STATISTICAL DISCRIMINATION OF BLUE BALLPOINT PEN INKS BY DIAMOND ATTENUATED TOTAL REFLECTANCE (ATR) FTIR

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INTRODUCTION

Determining the source of pen inks used on a variety of documents is impartial for forensic document examiners. The examination of inks is often performed to differentiate between inks in order to evaluate the authenticity of a document. A ballpoint pen ink consists of synthetic dyes in (acidic and/or basic), pigments (organic and/or inorganic) and a range of additives (Denman *et al*., 2010). Inks of similar color may consist of different composition and are frequently the subjects of forensic examinations. This study emphasizes on blue ballpoint pen inks available in market because it is reported that approximately 80% of questioned documents analysis involving ballpoint pen ink (Andrasko, 2001). Analytical techniques such as thin layer chromatography, high performance liquid chromatography, UV-vis spectroscopy, luminescence spectroscopy and infrared spectroscopy have been used in the analysis of ink samples (Kher *et al*., 2006).

In this study, application of Diamond Attenuated Total Reflectance (ATR) FTIR is straightforward but preferable in forensic science as it offers no sample preparation and minimal analysis time. The data obtained from these techniques were further analysed using multivariate chemometric methods which enable extraction of more information based on the similarities and differences among samples in a dataset (Panero and da Silva, 2008). It was indicated that some pens from the same manufactures can be similar in composition, however discrete types, can be significantly different.

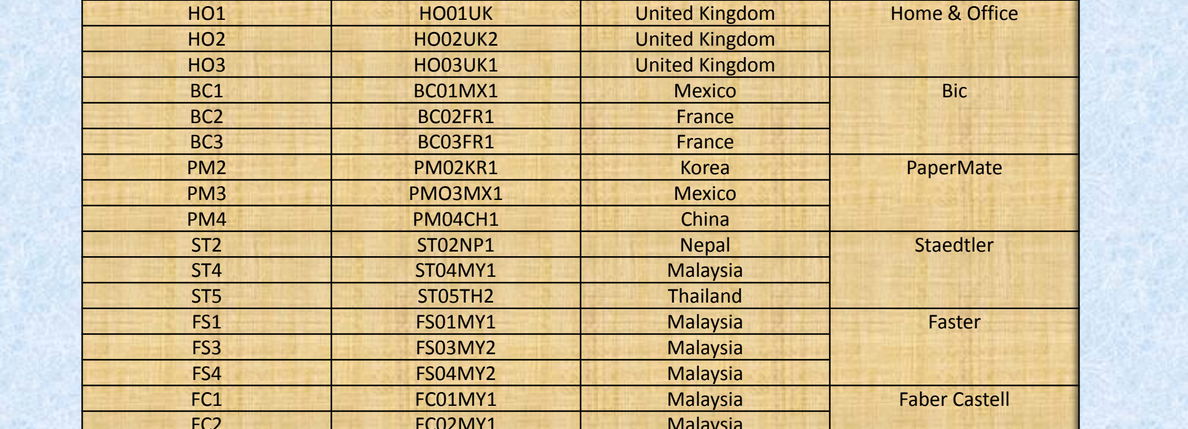
EXPERIMENTAL

21 blue ballpoint pens were evaluated. These included three pens from each brand purchased in different countries. All samples are presented in in Table 1

Table 1. Types of pens from seven different manufacturers

Sample		Country	Brand
Simplify Name	Labelled Name		
HO1	HO01UK	United Kingdom	Home & Office
HO2	HO02UK2	United Kingdom	
HO3	HO03UK1	United Kingdom	
BC1	BC01MX1	Mexico	Bic
BC2	BC02FR1	France	
BC3	BC03FR1	France	
PM2	PM02KR1	Korea	PaperMate
PM3	PMO3MX1	Mexico	
PM4	PM04CH1	China	
ST2	ST02NP1	Nepal	Staedtler
ST4	ST04MY1	Malaysia	
ST5	ST05TH2	Thailand	
FS1	FS01MY1	Malaysia	Faster
FS3	FS03MY2	Malaysia	
FS4	FS04MY2	Malaysia	
FC1	FC01MY1	Malaysia	Faber Castell
FC2	FC02MY1	Malaysia	
FC3	FC03MY1	Malaysia	
GS1	GS01MY1	Malaysia	G-Soft
GS3	GS03MY2	Malaysia	
GS2	GS02MY2	Malaysia	

The tip of ink barrel of each pen was removed carefully using plier. Small amount of inks were then spotted directly onto the diamond ATR accessory. The ideal absorption of IR was achieved by placing the ink just enough to cover the crystal area regardless the amount of ink. All samples were analyzed using an Agilent Cary 630 FTIR spectrometer with 2 scans and spectral range from 4000 cm^{-1} to 500 cm^{-1}. Each spectra was then subjected to multivariate analysis using XLSTAT 2015 add ins in Microsoft Excel.



RESULTS & DISCUSSION

Attenuated Total Reflectance (ATR) FTIR

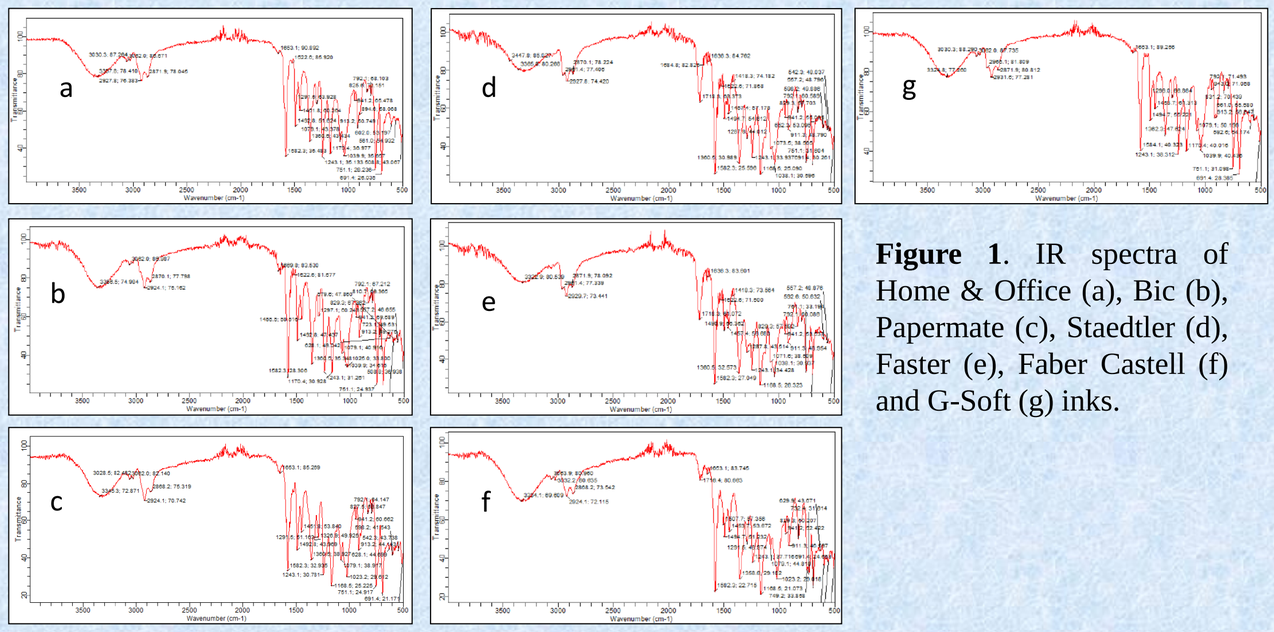


Figure 1. IR spectra of Home & Office (a), Bic (b), Papermate (c), Staedtler (d), Faster (e), Faber Castell (f) and G-Soft (g) inks.

The number of peaks as well as the peak positions and relative intensities were used as the basis for differentiation between the samples. Based on the visual spectral interpretation, comparing peak intensities between samples may give skewed results and interpretation of what major and minor peaks may be differ (Denman *et al*. 2010). In an attempt to improve this figure, multivariate analysis was employed. The most important region for ink analysis is from 1800 to 650 cm^{-1}, where typical absorption bands can be found (Silva *et al*. 2013). However in this work all peaks were considered and twenty five common wavenumbers across the samples from 4000 cm^{-1} to 500 cm^{-1} were included in the Principle Component Analysis (PCA).

Principal Component Analysis (PCA)

PCA was used to reduce the number of the variables and visually represent a clustering of the samples. The first four principal components (PCs) explained 86.2% of the total variance, of which 47.1% explained by PC1, 21.4% by PC2, 12.2% by PC3 and 5.4% by PC4 (table 2).

Table 2 Percentage variation associated with each principal component

	F1	F2	F3	F4
Eigenvalue	11.787	5.353	3.053	1.359
Variability (%)	47.148	21.412	12.214	5.438
Cumulative %	47.148	68.560	80.774	86.211

The PCA score plot of the first two principal components is shown in Figure 2. The pen inks have been clustered into five groups. The three pens from Home & Office, Faster and Bic are closely associated within their brands indicating that their compositions are strongly correlated. The three pens from each of the other brands were split between the identified clusters indicating more pronounced differences within these brands. The pens from different regions warrants further exploration as they show unique discrimination. In some cases these differences were quite marked for example with the Staedtler pens which clustered more readily into three different groups rather than with each other.

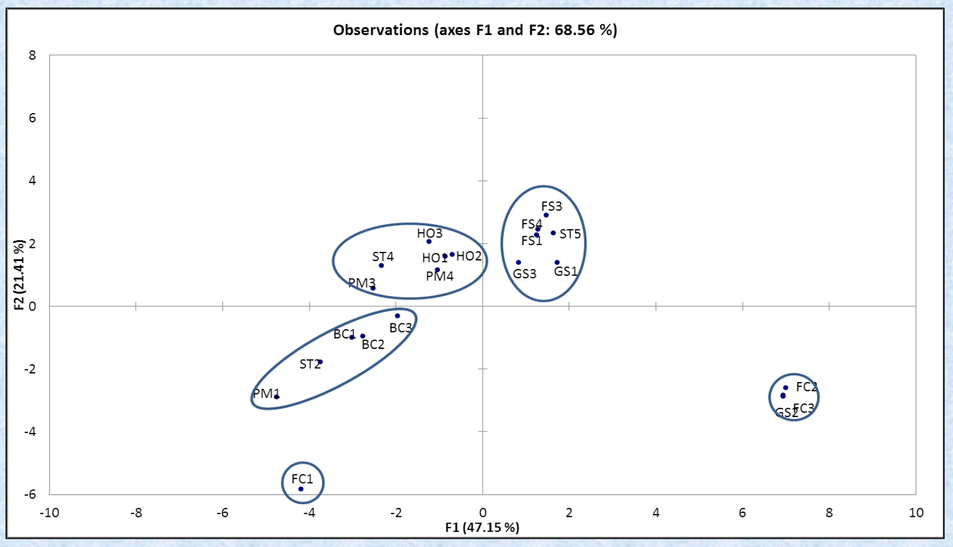


Figure 2. Score plot of PC1 vs. PC2

CONCLUSION

The results of this study indicate that IR spectra of pen inks when coupled with multivariate analysis can be a useful discrimination tool for certain brands of blue ball point pens. Inks from 3 manufacturers were closely associated by brand based on 25 selected wavenumbers. Distinct differences within brands possibly with a geographical influence need to be further explored to fully understand their implications in brand association for these types of inks.

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