




## Coupling ATR-FTIR Spectroscopy and Chemometric Analysis for Rapid and Non-Destructive Ink Discrimination of Forensic Documents

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### Abstract

The large increase of global counterfeit documents urges the need to explore novel methods for forensic examination toward efficient discrimination of forged and authentic documents. The attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy holds great promise for reliable chemical analysis. The chemometric analysis such as the principal component analysis (PCA) provides a very powerful analytical tool, especially when dealing with complicated multi-component spectral data sets. In this paper, we demonstrate a promising approach for the rapid and non-destructive discrimination of writing-pen inks using the ATR-FTIR spectroscopic technique coupled with the PCA. A variety of writing pens of different sorts were collected and the ink samples were applied onto one type of photocopier paper. The ATR-FTIR spectra of ink samples were measured triply over two spots yielding six spectra for each studied ink. The obtained FTIR spectra were compared to confirm the repeatable spectral profile. The ATR-FTIR spectral results obtained for the different inks indicate the presence of triarylmethane dye as a basic colorant in the studied writing-pen inks. Adopting the visual analysis of the FTIR spectra of the different inks, a relatively low discrimination power of only 72 % could be achieved which limits routine FTIR analysis in forensic documents examination. Interestingly, the coupling of the PCA as a multivariate chemometric technique with FTIR resulted in much improved spectral discrimination. The PCA score plot of the first two principal components (PC1 and PC2) using the spectral data of the 33 pen ink samples resulted in a significantly higher discrimination power of 100 % with all data points showing separately, indicating successful discrimination of all ink samples. Such high discrimination power is highly desirable in forensic examination of question documents to eliminate errors leading to poor ink identification due to human factors. The inks discrimination was achieved using samples of inks directly applied onto paper without any sophisticated sample preparation or processing. This ATR-FTIR/PCA analytical approach may serve as a potential method for reliable, and non-destructive forensic documents examination aimed at rapidly identifying a forgery.

**Keywords:** Spectroscopy; Infrared; Forensic; Forgery; Inks; Multivariate Analysis.

### 1. Introduction

Forensic document examination is a forensic science field that plays a key role in the analysis of questioned documents. It can provide valuable information in a multitude of counterfeiting investigations concerning the type of paper and ink as

well as the formulation and characterization of inks.[1] Given the large increase of counterfeit documents in Egypt and around the world, there is a pressing need to develop new forensic document examination methods for efficient discrimination between forged and authentic documents. A forged document is an imitating copy produced without the authorization of authoring customers, companies, agencies, or the government.[2] Analysis of

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documents whose authority or origin is doubtful usually involves chemical profiling of the ink that is used for writing or printing. The growing digital and printing technologies and the different internet-based communications modes have led to a reduced number of handwritten documents. Nevertheless, signing such documents with a wet-ink signature is still needed in many situations to authenticate these documents. In addition, other prevalent handwritten notes continue to be used in some circumstances. Forgery processes are still manipulated for producing a variety of illegal documents. Thus, several analytical methods have been adopted to offer the ability to investigate the document's origin or authenticity.[3]

The forensic examination of questioned documents mainly aims at authenticating the document by investigating the document inks. This can be achieved by determining if the inks used in the questioned and authentic documents are the same or different. In the case of handwritten documents, are they written with the same or different pens? The answer to this question requires a method to analyze the chemical composition of the writing inks and enable sourcing their types. Generally, the pen-writing inks are composed mainly of a colorant, carrier, and additive. The colorant is typically a dye or pigment suspended in the carrier that a solvent or resin forms a flowing liquid. Additives such as emulsifiers, surfactants, and anticorrosion are usually added to the ink to stabilize the emulsion and control the surface and physicochemical properties of the ink.[4] These main ink ingredients typically vary in their composition and combination from product to product, and such variation is crucial for forensic investigation of questioned ink.

The chemical analysis of ink profiling of its main components can lead to determining if more than one ink is used throughout a certain document and its type.[5] The forensic examination of writing inks involves the physical and chemical analyses of the questioned ink, typically using destructive or non-destructive analytical methods. The routine forensic analysis of inks is carried out using non-destructive analytical techniques based on the microscopic and optical examination of the ink material. Such examination can provide information about the physical characteristics of inks such as color, luminescence, and absorption properties which can be utilized to differentiate between different ink substances.[6] However, such routine analytical methods lack behind providing information about the

chemical composition of questioned ink. Thus, to identify an ink, it is necessary to determine its chemical composition to adopt physicochemical analytical methods.[7]

The spectroscopy-enabled examination of inks is of great interest as it allows forensic investigation and analysis of documents effectively and reliably.[8, 9] Besides, thin-layer chromatography (TLC), high-performance thin-layer chromatography (HPTLC), and capillary electrophoresis (CE) are often adopted for ink analysis. The routine analysis of inks relies on chromatographic or spectroscopic techniques requires etching a small portion of the ink from the surface of the questioned document. The etching can be achieved either by scratching or solvent extraction, making them harmful to nature.[10] These methods are based primarily on the separation of the dyes in questioned inks to enable their differentiation.[11]

The Fourier-transform infrared (FTIR) spectroscopy has shown great promise as an effective tool for chemical analysis and forensic analysis of documents and ink substances.[12-14] It is a quite simple tool that can determine the various components of a given ink in providing qualitative and quantitative information that facilitates the comparative analysis of writing-pen inks.[15] The FTIR is a straightforward tool allowing effective discrimination and classification of questioned ink samples.[16] Specifically, the attenuated total reflection Fourier-transform infrared (ATR-FTIR) technique allows examination of writing-pen inks without sophisticated sample preparation. It is a completely non-destructive technique that allows maintaining the overall integrity of the document.[6, 17] This makes the micro ATR-FTIR an ideal method of interest to forensic document examiners for the analysis of writing-pen inks.[17] The micro ATR-FTIR spectroscopy has been shown effective for the discrimination of blue-red ballpoint pen ink applied on paper when coupled with multivariate analysis.[16] In this regard, the coupling of spectroscopic and chemometric analysis can ease the rapid classification and individualization of inks.[18-20]

The chemometric techniques such as principal component analysis (PCA) and linear discriminant analysis (LDA) techniques have recently found their way in the forensic analysis of inks.[16] They provide forensic examiners with powerful analytical tools, especially when dealing with complicated multi-component or multi-variable data sets, as they

can maximize the information drawn from the large data sets. The PCA method involves two or more principal components. The first principal component (PC1) represents the features of the data sets that vary the most. The second principal component (PC2) and so on subsequent principal components introduce the second most variable features within the data sets.[21] A two-dimensional (2D) score plot of the first two principal components and a three-dimensional (3D) plot of the first three principal components are often used to display the cluster outcomes of given data sets.[20] The samples with similar scores are positioned close to each other on the plot, thus classifying and individualizing the samples in an objective and reproducible manner.[22, 23]

In this paper, a rapid approach for the discrimination of writing-pen inks based on the ATR-FTIR spectroscopy coupled with chemometrics is reported. The developed approach relied on the investigation of the chemical components of thirty-three writing pens of three different types (ballpoint, gel, and roller). The inks of the different writing-pen samples have been successfully discriminated by coupling ATR-FTIR and PCA techniques. The discrimination was achieved for writing-pen inks applied on paper simply without a need for any sophisticated sample preparation or processing. This technique has proven to be efficient, reliable, and completely non-destructive. The coupling of the PCA chemometric technique as a multivariate approach with FTIR resulted in improved discrimination and classification power close to 100%, which is highly desirable in forensic examination of question documents.

In the following sections of this paper, a description of the experimental methods used for the preparation of the ink samples is presented. This is followed by a detailed explanation of the spectral data acquisition, treatment, and the multivariate analysis of the obtained data. Afterward, the results and discussion section presents both spectroscopy and multivariate analysis results with a thorough discussion for each part. The ATR-FTIR results with routine visual analysis are presented first in light of previous literature data. Then the PCA analysis of obtained spectral data is explained and advantages over routine visual analysis are elaborated. The final section of this paper outlines the concluding remarks of the present work highlighting the potential ATR-FTIR/PCA for rapidly identifying forgery and authenticity of forensic documents.

## 2. Experimental

### 2.1. Preparation of Writing-Pen Ink Samples

The writing-pen inks investigated in this study were collected from the local market in Egypt. Amongst the best-selling pens, thirty-three blue writing pens were collected that comprise ballpoint, gel, and rollerball. **Table 1** lists the different writing pens used in this study with their coded names, type, brand, model, and manufacturer. The models of the thirty-three pens were as follows: five writing-pens models from the PRIMA brand that is widely used in Egypt, three models from the ROXI brand, three models from the Uni-Ball brand, and two different batches from one model from the BIC brand. The remaining models were chosen from some other less common brands as listed in **Table 1**. The preparation of the writing-pen ink samples relied on applying a square of 1 cm<sup>2</sup> area using each writing pen. All writing-pen ink samples were applied on the same photocopier paper type (multi-office paper 80 g/m<sup>2</sup>) 24 h before spectra acquisition.

### 2.2. FTIR Spectra Acquisition and Data Treatment

The FTIR spectra of the investigated ink samples were acquired using a Nicolet 6700 FTIR spectrometer, Thermo-Scientific, USA, equipped with an attenuated total reflection (ATR) accessory. The FTIR spectra were collected in the spectral range of 650-4000 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup> and a total number of scans of 20. The FTIR spectra were collected against that of the FTIR spectrum of the paper as the background. For accurate measurements, the FTIR spectra of each writing-pen ink were measured three times over two different positions with a total of six spectra for each investigated ink. The six FTIR spectra of each ink were compared, and a repeatable spectral profile had confirmed. For the inter-comparison of the different writing-pen inks, a single FTIR spectrum for each sample was assumed. The majority of the functional groups present in an ink appear in the FTIR region of 650-2000 cm<sup>-1</sup>. The 650-2000 cm<sup>-1</sup> range was utilized for the comparison to avoid any non-informative part of spectra and to reduce the numbers of variables in the principal component analysis.

### 2.3. Multivariate Analysis

The principal component analysis (PCA) is a statistical procedure that allows a huge number of

samples data sets described in terms of a much smaller number of variables called principal components (PCs). The first principal component describes the most variable of the data set, while the second and all consequent principal components introduce advanced specific features of decreasing significance. This procedure promotes the classification and individualization of sample data sets in a preferable and reproducible manner. In forensic science investigation, the statistical interpretation of multidimensional data is generally executed in either raw data or log-transformed data.

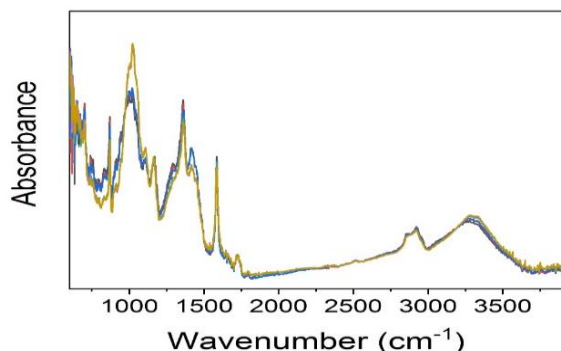
The spectroscopic data obtained for many samples with similar spectroscopic characteristics could be complex. Thus, the data were first normalized to a reference point. The normalization could not differentiate the ink samples but minimizes the errors due to the differences in the amount of ink applied at the spot point or the instrumental factors. The appropriate pretreatment of the raw data is crucial for valuable and effective data analysis. All the statistical analyses have been performed using Origin-Pro 2018 software (Origin Lab Corp.).

Table 1: A list of the 33 writing pens used in this study including their coded names, type, brand, model, and manufacturer.

No.	Code	Pen Type	Brand	Model	Manufacturer
1	PR1	B.P	PRIMA	SOLO	Egypt
2	PR2	B.P	PRIMA	MARGO	Egypt
3	PR3	B.P	PRIMA	FORMA	Egypt
4	PR4	B.P	PRIMA	FORSA	Egypt
5	PR5	B.P	PRIMA	UNOF	Egypt
6	RX1	B.P	ROXI	CLASSIC	Egypt
7	RX2	B.P	ROXI	RED BIRDS	Egypt
8	RX3	B.P	ROXI	GOLD	Egypt
9	CL1	B.P	CLARO	TECHNIK	India
10	CL2	B.P	CLARO	SIGMA	India
11	UB1	B.P	UNI-BALL	LAKUBO	Japan
12	UB2	B.P	UNI-BALL	SX-210	Japan
13	GF	B.P	UNBRANDED	N.A.	China
14	VN1	B.P	VINSON	ZERO Z3	Japan
15	VN2	B.P	VINSON	VIGOR C3	Japan
16	BCb	B.P	BIC	BIC	Egypt
17	BCa	B.P	BIC	BIC	Egypt
18	RO	B.P	ROTO	PACER	Egypt
19	PG	B.P	PREGO	FINE	Egypt
20	PK	B.P	PARKER	QUINK	UK
21	LZ	B.P	LAZOR	SIGNETTA	India
22	RE	B.P	REYNOLDS 045	CARBURE	Egypt
23	CE1	B.P	CELLO	SPEED	India
24	ST1	B.P	STAEDTLER	STICK 430 M	Germany
25	EU	B.P	EURO	POP	Egypt
26	WN	B.P	WIN	TOTEM-WISH	India
27	UB3	GEL	UNI-BALL	SIGNO	Japan
28	DE	GEL	DE MEI PEN	THE COLOR PEN	China
29	BR	GEL	BRIGHT COLOR	CS-956	China
30	ZU1	GEL	ZUIXUA	HY505	China
31	ZU2	GEL	ZUIXUA	DIAMOND G-520	China
32	UB4	ROLLER	UNI-BALL	EYE	Japan
33	ZR	ROLLER	ZEBRA	Z-1	Japan

### 3. Results and Discussion

This paper reports on the differentiation of blue writing-pen inks using the ATR-FTIR and PCA analysis. The FTIR analysis was performed using 33 writing-pen ink samples. The 33 ink samples were from three types as ballpoint, gel, and roller of different brands. A single type of paper was used in the preparation of all studied ink samples. **Table 1** shows a list of the 33 writing pens used in this study, including their code names, types, brands, models, and manufacturers. **Figure 1** shows the FTIR spectra of the selected ink sample (PR1 pen) with six individual spectra collected from two different spots of the selected PR1 ink on the paper. The six FTIR spectra of the PR1 pen sample exhibit similar FTIR characteristics with similar peak profiles and peak positions. The peaks of the different spectra can be differentiated based on the peak intensity arising from the variation of the quantity of ink present on the paper. Since the differences between the replica spectra stem only from the count and not from the nature of the peak, this indicates that the FTIR measurement is reliable and reflects the homogeneity of the ink sample on the surface.



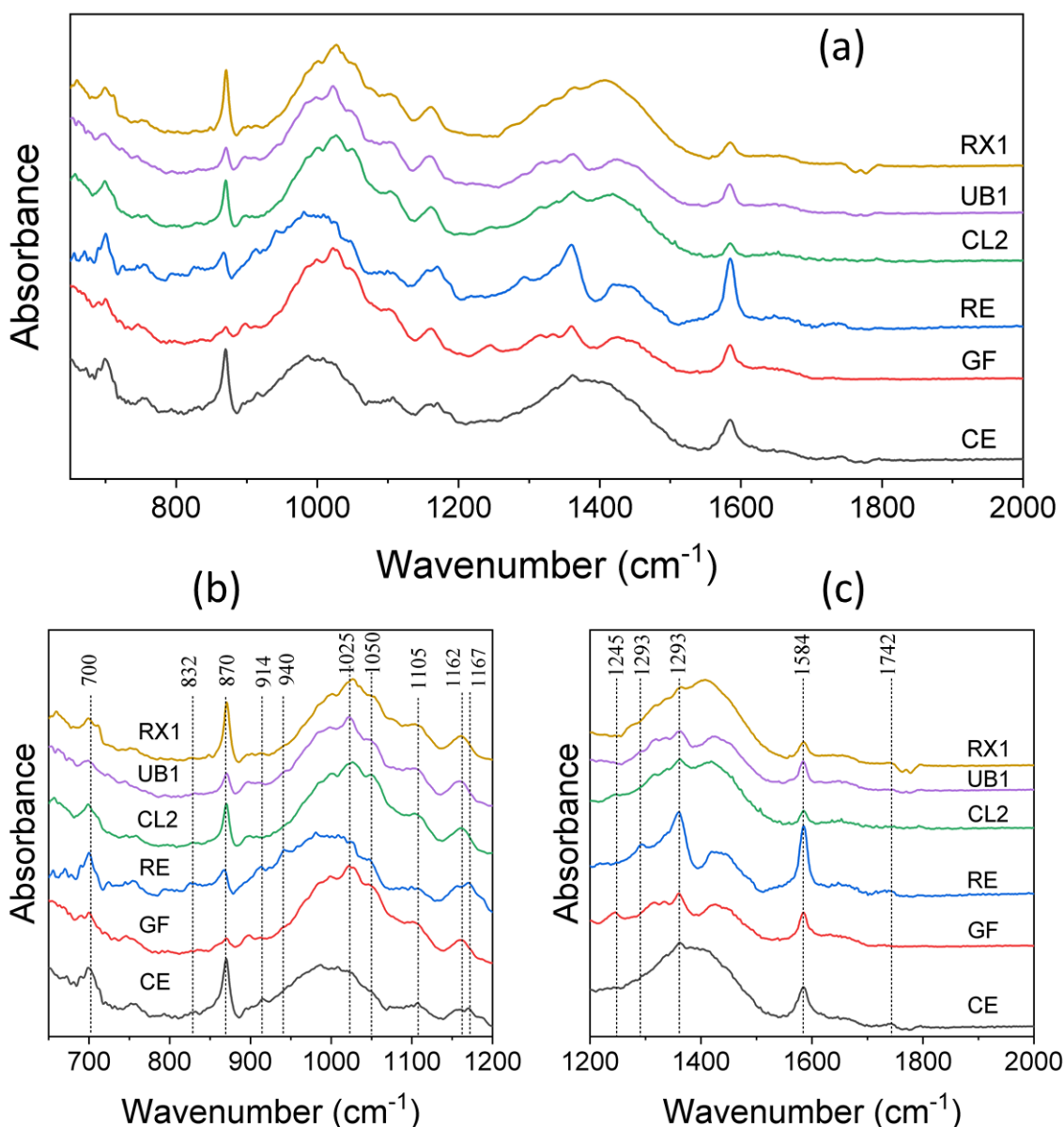
**Figure 1.** FTIR spectra of PR1 pen sample. A total of 6 individual spectra was collected from two different spots of the selected PR1 ink on the paper.

Based on this analysis, six replica spectra were collected for each ink sample similar to the PR1 pen sample. Only one FTIR spectrum was selected for each sample for the sake of judgment qualitative (visual) compared to quantitative (statistics) analysis of the different ink samples. The FTIR spectral data can provide valuable information about the chemical composition of the different ink constituents. However, the dyes and/or pigments, solvents, resins, and additives in the inks have different compositions

and concentrations. Such complexity of components varies a lot among different ink types, brands, and models that make the assignment of FTIR peaks challenging.[17] The visual differentiation of inks relies mainly on checking the spectra for the presence or absence of specific peaks or shoulders and the inter-comparison of the relative peak intensities of the various pens.[24]

**Figure 2** displays the FTIR spectra of the six different B.P pen samples, namely, CE, CL2, GF, RE, RX1, and UB1. As can be seen in **Figure 2-a**, the six pen samples can be distinguished with the visual comparison, as they exhibit slight differences in the peak positions and relative intensities. This could be used as reference parameters for visual spectral differentiation. The spectra were dominated by six main peaks centered at  $\sim 700\text{ cm}^{-1}$ ,  $870\text{ cm}^{-1}$ ,  $1025\text{ cm}^{-1}$ ,  $1162\text{ cm}^{-1}$ ,  $1360\text{ cm}^{-1}$ ,  $1584\text{ cm}^{-1}$ . Nevertheless, the FTIR spectra of the six B.P pen samples exhibit clear differences in the relative peak intensities for some samples and possess unique peaks in other samples. The spectrum of the CE sample was featured with small shoulders at  $914\text{ cm}^{-1}$  and  $1730\text{ cm}^{-1}$ . The so-called GF ink shows a small peak at  $1290\text{ cm}^{-1}$ , while two small peaks were observed at  $914\text{ cm}^{-1}$  and  $941\text{ cm}^{-1}$  for RE. Despite similar peak positions at  $1584$  and  $870\text{ cm}^{-1}$  of CL2, UB1, and RX1, they can be visually discriminated from each other by using the relative peak intensity. The CL2 and UB1 samples maintain lower intensity peaks at  $1584\text{ cm}^{-1}$  and  $870\text{ cm}^{-1}$  compared to an analog of RX1.

The peak assignment of the different FTIR spectra collected for the six B.P. pen samples can provide an insight into the nature of the different chemicals present in the ink samples. As shown in **Figures 2b&2c**, the spectra of the different samples have similar peaks at  $1167\text{ cm}^{-1}$ ,  $1360\text{ cm}^{-1}$ ,  $1584\text{ cm}^{-1}$ , agreeing with those reported for the ballpoint pen ink.[25] These three peaks are ascribed to the C-N, N-O, and N-H vibration, respectively, typically evidenced on a triarylmethane dye such as crystal violet.[15, 25] The peaks at  $700\text{ cm}^{-1}$  and  $745\text{-}755\text{ cm}^{-1}$  related to the mono-substituted arene group indicate the presence of 2-phenoxyethanol as a solvent in the inks, while that at  $1025\text{ cm}^{-1}$  could occur from traces of the primary alcohol in the solvent matrix.[2]



**Figure 2.** (a) FTIR spectra of the six B.P. pen samples, namely, CE, GF, RE, CL2, UB1, and RX1. (b,c) Same spectra in the narrow ranges of 650-1200  $\text{cm}^{-1}$ , and 1200-2000  $\text{cm}^{-1}$ , respectively.

The peak centered at  $\sim 870 \text{ cm}^{-1}$  may be related to the oxygen-containing functional groups of some additives present in ink and/or paper, such as the calcium carbonate.[2] The presence of aliphatic structures was suggested by the low-intensity peaks at around  $1050 \text{ cm}^{-1}$ ,  $1105 \text{ cm}^{-1}$ ,  $1293 \text{ cm}^{-1}$ . These peaks are ascribed to the asymmetric/symmetric stretch vibration of the aliphatic ether ( $-\text{C}-\text{O}-\text{C}-$ ).[7, 12] For the RE and GF pen samples, the peaks at  $914 \text{ cm}^{-1}$  and  $1245 \text{ cm}^{-1}$  can be assigned to the stretching vibration of the terminal epoxy resin [15], and the vibration of the aromatic ether ( $\text{Ar}-\text{O}-$ ) [7], respectively. The PR1 and CE pen samples show a

very small peak at  $1742 \text{ cm}^{-1}$  due to the stretching vibration of the carbonyl group ( $-\text{C}=\text{O}$ ) of aliphatic acids.[12] The FTIR results indicate the presence of triarylmethane dye, epoxy resin, 2-phenoxyethanol, and benzyl alcohol as the main ingredients in the 26 ballpoint pen samples. It has also been revealed that some samples contain aliphatic or aromatic ethers following the previous literature.[5, 26] It can be thus concluded that the visual examination of the FTIR spectra allowed to discriminate different inks if distinct differences in the chemical properties of the ink exist. It is worth mentioning that only 12 B.P pens could be discriminated with the visual

examination among the 26 B.P. pens used in this study (**Figure 2**, 6-samples are not shown). The other 14 non-discriminated B.P. pen samples exhibited similar peak profiles and positions with slight differences in peak widths and intensities.

The FTIR spectra which represent the five indiscriminate pen samples, namely, BCa, BCb, CL1, EU, and LZ, are shown in **Figure 3**. The capability of a given analytical method to differentiate the samples of two or more groups of spectral data is typically expressed using the discrimination power. Generally, the discrimination power (DP) can be calculated according to the method of Smalldon and Moffat [27] using equation 1:

$$DP = \frac{\text{Number of Discriminate Pairs}}{\text{Number of Possible Pairs}}$$

Eq. 1

The number of the possible pairs can be calculated using equation 2:

$$\text{Number of Possible Pairs} = \frac{n(n-1)}{2}$$

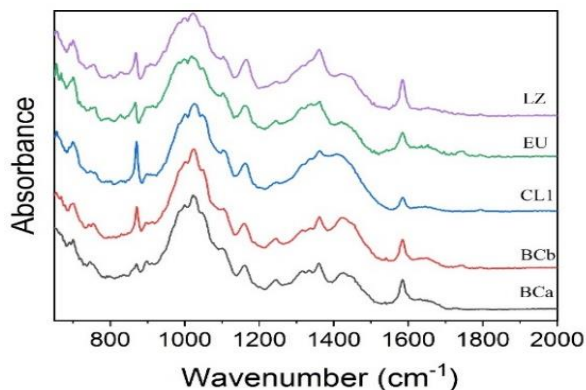
Eq. 2

A total number of 325 possible pairs was estimated for the 26 B.P. pen samples. Applying the number of the undifferentiated spectra (14) in eq. 2 gives a total number of 91 indiscriminate pairs. This results in a total number of 234 discriminate pairs. It gives a discrimination power of 72% when applying the numbers of the discriminant pairs and the total possible pairs in eq. 1. Such low discrimination power could hinder the practical implementation of the FTIR-based visual examination of forensic documents.

The ballpoint pens are known to be the most widely used for handwriting. The use of other types of writing pens such as gel, roller, and fill-tip is common. The use of gel pens has increased in recent years in both local and global markets. Forensic document examiners may face challenges discriminating different gel pen inks due to their increased use and a wide variety. Therefore, we examined a group of the most used five gel pens in the Egyptian market with the same approach of the FTIR-based visual examination.

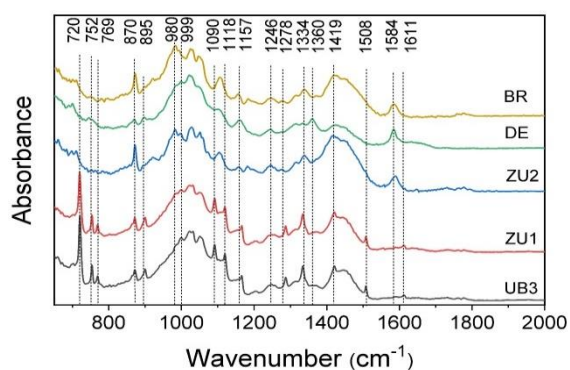
**Figure 4** shows the FTIR spectra of five different gel pens of four different brands (Uniball, Zuixua, De Mei, and Bright Color) and two different models of the Zuixua pens. The five different pens (coded UB3, ZU1, ZU2, DE, and BR) exhibit two common peaks at 1157 cm<sup>-1</sup> and 1584 cm<sup>-1</sup> assigned to the C-N, and N-H vibration, respectively. The UB3 and ZU1 samples show characteristics of azo pigments with

distinctive peaks at 1611 cm<sup>-1</sup>, 1419 cm<sup>-1</sup>, and 720 cm<sup>-1</sup> due to the aromatic ring quadrant stretching, the N=N stretch, and the naphthalene mode, respectively. The peak at 1334 cm<sup>-1</sup> is related to the aromatic nitro group.[28]



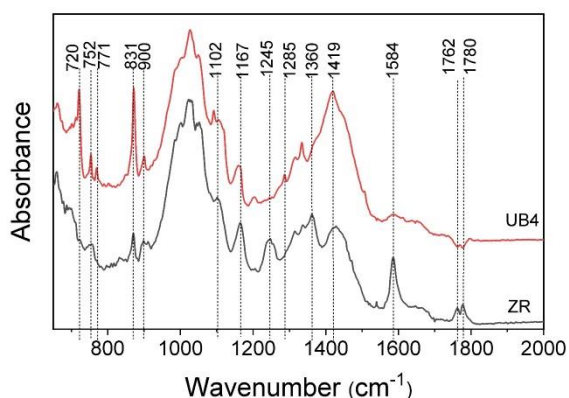
**Figure 3.** FTIR spectra of six similar B.P. samples, BCa, BCb, CL1, EU, LZ.

The visual comparison of the five spectra reveals that UB3 and ZU1 exhibit comparable FTIR spectral profiles with similar peaks positions and intensities. The similar spectral features of the UB3 and ZU1 inks obscure the visual discrimination against the two different brand inks. The three spectra of the ZU2, BR, and DE ink samples display comparable spectral features. The spectra of ZU2 and BR were slightly distinguished from that of DE in the sense that the peaks were at 1278 cm<sup>-1</sup> and 980 cm<sup>-1</sup>. The DE spectrum shows a peak at 1360 cm<sup>-1</sup> (N-O), along with two peaks at 1157 cm<sup>-1</sup> and 1584 cm<sup>-1</sup>, suggesting the existence of the triarylmethane dye as a basic colorant in this ink. This indicates the discrete chemical composition of DE than ZU2 and BR pens which helps differentiate the former from the latter. On the contrary, the spectra of the ZU2 and BR ink samples cannot be visually differentiated possibly due to their similar chemical nature. These results indicate that among the 10 possible pairs of the five spectra, only 8 pairs could be visually discriminated, and 2 pairs could not be analyzed (UB3/ZU1 and ZU2/BR), giving rise to a DP of 80%.



**Figure 4.** FTIR spectra of five different gel pens, namely UB3, ZU1, ZU2, DE, and BR.

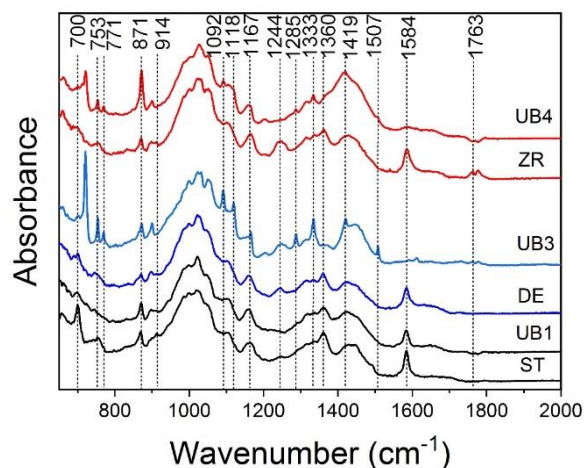
Further, checking the adequacy of the FTIR-based visual discrimination of the inks was extended to the roller pen samples. **Figure 5** shows the FTIR spectra of two different roller pens, namely ZR and UB4. The spectra of the two roller pen ink samples present comparable FTIR absorption peaks at 870  $\text{cm}^{-1}$ , 900  $\text{cm}^{-1}$ , 1313  $\text{cm}^{-1}$ , 1335  $\text{cm}^{-1}$ , and 1419  $\text{cm}^{-1}$ , as well as two peaks in 1762  $\text{cm}^{-1}$  and 1780  $\text{cm}^{-1}$  related to the aliphatic acids or their esters. The peaks positioned at 1584  $\text{cm}^{-1}$ , 1360  $\text{cm}^{-1}$ , and 1167  $\text{cm}^{-1}$  for ZR reflect the presence of the triarylmethane dye. The ZR spectrum is distinct from that of UB4 by the absorption bands at 912  $\text{cm}^{-1}$ , 1102  $\text{cm}^{-1}$ , and 1245  $\text{cm}^{-1}$ , though the latter is distinct from the former by the absorption bands at 720  $\text{cm}^{-1}$ , 752  $\text{cm}^{-1}$ , and 771  $\text{cm}^{-1}$ . Also, the difference in the relative intensity of the peaks at 831  $\text{cm}^{-1}$ , 900  $\text{cm}^{-1}$ , and 1584  $\text{cm}^{-1}$  increases the visual discrimination of the ZR and UB4 samples.



**Figure 5.** FTIR spectra of two roller pens, namely ZR and UB4.

The overall view of the above FTIR-based visual analysis of different inks with different types and brands demonstrates the presence of triarylmethane

dye as a basic colorant in the ballpoint, gel, and roller pens, as can be seen in **Figure 6**. The above analysis also shows the presence of the azo pigment in the gel and roller pens. The FTIR spectra reveal the prominent presence of the 2 phenoxyethanol in the ballpoint pens while being slightly present in gel pens and absent in roller ones. Although the visual inspection of the FTIR spectra might allow differentiating some ink samples, the inability to visually discriminate all studied ink samples challenges the routine visual FTIR analysis for forensic documents examination. Hence, we aimed at improving the discrimination power with the help of chemometric techniques such as principal component analysis (PCA).

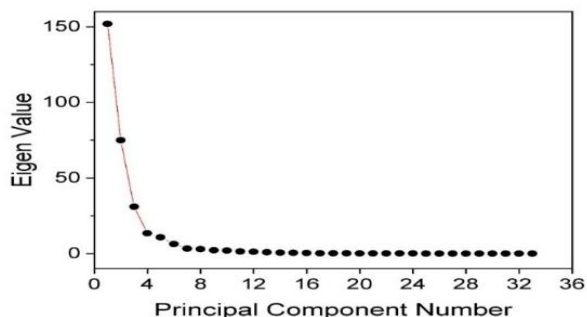


**Figure 6.** FTIR spectra of 6 different ink samples from 3 types, namely 2B.P (ST, UB1), 2 Gel (DE, UB3), and 2 Roller (ZR, UB4).

Herein, the PCA was employed as a chemometric tool to analyze the FTIR datasets of the different 33 ink samples in the range from 650-1200  $\text{cm}^{-1}$ . It is known that the PCA method involves two or more principal components (PCs), which explain a 100% total variance of the data. However, only those PCs whose eigenvalue is greater than 1 can be used to determine the variance present in the samples as reported by Kaiser.[29] **Figure 7** displays the Scree plot of the eigenvalues of the principal components. The first six PCs match the Kaiser criteria giving a variance value at 94.31% (PC1 =49.60, PC2 =24.53, PC3= 10.14, PC4=4.39, PC5= 3.52 and PC6=2.06), which is a very significant variance value. The remaining PCs represent 5.69% of the total variance. As can be seen in **Figure 7**, the eigenvalue possesses a magnitude greater than unity till PC12. The



eigenvalue was less than unity for up to PC13, suggesting all PCs beyond PC13 are meaningless. The first three PCs reveal 84.34% cumulative variance, clear enough for discrimination.

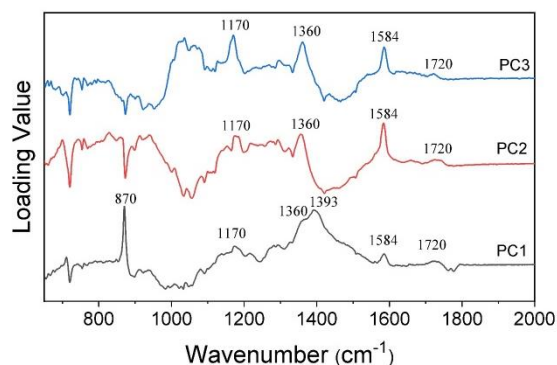


**Figure 7.** A Scree plot of eigenvalues to decide on the number of components to be used in discriminant analysis.

To elucidate the reason behind the maximum variance explained by the first 3 PCs, the wavenumber was plotted versus the loading value (regression score) for the first 3 PCs (**Figure 8**).[21] The analysis of this loading plot reveals that the first three PCs can give information about the dataset. The positions of the different peaks reflect the main chemical components utilized in the ingredients of the different ink formulations.[2] On the other hand, the variation of the loading value of the different bands reflects the variation of the chemical components between the different pen ink samples.

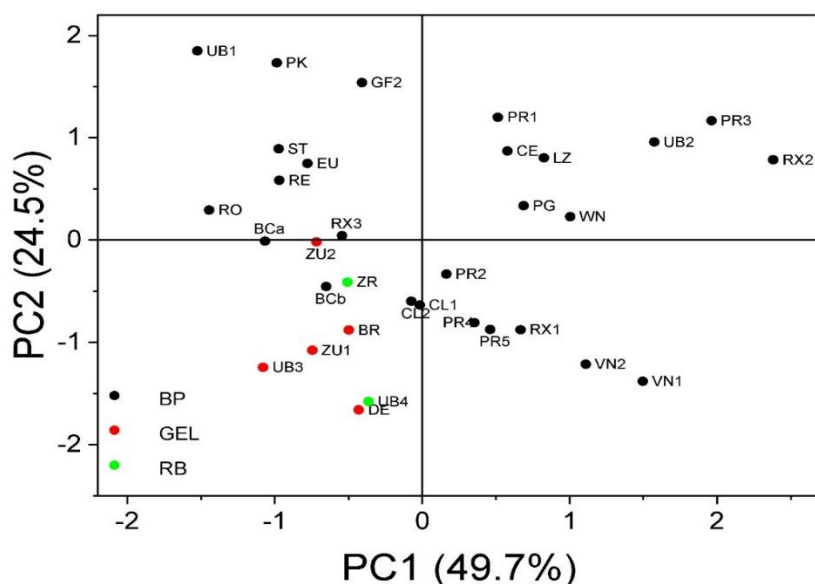
The loading plot encounters various peak shapes, including convoluted, deconvoluted, and partially resolved bands (**Figure 8**), which adds an interpretive task to forensic experts. It is clear from the loading plot that PC1 reflects two main peaks at about 870  $\text{cm}^{-1}$  and 1393  $\text{cm}^{-1}$  and the other two weak peaks at 1285  $\text{cm}^{-1}$  and 1730  $\text{cm}^{-1}$ . Although the FTIR spectra of the different ink samples exhibit a common peak at 870  $\text{cm}^{-1}$ , the varying intensities of this peak amongst different inks led to the highest value of PC1. The band around 1393  $\text{cm}^{-1}$  in the loading plot shown in **Figure 8** was found not related to any FTIR absorption peak in the crude FTIR spectrum. It falls between the two prominent 1360  $\text{cm}^{-1}$  and 1419  $\text{cm}^{-1}$  peaks considering a great variance in the spectral profiles at this point should give rise to a high value in PC1. The PC1 also clearly exhibits two peaks at 1285  $\text{cm}^{-1}$  and 1720  $\text{cm}^{-1}$  that correspond to the C-O and C=O stretch of the aliphatic acids/their esters,

respectively. Some other peaks at about 1584  $\text{cm}^{-1}$ , 1360  $\text{cm}^{-1}$ , and 1176  $\text{cm}^{-1}$  are also shown in the spectrum of PC1. These peaks have conferred low loading values for PC1, due to the presence of triarylmethane dye as a common basic colorant in all ballpoint, gel, and roller pens. The second important PC is PC2 which is characterized by peaks at 1720  $\text{cm}^{-1}$ , 1584  $\text{cm}^{-1}$ , 1360  $\text{cm}^{-1}$ , 1176  $\text{cm}^{-1}$ , and 1150  $\text{cm}^{-1}$ . The PC2 exhibits higher loading values than PC1 at 1584  $\text{cm}^{-1}$ , 1360  $\text{cm}^{-1}$ , and 1176  $\text{cm}^{-1}$  which are related to the triarylmethane dye. The band at 1150  $\text{cm}^{-1}$  in the PC2 can be related to the benzyl alcohol solvent. In addition to the peaks shown in PC1 and PC2, the PC3 reveals additional peaks appear at 1430  $\text{cm}^{-1}$ , and 1033  $\text{cm}^{-1}$  which could be due to some ink additives. The PC1, PC2, and PC3 mainly show the spectral characteristics of the fingerprint region of the different ink samples such as triarylmethane dye, solvents, resins, and additives.



**Figure 8.** A plot of the wavenumber versus the loading value for the first 3 PCs.

The PCA score plot of the first two PCs (PC1 and PC2) showing the discrimination analysis of the 33 pen ink samples is shown in **Figure 9**. Each data point on the 2D graph represents the total loading values of PC1 and PC2 for each ink sample. All data points representing different samples are shown separately, indicating the successful discrimination of all ink samples. The PCA-assisted examination of the FTIR spectra of the 33-pen resulted in a discrimination power of 100%, which is significantly higher than those obtained with the FTIR-based visual examination. This indicates the promise of coupling PCA with the FTIR analysis toward the reliable rapid and non-destructive forensic document examination.



**Figure 9.** The PCA score plot of the first two PCs shows the discrimination analysis of the 33 pen ink samples.

#### 4. Conclusions

Forensic document examination plays a key role in the analysis of questioned documents. The micro ATR-FTIR is a powerful technique for chemical analysis that can contribute valuable information on the chemical composition of writing-pen inks. The chemometric techniques such as PCA have already found their way into the forensic analysis of inks. In this paper, a non-destructive and rapid approach for the discrimination of writing-pen ink samples using ATR-FTIR spectroscopy assisted with chemometric analysis is reported. A broad range of writing pens available in the local market in Egypt which are often used in forensic documents was collected and investigated in this study. The samples were prepared by directly applying ink samples onto paper followed by spectral data acquisition, and multivariate treatment. The routine FTIR-based visual examination of the different ink samples resulted in a discrimination power of only 72% and 80% in the case of the studied ballpoint pens and gel pens, respectively. The multivariate analysis of the FTIR datasets based on PCA enabled the successful discrimination of all studied inks with a discrimination power of 100%. The results indicated that coupling the PCA with the ATR-FTIR holds a great promise for forensic examination toward reliable identification of authentic and forged documents.

#### 5. Conflicts of interest

There are no conflicts to declare.

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