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Original Article

Fourier Transform Infrared (FTIR) Spectroscopy with Chemometric Techniques for the Classification of Ballpoint Pen Inks

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Abstract

FTIR spectroscopic techniques have been shown to possess good abilities to analyse ballpoint pen inks. These in-situ techniques involve directing light onto ballpoint ink samples to generate an FTIR spectrum, providing "molecular fingerprints" of the ink samples thus allowing comparison by direct visual comparison. In this study, ink from blue (n=15) and red (n=15) ballpoint pens of five different brands: Kilometrico®, G-Soft®, Stabilo®, Pilot® and Faber Castell® was analysed using the FTIR technique with the objective of establishing a distinctive differentiation according to the brand. The resulting spectra were first compared and grouped manually. Due to the similarities in terms of colour and shade of the inks, distinctive differentiation could not be achieved by means of direct visual comparison. However, when the same spectral data was analysed by Principal Component Analysis (PCA) software, distinctive grouping of the ballpoint pen inks was acheived. Our results demonstrate that PCA can be used objectively to investigate ballpoint pen inks of similar colour and more importantly of different brands.

Key words: Forensic Science, Principal Component Analysis (PCA), FTIR spectroscopy, Ballpoint pen inks, Direct Visual Comparison.

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تصنيف أحبار الأقلام الجافة باستخدام تقنية مطيافية تحويل فورير بالأشعة تحت الحمراء (FTIR) والتقنيات الكيميائية

المستخلص

لقد أثبتت تقنية مطيافية تحويل فورير للأشعة تحت الحمراء كفاءتها الجيدة لتحليل الأحبار الجافة. يتم في هذه التقنيات، والتي تستعمل في الموقع، توجيه ضوء على عينات الحبر الجاف للحصول على طيف تحويل فورير بالأشعة تحت الحمراء(FTIR) ما ينتج عنه بصمة جزيئية لعينات الحبر وهو ما يتيح المقارنة البصرية المباشرة.

في هذه الدراسة تم تحليل أحبار من خمسة عشر قلم أزرق وكذلك أحبار من خمسة عشر قلم أحمر باستخدام تقنية مطيافية فورير للأشعة تحت الحمراء (FTIR) من خمس علامات تجارية مختلفة (كيلومترك،جي سوفت، ستابيلو، بايلوت، فابر كاستل) بهدف إنشاء مجموعات مميزة وفقاً للعلامات التجارية.

أولاً تمت مقارنة وتجميع الاطياف الناتجة يدوياً، ونظرا لأوجه

تشابه الأحبار فيما يخص اللون والطيف فإنه لا يمكن أن يتم التحقق من مجموعات متميزة من خلال المقارنة البصرية المباشرة. ولكن باستخدام نفس البيانات وتحليلها عن طريق برنامج تحليل المكونات الرئيسية (PCA) فقد تم الحصول على مجموعات مميزة من الحبر الجاف.

أثبتت نتائج هذه الدراسة أن برنامج تحليل المكونات الرئيسية (PCA) يمكن أن يستخدم بموضوعيه للتحقق من الأحبار التي تتشابه في اللون وتتركز أهميته في التحقق من العلامات التجارية المختلفة.

الكلمات المفتاحية: الأدلة الجنائية، تحليل العناصر الرئيسية (PCA)، مطيافية (FTIR)، أحبار الأقلام الجافة، مقارنة بصرية مباشرة

Introduction

Forensic examination of questioned documents routinely involves both physical and chemical analyses of inks. As the methods of perpetrating forgery and alteration of documents are becoming increasingly more sophisticated, it is often difficult to determine which individual writing implement was responsible for making entries in a document; however, it is usually possible to identify the ink [1].

There are two techniques generally used in forensic ink analysis, namely, destructive and non-destructive. The destructive technique requires removal of a small portion of the ink from the questioned document using an appropriate solvent followed by analysis using chromatographic, electrophoretic and spectroscopic techniques. On the contrary, in the non-destructive technique ink from the questioned text is analysed by in-situ Raman [2] or Infrared Spectroscopy [1,3].

FTIR has proven to be a useful tool in the analysis of bulk blue ballpoint pen ink [4]. By this technique, not only were the components of the ink determined, but also the classification of ballpoint inks had been made. On the basis of the components of the ink and classification of ballpoint inks, a pattern recognition system of artificial intelligence was made to describe the frequency and absorbance of the spectra in detail. More importantly, the pattern recognition technology could identify inks automatically and digitally. This pattern recognition technology is a new way to determine bulk blue ballpoint pen inks; it is fast, accurate, and nondestructive [4].

Red seal inks were studied to investigate the feasibility of micro-attenuated total reflectance (ATR) FTIR spectroscopy [5]. The technique successfully differentiated red seal inks of similar colours from different manufacturers. A blind test conducted by Dirwono et al [5] showed that micro-ATR-FTIR can easily identify the origin of unknown red seal inks with high accuracy and preciscion. This technique was also successful in determining the sequence of heterogeneous line intersection from a personal seal and a ballpoint pen. The study showed that micro-ATR-FTIR is a valuable nondestructive tool for objective analysis of red seal inks [5].

The FTIR technique provides both quantitative and qualitative information. The former is normally used in forensic science for comparative analysis of inks. It is a straightforward and fairly simple technique which can be used to determine the source origin of inks. The latter information is commonly subjected to chemometric analysis which helps to facilitate classification and individualisation of inks. The problem associated with presenting qualitative information in a court of law is that it is highly subjective, and the success of presenting such information will entirely depend upon the level of experience knowledge, and skills an examinar possesses.

In forensic ink analysis, even though the efficiency of instrumentations and analytical methods regarding the composition of ink have been successfully developed and established, the chemometrics area is not being extensively utilized to explore and support the analytical outcomes. Chemometrics is a powerful tool, especially when dealing with complicated multi-component or multi-variable data sets, as it allows the extraction of maximum information from the complex data sets [6]. In forensic ink analysis, Principal Component Analysis (PCA) is a chemometric technique that is commonly applied to aid forensic scientists in the interpretation of ink analysis outcomes [7-11].

1.1 Principal Component Analysis (PCA)

PCA is a multivariate statistical method which allows a large number of sample data sets to be described in terms of a much smaller number of principal components. The first principal component, i.e. PC1, describes the gross average features of the data sets, while the second (PC2) and subsequent principal components introduce further specific features of decreasing significance. A score plot of the first two principal components is most commonly used to display the cluster outcomes of given data sets where samples having similar scores are positioned closely together. This technique facilitates classification and individualization of samples in an objective and reproducible manner [12].

The aims of this study were to characterise blue and red ballpoint pen inks using FTIR spectroscopy, analyse the spectroscopic data of the ballpoint pen inks using the chemometric technique of Principal Component Analysis (PCA) and finally to establish objective and definite differentiation of the ballpoint pen inks using PCA.

2.Materials and Methods

2.1 Sample Collection

Inks from 15 blue and 15 red ballpoint pens were analyzed in this study. Pens were manufactured by five different manufacturers (Faber Castell®, Pilot®, Stabilo®, G-soft®, Stabilo®) and were purchased from the local bookstores in the Kubang Kerian and Kajang areas (table 1).

2.2 FTIR Spectroscopy

An ink spot measuring approximately 2 cm in diameter was scribbled directly onto white filter paper. The spot was left to stand at room temperature for 10 minutes prior to the analysis. All spectra were obtained from an FTIR spectrometer (Bruker Technologies,USA) which incorporates an ATR sampling interface. The sample interface was wiped clean using tissue soaked with ethanol before and after the analysis. A reference spectrum of air was taken at the start of each day prior to any measurements to ensure the spectrometer was working correctly. The spectrum of the white filter paper was recorded and this served as a "Blank". The repeatability of the analysis was assessed by calculating the percent relative standard deviation (%RSD) of peak absorbancies at each wavenumber position for a set of three spectral measurements. All samples were analysed in triplicates. The spectral range used in the acquisition of data was from 1200-1800 cm^{-1}. The entire range, consisting of 344 data points, was used for PCA.

2.3 PCA

PCA was performed using MINITAB® Version 16.2.3 statistical software (Minitab Incorporated, State College, PA, USA). Prior to the introduction to the Minitab® environment, all FTIR spectra were prepared and processed in Microsoft Excel (Microsoft, Inc.).

3.Results and Discussion

The blank and FCB ballpoint pen inks were used for both repeatability and reproducibility studies to assess the robustness of the FTIR analysis. Figure 1 shows the spectral variations of the three FCB ballpoint pen inks with the blank. Direct visual observation of the spectra shows that the spectra of FCB ballpoint pens are overlapped and are not inundated by the spectra contributed by the blank, which is composed of a variety of organic and inorganic components. Furthermore, the %RSD of the readings was less than 5%, indicating that the variation within the sample is small. Thus, the FTIR analysis gave very good repeatability.

Figure 2 shows the spectra generated from three different FCB ballpoint pens. Direct observation of the spectra shows that they are closely overlapped. The %RSD of the readings was less than 5%, indicating that the variation between the samples is small.

Table 1- ***Description of the pens used in the study***

Brand and Model	Ink Manufacturer	Local Trader	Reference Code	Colour and Quantity of Pens	
				Red	Blue
Pilot Super GP	Namiki, Japan	Pilot Pen Corp	PLB, PLM	3	3
Faber Castell	Nuremberg, Germany	A.W. Faber Castell Public Limited Company	FCB, FCM	3	3
Stabilo Galaxy 818	Weiβenburg, Germany	Swan Malaysia	STB, STM	3	3
G Soft R 100 Fine	Rennes, France	Famous Stationers Public Limited Company	GSB,GSM	3	3
Kilometrico	Ogdensburg, New York	Papermate Public Limited Company	KMB, KMM	3	3

3.1 Red Ink Group

In general, all spectra from five different red ballpoint pen inks showed quite dissimilar spectral patterns. All spectra exhibited two prominent peaks at approximately 1350 cm^{-1} and 1600 cm^{-1}, respectively. However, they were different in the form of relative peak height and its shape, as illustrated in Figure 3. Closer inspection of some of the spectra revealed the presence of weaks or shoulders that could arguably provide further discrimination. The differences in the five spectra of FCM, PLM, STM, KMM and GSM are shown in the region between 1450-1550 cm^{-1} and 1724-1755 cm^{-1}.

3.2 Blue Ink Group

The five spectra of the blue ballpoint pen inks of FCB, PLB, STB, GSB and KMB are shown in Figure 4. The same prominent peaks are readily observable at 1600 cm^{-1} in the five spectra. The differences between the five spectra can be seen between 1425–1500 cm^{-1} and 1701–1751 cm^{-1} regions.

It is difficult to differentiate the ballpoint pen inks on the basis of direct manual examinations alone as evident in Figures 3 and 4 above. No distinct classification or identification could be achieved; therefore, a technique that can conclusively differentiate between ballpoint pen inks of similar color is needed.

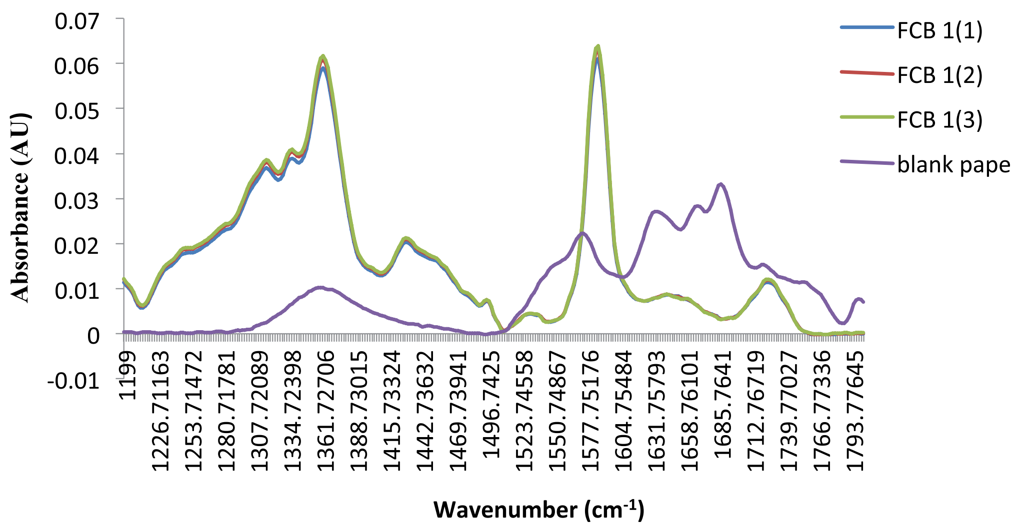

Figure 1- *FTIR spectra of three same FCB ballpoint pen inks*

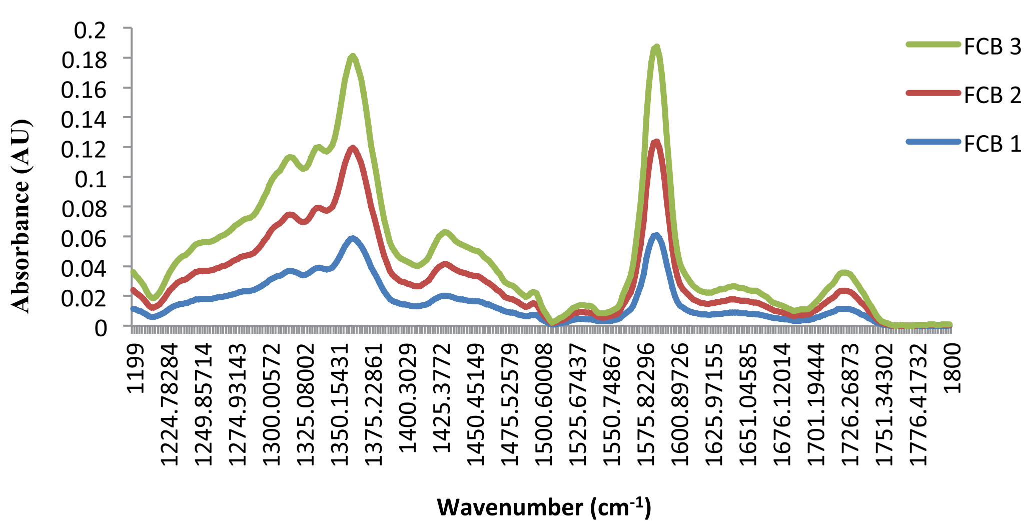

Figure 2- *FTIR spectra of three different FCB ballpoint pen inks*

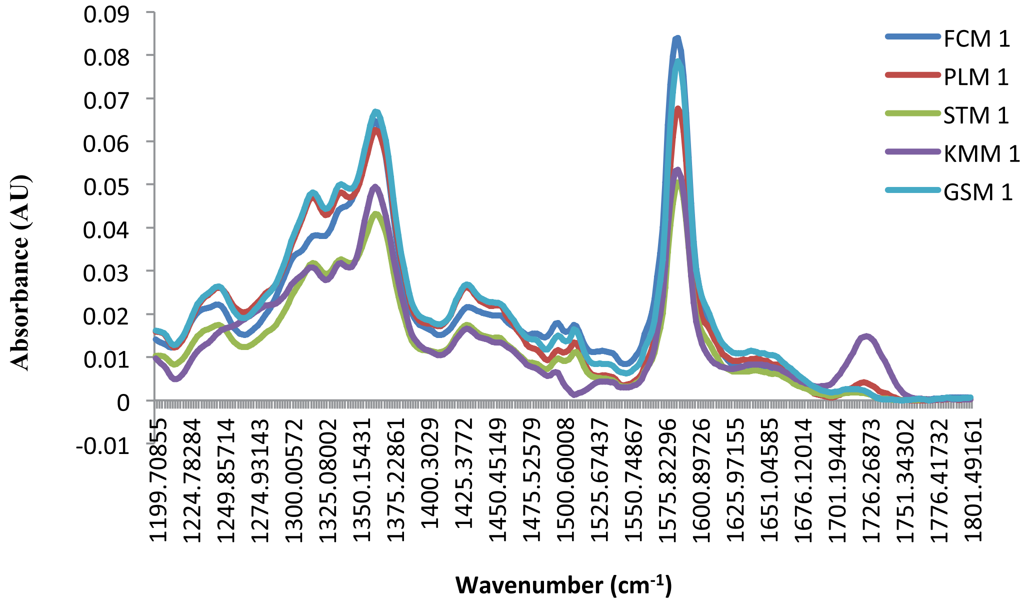

Figure 3- *Respective spectral pattern of five different red ballpoint pen inks analyzed by ATR-FTIR spectroscopy in the region 1200-1800 cm^{-1}*

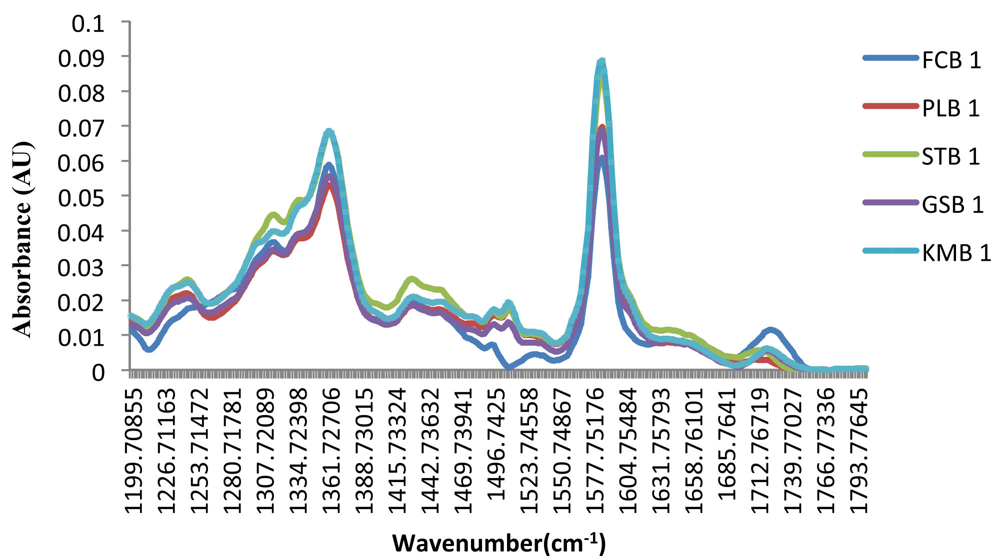

Figure 4- *Respective spectral pattern of five different blue ballpoint pen inks analyzed by ATR-FTIR spectroscopy in the region 1200-1800 cm^{-1}*

3.3 PCA

PCA was applied to the FTIR spectra obtained from all the ballpoint pen inks using MINITAB® Version 16.2.3 statistical software (Minitab Incorporated, State College, PA, USA) in order to distinguish between the pen inks according to their brands. The wavelength region of 1200 – 1800 cm^{-1} was subjected to PC analysis. The interpretation of the PCA was achieved using the score plot of the first two PCs, i.e. PC1 and PC2.

3.3.1 PCA of Red Ballpoint pen Inks

The PC score plot of the first two PCs, i.e. PC1 and PC2 for the red ballpoint pen inks is shown in Figure 5. As is evident in the score plot, the red ballpoint pen inks can be successfully grouped into five distinctive clusters corresponding to the five different ballpoint pen brands considered in this study. Cluster A, B and C, which are positioned at the right hand side of the score plot, constitute red ballpoint pen inks of FCM, GSM and PLM,

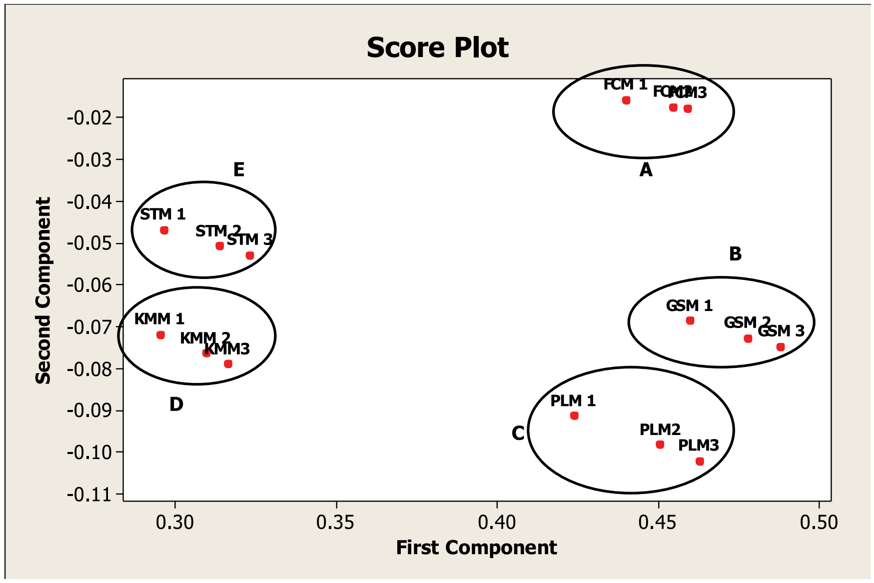

Figure 5- *Principal component score plot of red ballpoint pen inks from FTIR Spectroscopy*

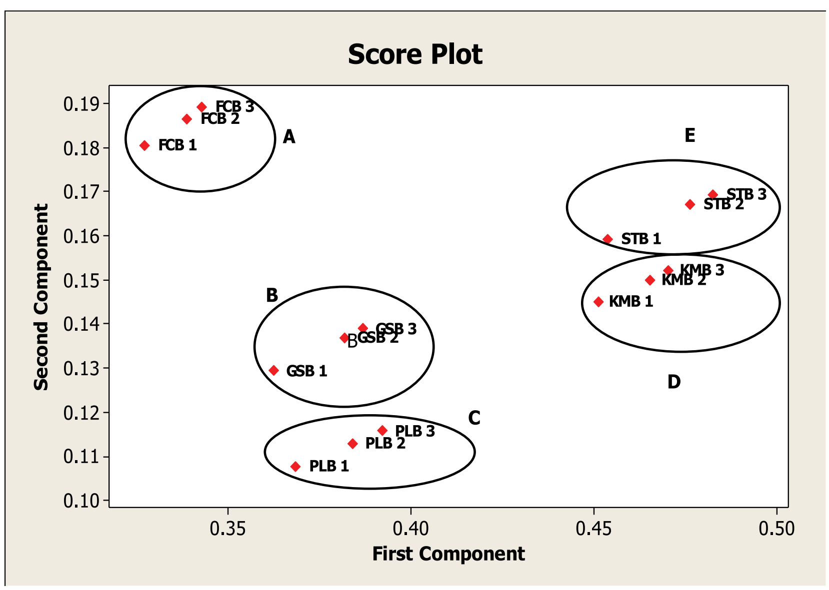

Figure 6- *Principal component score plot of blue ballpoint pen inks from FTIR Spectroscopy*

respectively. Cluster D and E, positioned on the left hand side of the score plot, are constituted of red ballpoint pen inks of KMM and STM, respectively. The five distinctive clusters suggest that the red ballpoint pen inks investigated in this study have different ink formulations.

3.3.2 PCA of Blue Ballpoint pen Inks

The PC score plot of the first two PCs, i.e. PC1 and PC2 for the blue ballpoint pen inks is shown in Figure 6. As is evident in the score plot, the blue ballpoint pen inks can be successfully grouped into five distinctive clusters corresponding to the five different ballpoint pen brands considered in this study. Cluster A, B and C, positioned at the left hand side of the score plot, constitute blue ballpoint pen inks of FCB, GSB and PLB, respectively. Cluster D and E, which are positioned on the right hand side of the score plot, constitute blue ballpoint pen inks of KMB and STB, respectively. Similar to the red ballpoint pen inks, the five distinctive clusters suggest that the blue ballpoint pen inks considered in this study also used different ink formulations, which enabled their differentiation.

4.Conclusion

FTIR spectra of ballpoint pen inks generated from an FTIR spectrometer when coupled with Principal Component Analysis (PCA) is a powerful approach for characterizing blue and red ballpoint pen inks compared to conventional direct manual examinations of the FTIR spectra alone. Although simple and quick to perform, the interpretation of direct manual examination of FTIR spectra of ballpoint pen inks depends on the experience of the examiner. In contrast, chemometric techniques of PCA afforded more objective and meaningful outcomes. As shown in this study, ballpoint pen inks of two different colours i.e. blue and red of five different brands were successfully resolved and differentiated after undergoing chemometric treatments of PCA. Our results have shown that PCA can be used as an effective tool for examining questioned documents in order to characterise the ballpoint pen inks used in them.

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