grupo Banco Espirito Santo (BES)
FB7	Paper Mate	Flair Original M	**FK7**	White label	note it
FB11	ergo marker	CD/DVD FINE LINER 4001 0.7 mm	**FK8**	White label	fiber liner 1 mm (LUS I HF — LINE)
FB16	White label	Note it (nylon writing markers)	**FK11**	Rotring	Tikky Graphic 0.5 (pigmented ink)

Table 2.4
Samples of blue (FOB) and black (FOK) fountain pen ink

Code	Brand	Model	Code	Brand	Model
FOB1	HERO	202 (60 mL)	**FOK1**	HERO	Black ink 204 (Glass Bottle 60 mL)
FOB5	Pelikan	LEVEL (tinta:329441)	**FOK5**	LAMY	Black ink (50mL)
			FOK6	LAMY	Rotring (Levenger)
			FOK9	PARKER	Quink (SOLV-X)
			FOK13	WATERMAN	Black ink (50mL)
			FOK17	CROSS	Black ink (62,5mL)
			FOK21	AURORA	Aurora 88
			FOK25	MONT BLANC	ink with super-cleaner SC21
			FOK29	Pelikan	LEVEL (ink:329524)
			FOK30	Pelikan	Bright black permanent (4001)

The experimental procedure consisted in drawing lines on a white printing paper (80 g/m^2, A4, Inacopia office®), which was then fixed to a microscope base slide, and placed on the stage of the microscope with the microspectrophotometer instrument (Figure 2.1). For acquisition of the absorption spectra a TIDAS MSP-800 microspectrophotometer, consisting of a microscope (Zeiss®, Axiotech 100) coupled to a spectrophotometer (J&M Tidas®), was used.

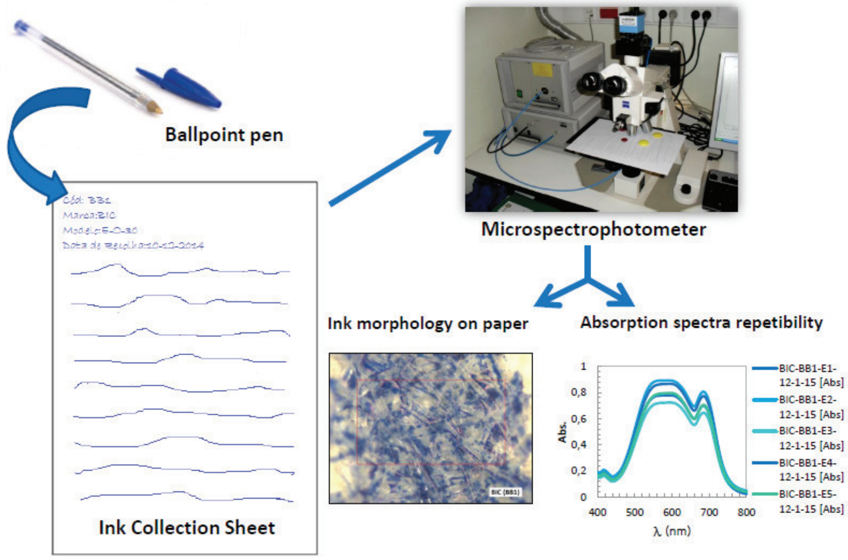


Figure 2.1 — Scheme for the study of ink characteristics: physical (ink morphology) and spectral (spectra obtained in five analysis in different areas).

The blue and black inks were analysed in the visible region between 400 and 800 nm in the reflectance mode. In this work, the spectra were obtained in the reflectance mode. This mode of obtaining the spectra, besides being non-destructive, allows to have a sample with no previous treatment for analysis (in contrast for example with the spectra in transmittance mode) (Zięba-Palus, 2006; Martyna et al., 2013; Pfefferli, 1983). For each ink, five measurements were obtained in five different lines and areas of the collected traces of ink, using a diaphragm to select each area, under the following conditions: for the microscope [Diaphragm dimensions (220.0 × 127.0 µm), image resolution (640 × 80), objective with 20× magnification and light intensity of the microscope 10 (maximum)] and for the spectrophotometer [Interpolation (YES), Step (1 nm), Representation (Absorbance AU), Scan type (Single Scan), Accumulations (3), Bunching (1 Pixel)]. As reference, a white area (i.e. with no ink) of the same sheet, where the ink was collected, was used.

Formation of groups for hierarchical cluster analysis (HCA)

The hierarchical cluster analysis interconnects objects by their associations, giving rise to a dendrogram (bidimensional representation) wherein like objects, according to the chosen variables, are grouped together. The smaller the distance between objects, the greater the similarity between them. (Kaufman et al., 1990; Wu et al., 2007; Mendlein et al., 2013). To group the analysed samples the Euclidean distance (to calculate the distance between each pair of objects), and the Ward method (of connection as binding criteria for the formation of groups) were used. A program written in R (version 3.0.1) was used to make the clustering of the samples, and consequently produce the dendrogram.

The HCA analysis which was based on the five parameters [(i) number of visible bands and (ii) associated wavelength, (iii) absorption value at the wavelengths in (ii) and (iv) the values of the 1st derivative for the wavelength maxima and (v) the presence/absence of fluorescence in the investigated samples] lead to the association in 3-5 different groups (subdivided in other subcategories). With regard to the fluorescence (an additional parameter for the construction of dendrograms), the samples were excited in the visible region between 485 and 610 nm and the presence or absence of luminescence was observed with the naked eye through a spectral video comparator (foster + freeman®, VSC5000).

Results and discussion

Characterisation of the writing ink instruments

All inks in study were collected on paper and attached to a characterisation sheet containing: (i) a photograph of the manual writing instrument (pen) from which the ink was taken; (ii) an image of the morphology of the deposited ink on the paper sheet corresponding to one of the areas selected for analysis, magnified 200×; and (iii) the absorption spectra consisting of five measurements performed for each sample, was obtained. To illustrate this, an example for ballpoint pens and liquid ink pens (rollerball and gel pens) is given in Figure 3.1.

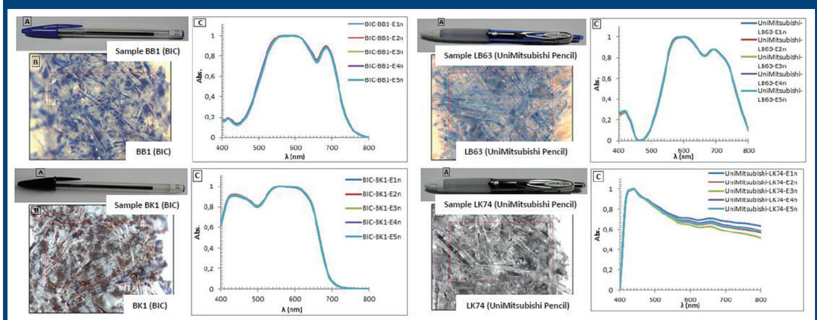


Figure 3.1 — Physical (ink morphology) and spectral characteristics of the BB1 (upper, left), BK1 (bottom, left), LB63 (upper, right) and LK74 (bottom, right) samples in which A corresponds to writing instruments, B corresponds to the image of the morphology of the paint, and C corresponds to the absorption spectra of the five measures conducted for the BB1, BK1, LB63 and LK74 samples, respectively.

Database

The collection of the 167 inks led to the creation of an absorption spectra database. The different types of collected ink allowed the construction of libraries according to the physical (ink morphology) and spectral characteristics of each ink. The average spectrum, obtained from five spectra for each of those inks, was added to the appropriate library. This procedure leads to the creation of eight libraries, including: *Ballpoint pen blue ink* — code BBn, *Ballpoint pen black ink* — code BKn, *Liquid (rollerball/*gel) *pen blue ink* — code LBn, *Liquid (rollerball/*gel) pen black *ink* — code LKn, *Felt-tipped pen blue ink* — code FBn, *Felt-tipped pen black ink* — code FKn, *Fountain pen blue ink* — code FOBn and F*ountain pen black ink* — code FOKn.

To further validate the generated database libraries, i.e. if they are functional, a preliminary test with 22 blind samples (knowing that 14 were already entered in the database and the remaining eight were not) taken on white printing paper (80 g/m^2, A4, Inacopia office®) was made. This set of samples is composed of writing instruments inks of blue (9) and black (13) colour. In order to have the preliminary test as close as possible to a practical case, it was initially assumed that all samples were unknown (considered blind samples). With the aid of optical microscopy (e.g. magnifying lens), a pre-selection of the type of ink present on each sample was made, thus facilitating the choice of the most appropriate library. Out of the 22 samples, 13 have been correctly identified. The remaining nine were totally unknown and have been added to the generated libraries after analyses. Table 3.1 summarises the results for the 22 blind samples.

For the matching process the following parameters were used: Minimum Quality (80); Comparing Algorithm (Squared Difference) and Normalise Each Search Range. Below are two examples to demonstrate the results obtained for the blind samples using the matching process of the *paronama 3* software program.

Figure 3.2 — Results for correspondence of BS2 sample with the data entered in the library.

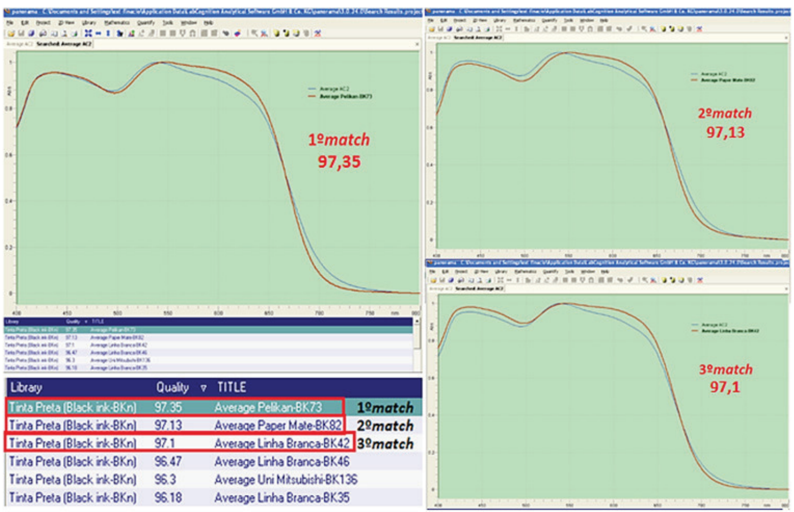


Table 3.1
Obtained result for the match of 22 blind samples (marked with blue and grey colours are blind samples of blue and black colours, respectively)

Blind Sample	1st match		Writing instrument used as Blind Sample	Blind sample identification
BS1	94,54	Paper Mate (FB7)	Paper Mate Ink Joy 100 (BBn)	✗
BS2	97,35	Pelikan (BK73)	Pelikan (BKn)	✓
BS3	99,44	Pentel (BB21)	Pentel (BB21)	✓
BS4	98,73	LINC (BB151)	LINC GLYCER (BB151)	✓
BS5	98,29	Uni Mitsubishi (BB81)	Uni Lakubo-Mitsubishi (BB81)	✓
BS6	98,25	mab (BK92)	mab (BK92)	✓
BS7	99,01	BIC (BK5)	BIC (BK1)	✗
BS8	99,09	Pentel (BK22)	Pentel (BK22)	✓
BS9	98,08	"White label" (BK39)	"White label" (BKn)	✓
BS10	99,16	Office Cover (BB136)	Office Cover-Astro (BB136)	✓
BS11	98,44	Paper Mate (FB7)	Paper Mate flair M (FB7)	✓
BS12	98,79	ergo marker (FB11)	Ergo Marker (FB11)	✓
BS13	99,47	Paper Mate (FK1)	Paper Mate flair M (FK1)	✓
BS14	98,1	Uni Mitsubishi (LK73)	Zebra J-Roller (LK51)	✗
BS15	97,95	"White label" (LK21)	Uni Mitsubishi (LK73)	✗
BS16	92,3	"White label" (LB25)	"White label" (LB25)	✓
BS17	97,8	Uni Mitsubishi (LB61)	Uni Mitsubishi (LB61)	✓
BS18	82,81	PARKER (LK81)	Refill AURORA (BKn)	✗
BS19	84,94	PARKER (BK146)	Paper Mate Replay USA (BKn)	✗
BS20	95,01	PARKER (LK81)	Permanent ink LAMY (FOKn)	✗
BS21	95,22	PARKER (FOK9)	Rotring (BKn)	✗
BS22	91,77	"White label" (BK41)	Fisher Space Pen (BKn)	✗

For instance, Blind Sample 2 (BS2) shows a 1st match value of 97.35 (out in 100) with the black ballpoint pen brand Pelikan (BK73). This ink was correctly identified. The 2nd and 3rd match have little spectra differences and shows a good match result, close to the first match (Figure 3.2). Noteworthy is the fact that 1st, 2nd and 3rd matches show little spectral differences between them. The spectrum in red represents the data that is entered in the library while the blue spectrum is the sample under analysis.

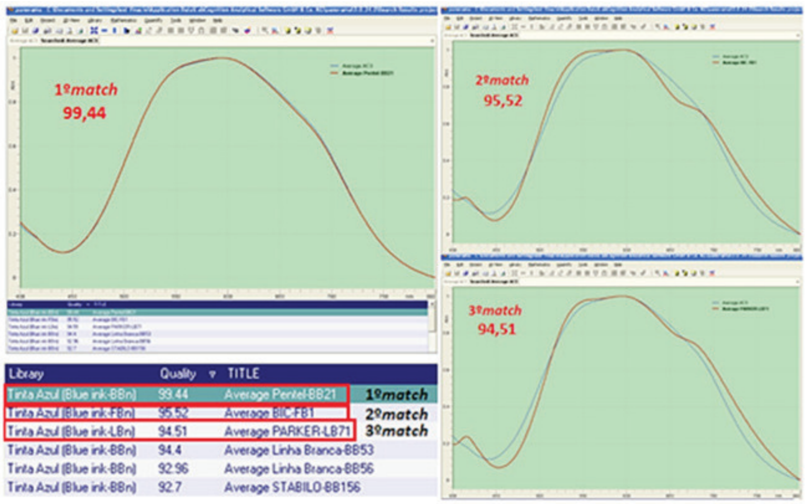


Figure 3.3 — Results for the correspondence of BS3 sample with the data added into the library

With the results of Blind Sample 3 (BS3) we observe that the value of the 1st match was 99.44 for a blue ballpoint pen Pentel brand (BB21). This sample was correctly identified too but in this case, the second and third match spectra exhibit accentuated differences which resulted in values of match significantly lower than the first one (Figure 3.3). Noteworthy is the fact that 1st, 2nd and 3rd matches show significant spectral differences between them. The spectrum in red represents the data that is entered in the library while the blue spectrum is the sample under analysis.

Blind Sample 7 (BS7) was correctly identified only on the 3rd match (BIC-BK1). This result can be explained by the high similarities in the formulation of constituent inks of samples BK151 (Waterman brand) and BK5 (BIC brand).

With the 22 blind samples, it was possible to obtain a correct functional match for 13 of the samples: 8 blue and 5 black.

Due to the large number of samples analysed and knowing that some of these exhibit similar spectral characteristics from each other, there was a need for clustering, to ease its characterisation and consequently its identification. In order to achieve this, two types of procedures were considered. One procedure can be considered more indicative (with a high degree of subjectivity) and the other more analytic (which can be considered more objective).

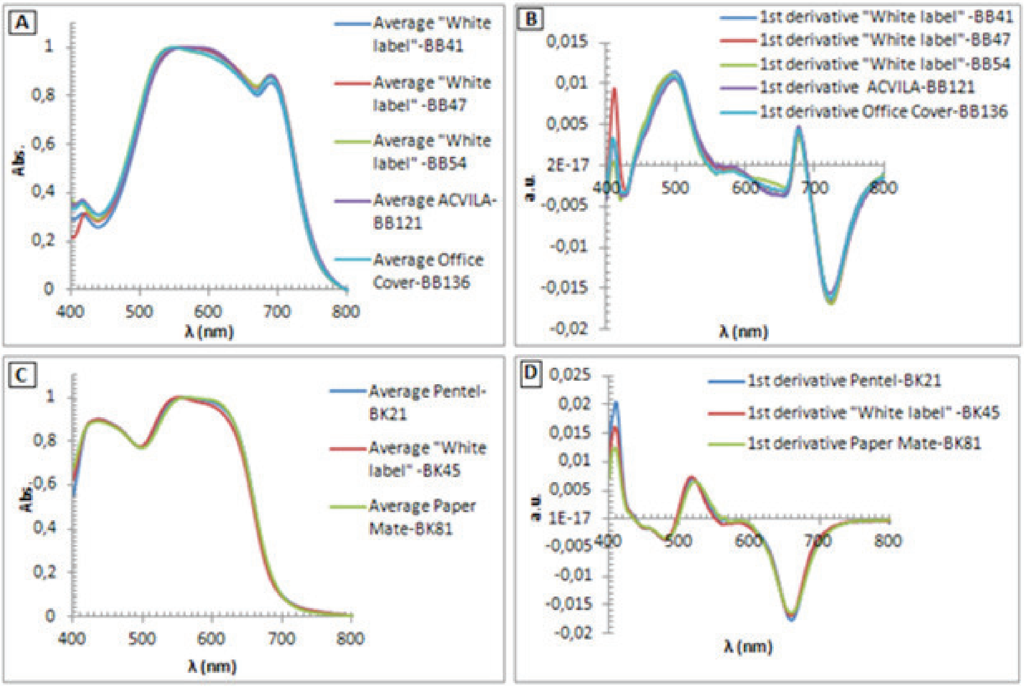
The first was based on the observation of the spectra comparison and is based upon the 1st derivative, i.e. these values are used to group samples. The 1st derivative allows us to observe the maximum and the minimum of the spectra and thus to facilitate the grouping.

This process is considered to have a high dose of subjectivity because it strongly depends on the observer and its degree of subjectivity. The second process should be considered more objective because it uses a multivariate analysis: hierarchical cluster analysis (HCA). This method allows testing how a set of elements relates to each other, and how they are similar according to the variables used.

Data clustering using 1st derivative

To group the samples analysed, the 1st derivative was calculated from the plots resulting from the average five measurements made for each sample. Comparisons between graphics overlays and the 1st derivative were obtained in order to form groups of the samples analysed. In Figure 3.4 an example of two groups is given: a blue (BBn) and black (BKn) ballpoint pens.

Figure 3.4 — *From left to right*. Absorption spectra corresponding to the average of five measurements performed with each of the samples BB41, BB47, BB54, BB121 and BB136 (A) and respective graphics of the 1st derivative (B). Absorption spectra corresponding to the average of five measures performed to samples BB41, BB47, BB54, BB121 and BB136 (C) and respective graphics of the 1st derivative (D).



In general, certain groups could be created using the graphic overlay of the 1st derivative of the samples. In Table 3.2 the number of generated groups and respective number of samples per group is summarised.

The association into these types of groups (solely based on the overlapping of the graphs of the 1st derivative) reveals that microspectrophotometry may be considered an excellent non-destructive technique for ink differentiation. The problem is that when there are a large number of samples to analyse, this grouping becomes insufficient, making this type of analysis impractical, since this is done manually. Therefore, it is necessary to use another type of analysis in order to be able to associate all the samples analysed in groups. To do this, we have used the hierarchical cluster analysis (HCA).

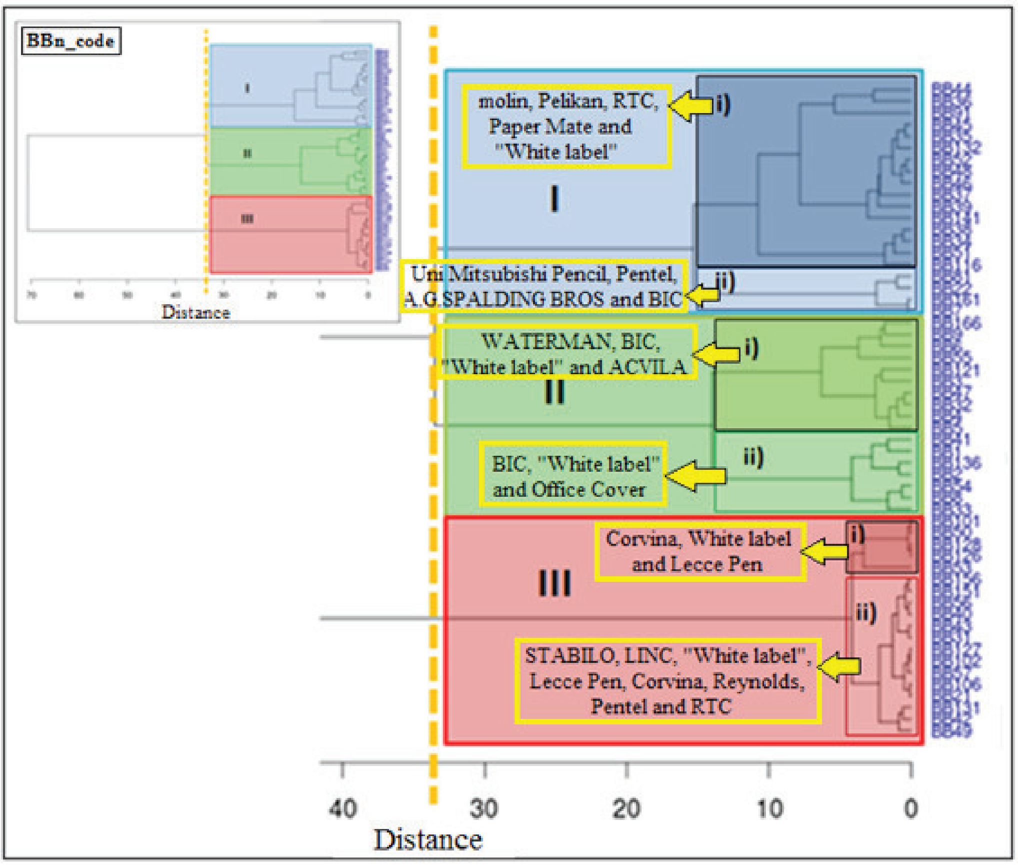
Table 3.2
Number of groups formed using the superposition of the graphics 1st derivative, taking into account the number of available samples for each type of ink

Writing instruments		Groups	Samples	Number of samples per group (G1 to G26)
Ballpoint pens	Blue ink	26	56	2, 3, 1, 3, 1, 3, 1, 3, 2, 2, 4, 2, 5, 2, 2, 1, 1, 3, 2, 5, 2, 1, 2, 1, 1,1
	Black ink	26	55	13, 2, 2, 3, 3, 1, 3, 3, 2, 2, 2, 1, 2, 1, 1, 1, 1, 2, 1, 2, 2, 1, 1, 1, 1,1
Liquid ink pens	Rollerball and gel blue ink	12	17	5, 1, 1, 1, 2, 1, 1, 1, 1, 1, 1, 1
	Rollerball and gel black ink	5	17	13, 1, 1, 1, 1
	Felt blue ink	5	5	1, 1, 1, 1, 1
	Felt black ink	4	5	1, 2, 1, 1
	Fountain blue ink	2	2	1, 1
	Fountain black ink	7	10	2, 3, 1, 1, 1, 1,1

Data clustering using hierarchical cluster analysis (HCA)

The formation of groups using hierarchical cluster analysis (HCA) was already explained. For each set of data (BBn, BKn, LBn, LKn, FBn, FKn, FOKn) there is a dendrogram in which each object is represented by the sample code. As an example, for the blue ballpoint pens, the following brands were grouped in the following three groups (Figure 3.5).

Figure 3.5 — Dendrogram constructed by hierarchical clustering (Ward binding method) on the data set of 56 samples ballpoint pen ink of blue colour (BBn) ([1]). Different colours are used to represent the groups formed according to their similarities. Each formed group is represented by two sub-groups (i) and (ii).



According to the dendrogram shown in Figure 3.5, for the ballpoint pens of blue (BBn) there are three major groups: Group I (blue): Molin, Pelikan, RTC, Paper Mate, 'White label', Uni Mitsubishi Pencil, Pentel, A.G.SPALDING BROS and BIC. Group II (green): WATERMAN, BIC, 'White label', ACVILA; BIC and Office Cover. Group III (red): Corvina, 'White label', Lecce Pen, STABILO, LINC, Reynolds, Pentel and RTC.

For black ballpoint pens there are also three major groups: Group I (PARKER, RTC, BROS AG-SPALDING, Pentel, Mitsubishi Pencil Uni, Paper Mate, 'White label' BIC Epene, and Pelikan); Group II (Fisher Space Pen, PLUS B-2, Pelikan, BIC, Epene, Paper Mate, 'White label' Rotring, Office Cover, WATERMAN, Pentel, Fegol); Group III (MONTE LEMA, Pelikan, AURORA, Unix, mab, 'White label' Uni Mitsubishi Pencil, BIC, Q-CONNECT).

([1]) There are cases in which the same brand appears in different groups (examples: RTC, Pentel, Bic, 'White label'); this is because the analyses were made with different models for each brand.

Blue rollerball and gel pens have five major groups: Group I ('White label', BIC, Paper Mate and Uni Mitsubishi Pencil); Group II ('White label'); Group III (PARKER, PILOT and 'White label'); Group IV ('White label'); Group V (Pentel). For black rollerball and gel pens have four major groups: Group I (PARKER); Group II (Uni Mitsubishi Pencil); Group III ('White label', BIC, Uni Mitsubishi Pencil, Pentel); Group IV ('White label', Uni Mitsubishi Pencil, PILOT, ZEBRA, STAEDTLER).

Blue felt-tip pens have two major groups: Group I ('White label', ergo marker, Paper Mate); Group II (Paper Mate, BIC). For black felt-tip pens exists two major groups: Group I ('White label', Rotring); Group II ('White label', Paper Mate).

Black colours fountain pens have four major groups: Group I (Pelikan, LAMY, MONT BLANC); Group II (HERO); Group III (AURORA, CROSS, WATERMAN, PARKER); Group IV (Pelikan). The two blue Fountain pen (Hero and Pelikan brand) were not submitted to HCA analysis.

In Table 3.3 the number of generated groups/subgroups, and respective number of samples per group/subgroup is summarised.

Table 3.3
Number of groups formed using hierarchical cluster analysis (HCA), taking into account the number of available samples for each type of ink

Writing instruments		Groups	Samples	Number of samples per subgroup (Sb)
Ballpoint pens	Blue ink	3	56	G1:SbI:16 + SbII:4 G2:SbI:7 + SbII:10 G3:SbI:5 + SbII:14
	Black ink	3	55	G1:SbI:7 + SbII:13 G2:SbI:7 + SbII:17 G3:SbI:4 + SbII:7
Liquid ink pens	Rollerball and gel blue ink	5	17	G1:SbI:3 + SbII:6 G2:SbI:2 G3:SbI:2 + SbII:1 G4:SbI:2 G5:SbI:1
	Rollerball and gel black ink	4	17	G1:SbI:1 G2:SbI:1 G3:SbI:4 + SbII:5 G4:SbI:5 + SbII:1
	Felt blue ink	2	5	G1:SbI:2 + SbII:1 G2:SbI:2
	Felt black ink	2	5	G1:SbI:2 G2:SbI:2 + SbII:1
	Fountain black ink	4	10	G1:SbI:3 + SbII:1 G2:SbI:1 G3:SbI:4 G4:SbI:1

The HCA data analysis suggests that for the blue ballpoint pens, black rollerball and gel pens, black and blue felt tip pens and fountain pens, there is no brand with more than one model found in the same group. In the black ballpoint pens, the mab brand appears in the same group and sub-group, and the same happens with the blue rollerball and gel pens from the Uni Mitsubishi Pencil brand.

Discriminating power

The analysed ink samples were grouped in two different ways by visual comparison through the superimposition of the absorption spectra and their respective first derivatives and by the application of a hierarchical cluster analysis (HCA) statistical method. In order to evaluate the discriminating power of microspectrophotometry, several authors used discriminating power (DP) according to the work developed by Smalldon and Moffat (Smalldon et al., 1973).

The discriminating power (DP) is defined as the 'probability that two distinct samples selected at random from the parent population would be discriminated in at least one attribute if the series of attributes were determined' and is calculated using the formula DP = 1 – [(Number of discriminated pairs)/(Number of possible sample pairs)] (Smalldon et al., 1973). The number of possible pairs is calculated using the formula [n (n-1)]/2, where n is the total number of samples. For example, in the qualitative analysis of blue ballpoint inks we have [56 (56-1)]/2 = 1 540 possible pairs of compared samples. For this class of inks the qualitative analysis of the results obtained with this technique has a power of discrimination of 72 %. Table 3.4 shows the DP values obtained for the classes of inks studied.

Table 3.4
Discriminating powers (DP) of qualitative analysis

Writing instruments		DP (qualitative analysis)
Ballpoint pens	Blue ink	0.72
	Black ink	0.73
Liquid ink pens	Rollerball and gel blue ink	0.93
	Rollerball and gel black ink	0.51
	Felt blue ink	1
	Felt black ink	1
	Fountain blue ink	1
	Fountain black ink	0.93

Considering the high number of inks under study, the values obtained for DP are high and demonstrate once again the good differentiation ability of microspectrophotometry in reflectance mode, thus allowing a non-destructive analysis of the documents being studied.

Totty et al., 1985, obtained a DP of 0.86 for black inks and 0.84 for a total of 16 blue inks. These inks were taken from porous tip pens and spectras were obtained in transmission mode in the visible region. Roux, et al., 1999, obtained DP of 0.83 to both 49 blue and 42 black ballpoint pen inks with the Olympus microspectrophotometer in reflection mode. More recently, Causin, V. et al., 2008, obtained a DP value of 0.96 for the 21 black ballpoint pen inks and 0.79 for the 12 blue ones. In this study, the spectra were obtained in the transmission mode in the UV-VIS region. The microspectrophotometry system used in our study and the differentiation of spectra in a visual form allows the obtaining of a good DP, however the different modes of acquisition and different types of pens used in the previous studies do not allow a linear comparison for all class of inks. The final result of the differentiation using this statistical method should always be obtained based on the last subgroups (and not the first ones); however this result should always be validated by the forensic expert.

Conclusions

The identification and dating of writing inks remain a major challenge in the forensic examination of questionable documents. Given the need to increasingly provide relevant information to our justice system, we explore and develop techniques and methodologies to generate forensic intelligence. Microspectrophotometry is undoubtedly a very effective technique to differentiate inks. This study demonstrated a wide applicability in terms of ink writing instruments and its high discrimination power for the different type of inks in analysis.

The 167 analysed ink samples were grouped into 87 distinct groups by overlapping the spectra of the 1st derivative and 37 groups using a hierarchical clustering analysis (HCA). Despite the HCA analysis showing a smaller number of groups, this type of chemometric method provides us with a sophisticated and efficient approach to differentiate ink samples essential when we have a large number of samples to compare.

The creation of the database constitutes a way to provide a list of inks with the same spectral characteristics as the analysed sample, however these groups show that different ink brands have similar spectral characteristics. This is an ongoing work, whose subsequent steps will (i) increase the number of samples analysed, (ii) analyse through HPLC and HPTLC all the inks to establish a more powerful database, (iii) add other variables to HCA method, (iv) another chemometric algorithms.

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