*Research Article*

# Chemical Research and Technology

# Forensic examination and comparison of blue colored pen inks commercially sold in Nigeria using spectroscopic and chromatography method

Ogochukwu Ifeagwu[1], Uche Eunice Ekpunobi[1], Daniel Omeodisemi Omokpariola[1]*, Daniel Eliagwu Enenche[1]

*[1] Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Nigeria*

ARTICLE INFO

ABSTRACT

The evaluation of pen inks used in written document has created enormous financial threats and other issues over the decade due to lack of forensic databank to examine fraudulent activities perpetrated with pen ink in Nigeria. In this study, twenty (20) blue pens composed of 10 ballpoint pens, 9 rollerball pens and 1 fountain pen were extracted to conduct forensic examination and comparison using Ultraviolet–visible spectroscopy (UV-Vis), Thin layer chromatography (TLC) and Fourier transformed infrared spectroscopy (FTIR) as the analytical results were assessed for deviation or comparison using discrimination power (DP) and principal component analysis (PCA). The DP results of UV-Vis., TLC and FTIR were significant at 93.33%, 97.77% and 77.77% for blue ballpoint pens, as blue rollerball pens were significant at 100%, 97.22% and 86.11% respectively. The PCA results of UV-Vis., TLC and FTIR formed 6, 10 and 6 clusters for blue ballpoint pens, as blue roller pens had 9, 3 and 6 clusters. DP and PCA were not conducted due to limited sample size but it will serve as a reference guide for forensic evaluation and comparison. Overall, UV-Vis., TLC and FTIR results were similar and vice versa, across samples, which gives absorption band, composition and colour spectra. The study has confirmed that pen ink examination remains an interesting area to mitigate forgery in Nigeria..

## 1. Introduction

According to section 465 of Nigeria's criminal code Act states that "*A person who makes a false document or writing knowing it to be false and with intent that it may in any way be used or acted upon as genuine, whether in the state or elsewhere, to the prejudice of any person or with intent that any person in the belief that it is genuine be induced to do or refrain from doing any act whether in the state or elsewhere is said to forge the document or writing*" [1-3]. Forgery has been prevalent in all institution in Nigeria and beyond, which has made various institutions to create further authenticating measure that has been further made forgers sophisticated in their misdeeds. Forgery can be in various forms such as imitation someone signature,

forging letters or certificates, altering government issued passport or identity cards or driver's license, counterfeiting financial instruments (currencies, cheques, stock and shares certificates) and duplicating other documents (patents, medical prescription, wills). Although there are punishments for forgery or forging documents in Nigeria and beyond, this has not mitigated these menace as it is perpetrated using inks [2, 4]. The evaluation of inks used in issued document has potential to establish connection between authentic and forged documents using forensic tools, which determines the chemical composition of inks [5-7]. Different forensic methods have been developed and adopted to evaluate documents that is divided into destructive and non-destructive. Destructive methods include thin layer chromatography [5,8-11], capillary electrophoresis [8,12], mass spectrometry [13-15], ultra violet – visible

spectroscopy [16-19], while non-destructive methods are luminescence spectrometry [20, 21], Fourier transformed infrared spectroscopy [22, 23] Raman spectroscopy [23], X-ray fluorescence [24, 25], image processing using software tools (digital microscope, Adobe Photoshop and Picasa) [13, 26-28].

Inks are made from a variety of materials such as dyes, resins, pigments, lubricants, emulsifiers and other additives as the composition and manufacturing processing are useful in production of different type of pens, which include water based pens and oil soluble pens [8, 29-31]. The type of pen applied on a written document possesses potential in detecting deviation and discrepancy as literature reviews has shown that crime and forgery has strong correlation with pen utilization [30, 32-35]. The purpose of this study it to carryout forensic discrimination of ballpoint pens, rollerball pens and fountain pens used in Nigeria as data are limited to the best of our knowledge using analytical tools such as ultraviolet visible spectroscopy, Fourier transformed infrared spectroscopy and thin layer chromatography. In addition, carry out statistical assessment such as discrimination potential and principal component analysis, which will assist relevant government and private stakeholders involved in forensic studies.

## Materials and Methods
### Samples Collection
A total of twenty blue pen inks of different brands of ballpoint pens and rollerball pens and fountain pens, commercially used in Nigeria were acquired from Onitsha main market of Anambra state, Nigeria, which were assigned sample code as presented in **Table 1**.

### Sample Preparation
Ballpoint and Roller ball ink samples were prepared by shading the ink onto an area of 1cm x 5 cm on a white A4 writing paper [13, 16]. The paper was then soaked in 100 mL of methanol in a test tube, which were extracted totally as blank paper were treated with methanol with sample procedure to quantify the matric effect [37, 38]. Fountain inks were applied on a white A4 writing paper of same dimension (1cm x 5 cm) and allowed to dry for 25 minutes, which were extracted using distilled water as solvent in a test tube; same procedure were done using blank paper as control to compare effect of the matrix [34].

### Instrumentation
The discrimination of pen ink sample was carried out using UV-Visible Genisys spectrometer, thin layer chromatography equipped with developing tank and Agilent FTIR spectrometer as the procedures for each instrument differ from others.

Samples for ultraviolet visible spectroscopy were prepared by transferring 10 $\mu$L ink extracts into separate sample vial and thereafter diluted with 3.5mL diluted water. The results were recorded in the spectral range of 200 – 800nm with quartz cell having path length of 1cm used to measure absorbance of all samples [10, 18].

Thin layer chromatography was done by applying ink extract on a TLC plate (silica gel) using a capillary tube of 0.5mm with dimension (5cm $\times$ 20cm). Diverse solvent solution was tried for the experiment to achieve better elution using ethyl acetate: ethanol: ammonia (70:35:30 v/v); butanol: acetic acid: distilled water (60:15:25 v/v); butanol: ammonia: distilled water (60: 15: 25 v/v) and n-butanol: ethanol: distilled water: acetic acid (18:2:2:1 v/v). The samples were placed in a developing tank with the different solvents and closed tightly for 30 minutes as the procedure were repeated five times to obtain better colour separation and retention factor (Rf). The chromatograms were removed from the developing tank and allowed to dry, then examined under incident daylight [34, 39-41]. The Rf value were calculated using the formula:

$$Rf = \frac{\text{Distance travelled by solute}}{\text{Distance travelled by the solvent front}} \quad (1)$$

Infrared analysis was conducted on ink extracts within spectral range of 4000cm$^{-1}$ – 650cm$^{-1}$. 10 $\mu$L methanolic ink extracts (ballpoint and rollerball pens) were added to 100mg of potassium bromide (KBr) powder, which were ground and allowed to dry, thereafter, pressed into KBr disc with 5 tonnes pressure and allowed to run [10, 32, 42]. Similar quantity (10 $\mu$L) of water ink extract (fountain pen) were directly spotted on diamond crystal area (Attenuated Total Reflectance, ATR accessory) and allowed to run [34, 43].

### Statistical Analysis
Two statistical tools were used to analyse instrumental results such as discriminating power (DP) and principal component analysis (PCA).

Discriminating power (DP) were calculated according to Lee *et al.* equation [44]:

$$\text{DP} = \frac{\text{Number of samples (n)}}{\text{Total number of possible samples}} \quad (2)$$

Where:

n = number of samples

Total number of possible sample pairs $= \frac{n(n-1)}{2}$

Discriminating power (DP) is significant if the result is greater than 0.9 or 90% and vice versa (rejected) if less than 0.9 or 90%.

| S/N | Name of pen | Sample Code | Type of Pen |
|---|---|---|---|
| 1 | Papilon | S1 | Ballpoint |
| 2 | Crystal original | S2 | Ballpoint |
| 3 | Normal biro | S3 | Ballpoint |
| 4 | Avanti Magna | S4 | Ballpoint |
| 5 | Lucky Corer | S5 | Ballpoint |
| 6 | Eezee | S6 | Ballpoint |
| 7 | Premium | S7 | Ballpoint |
| 8 | Crystal | S14 | Ballpoint |
| 9 | Ash | S17 | Ballpoint |
| 10 | White | S19 | Ballpoint |
| 11 | Slip biro | S8 | Roller-ball |
| 12 | Beifa R2via | S9 | Roller-ball |
| 13 | GP-2839 | S10 | Roller-ball |
| 14 | JC 368 | S11 | Roller-ball |
| 15 | Roller-tip | S12 | Roller-ball |
| 16 | Roller-ball blue | S13 | Roller-ball |
| 17 | Vip 908 | S15 | Roller-ball |
| 18 | Gp 2898 | S16 | Roller-ball |
| 19 | Gp 732 | S18 | Roller-ball |
| 20 | Yuan chang | S20 | Fountain |

**Table 2**: Ultraviolet – visible spectra results for ballpoint pen samples

| Peaks | S1 (nm) | S2 (nm) | S3 (nm) | S4 (nm) | S5 (nm) | S6 (nm) | S7 (nm) | S14 (nm) | S17 (nm) | S19 (nm) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 216.00 | 216.00 | 216.00 | 0.00 | 0.00 | 216.00 | 0.00 | 216.00 | 216.00 | 216.00 |
| 2 | 0.00 | 0.00 | 0.00 | 218.00 | 218.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 220.00 | 220.00 | 0.00 | 0.00 | 0.00 |
| 4 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 302.41 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 576.00 | 0.00 | 0.00 | 0.00 | 579.22 |
| 6 | 581.84 | 587.44 | 580.69 | 580.00 | 582.39 | 0.00 | 582.35 | 581.78 | 581.11 | 0.00 |
| 7 | 0.00 | 665.67 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

**Table 3**: Discriminating Power of ballpoint pen using Ultraviolet – visible spectroscopy

| n = total number of samples | Total number of sample pairs = n(n-1)/2 | Discriminating Pairs = total number | Non Discriminating pairs = total number | DP |
|---|---|---|---|---|
| 10 | (10×9)/2 = 45 | S1,S2; S1,S3; S1,S4; S1,S5; S1,S6; S1,S7; S1,S19; S2,S3; S2,S4; S2,S5; S2,S6; S2,S7; S2,S14; S2,S17; S2,S19; S3,S4; S3,S5; S3,S6; S3,S7; S3,S14; S3,S17; S3,S19; S4,S5; S4,S6; S4,S7; S4,S14; S4,S17; S4,S19; S5,S6; S5,S7; S5,S14; S5,S17; S5;S19; S6,S7; S6,S14; S6,S17; S6,S19; S7,S14; S7,S17; S7,S19; S14,S19; S17,S19 = 42 | S1,S14; S1,S17; S14,S17; =3 | 42/45 = 0.9333 |

DP: Discriminating Power

Principal Component Analysis (PCA) is a multivariate tool for large number of sample data, which loading plot of first principal component (PC1) and second principal component (PC2) is assessed to form clusters [45, 46]. PCA were applied on instrumentation results using Minitab version 18 statistical software to distinguish pen inks according to brand.

## Results and Discussion

The instrumental result of blue ink of ballpoint pen, roller ball pen and fountain pens were analyzed to provide forensic information.

### Ultraviolet visible spectroscopy

**Table 2** shows the result of ultraviolet-visible spectra analyzed for blue ballpoint pens presented in nanometer (nm). Sample S1, S14 and S17, a prominent absorption band appears at 581nm with a small shoulder at 216nm. However, this shoulder does not appear in samples S4, S5, S6, and S7. Another band at 587 nm and 665nm seen in sample S2 with small shoulder at 216nm. Samples S3 and S4 show bands at 580nm but different shoulders at 216nm and 218nm respectively. Sample S19 has band at 579 nm and a small shoulder at 216nm. In samples S5 and S7, absorbance band is seen at 582nm but had different shoulders at 218nm and 220nm respectively. Another band at 576nm and 302nm is seen in sample S6 with small shoulder at 220nm. Samples S1, S2, S3, S14, S17 and S19 show a minor peak at 216 nm while this peak is less significant in samples S4, S5, S6 and S7 have not shown that peak.

Discriminating power (DP) analyzed as shown in **Table 3**, produced 42 discriminating pairs and 3 non-discriminating pairs (S1,S14; S1,S17 and S14,S17) as DP value were significant at 0.93 (93.33%). Similar ballpoint pen assessment by Lee *et al.* [16] produced lower DP value of 72. 12% after assessing 48 blue ballpoint pens of 12 different brands accordingly.

Principal Component Analysis were applied to ultraviolet-visible absorption spectra obtained from all blue ballpoint pen as shown in **Figure 1** in order to distinguish between the pen inks according to their brands. The interpretation of the PCA were achieved using the loading plot of the first two principal components (PC1 versus PC2). As is evident in the loading plot, the ballpoint pen inks were successfully grouped into six (6) distinctive clusters corresponding to the ten (10) different ballpoint pen brands considered in this study. Cluster A constitute blue ballpoint pen inks of S1, S3, S14 and S17. This suggests that these pen inks are from the same brand. Cluster B, D, E and F

constitute blue ballpoint pen ink of S7, S2, S6 and 19 respectively. Cluster C constitute blue ballpoint pen inks of S4 and S5. The six distinctive clusters suggest that the blue ballpoint pen inks considered in this study are of different formulations except the cluster A and cluster C.

**Table 4** shows the result of ultraviolet-visible spectra analyzed for blue rollerball pens. Sample S8 depicts a large band at 574nm and at 216nm. Sample S9 had absorption band at 590nm, 353nm, 305nm and at 216nm, which does not appear in the UV spectrum of the rest of the samples except the band at 216nm. Samples S10 had band at 208nm, 329nm and 607nm, as sample S11 gave spectra band at 214nm, 330nm, 609nm and 704nm. Sample S12 has band at 216nm, 558nm and 593nm. Sample S13 shows bands at 202nm, 266nm and 602nm. Sample S15 has bands at 216nm, 264nm, 330nm, 608nm and 704nm. Sample S16 has bands at 267nm, 328nm and 607nm. Sample S18 has bands at 216nm and 608nm.
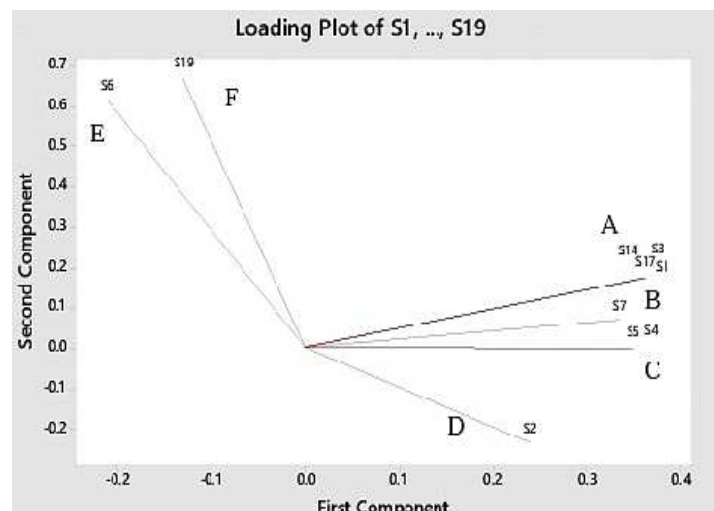


**Fig. 1**. Principal component analysis of UV-Vis. ballpoint pen

Discriminating power (DP) evaluated as shown in **Table 5**, depict that all sample pairs of rollerball pen inks were completely discriminated as non-discriminating pairs were absent. Therefore, the DP were significant at 100%, as Laser induced breakdown spectroscopy of blue rollerball pens by Kula *et al.* [29] showed that DP were 83%.

**Figure 2** displays principal component analysis (PCA) of blue roller ball pens, which produced nine (9) clusters. Cluster A, B, C, D, E, F, G, H and I constitute blue roller-ball pen inks of S11, S15, S13, S18 S16 S10, S8, S12 and S9 respectively.
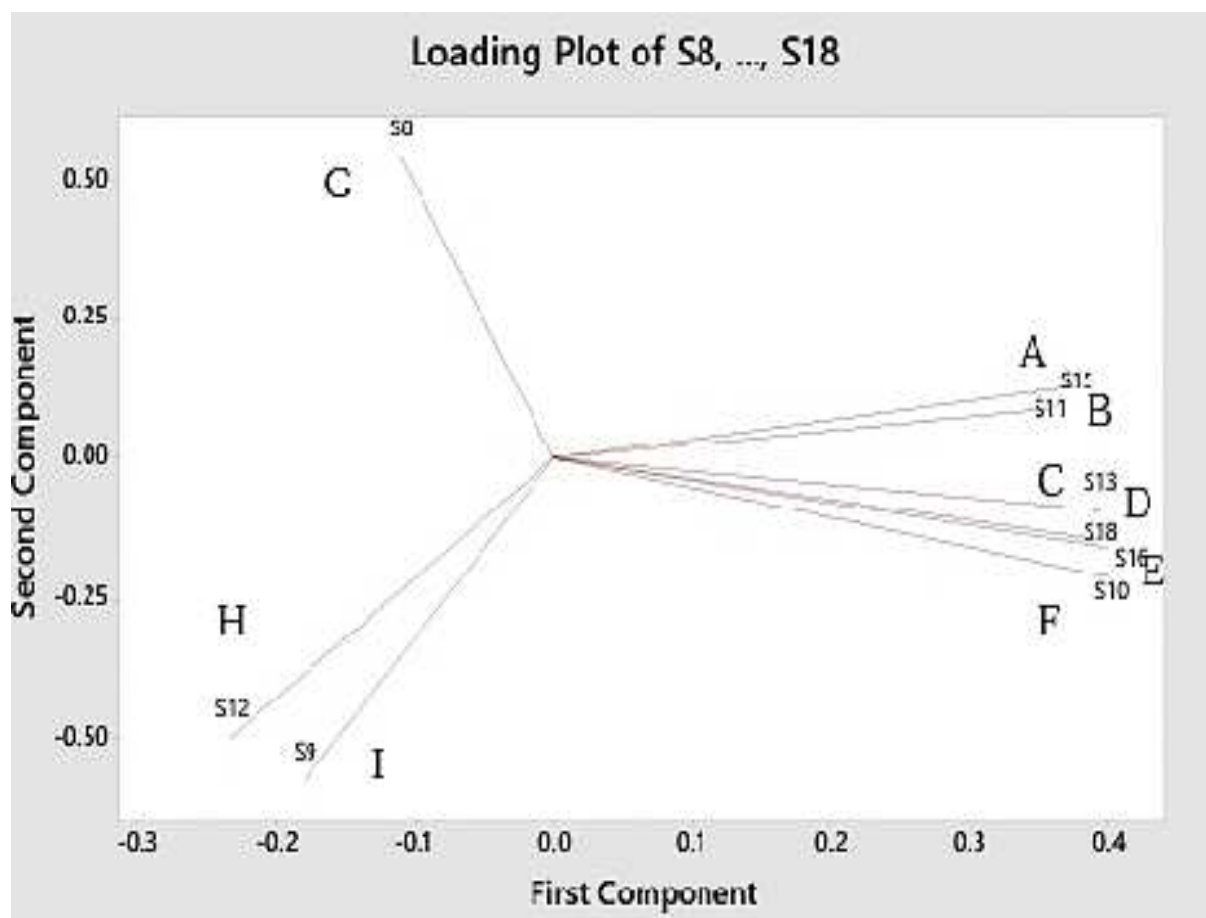
**Table 4**: ultra violet- visible spectra results for rollerball pen samples

| Peak | S8 (nm) | S9 (nm) | S10 (nm) | S11 (nm) | S12 (nm) | S13 (nm) | S15 (nm) | S16 (nm) | S18 (nm) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 216.00 | 216.00 | 208.00 | 214.00 | 216.00 | 202.00 | 216.00 | 0.00 | 216.00 |
| 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 266.00 | 264.88 | 267.44 | 0.00 |
| 3 | 0.00 | 305.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 4 | 0.00 | 353.50 | 329.18 | 330.35 | 0.00 | 0.00 | 330.03 | 328.81 | 0.00 |
| 5 | 574.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6 | 0.00 | 0.00 | 0.00 | 0.00 | 558.57 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 0.00 | 590.00 | 0.00 | 0.00 | 593.73 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 0.00 | 0.00 | 607.67 | 609.40 | 0.00 | 602.50 | 608.33 | 607.80 | 608.00 |

**Table 5**: Discriminating Power for rollerball pen using Ultraviolet – visible spectroscopy

| n = total number of samples | Total number of sample pairs = n(n-1)/2 | Discriminating Pairs = total number | Non Discriminating pairs = total number | DP |
|---|---|---|---|---|
| 9 | (9×8)/2 = 36 | S8,S9; S8,S10; S8,S11; S8,S12; S8,S13; S8,S15; S8,S16; S8,S18; S9,S10; S9,S11; S9.S12; S9.S13; S9,S15; S9,S16; S9,S18; S10,S11; S10,S12; S10,S13; S10,S15; S10,S16; S10,S18; S11,S12; S11,S13; S11,S15; S11,S16; S11,S18; S12,S13; S12,S15; S12,S16; S12,S18; S13,S15; S13,S16; S13,S18; S15,S16; S15, S18; S16,S18 = 36 | 0 | 36/36 = 1.0000 |

DP: Discriminating Power

**Figure 2**: Principal component analysis of UV-Vis. rollerball pen

**Table 6**: Ultraviolet – visible spectra results for fountain pen samples

| Peaks | S20 (nm) |
|-------|----------|
| 1 | 276.00 |
| 2 | 369.54 |
| 3 | 592.00 |

**Table 7**: TLC Rf results for ballpoint pen samples

| Sample ID | Blue (Rf) | Light blue (Rf) | Violet (Rf) |
|-----------|-----------|-----------------|-------------|
| S1 | - | 0.7 | 0.85 |
| S2 | - | 0.08 | 0.75 |
| S3 | - | 0.16 | 0.44 |
| S4 | 0.52 | - | 0.53 |
| S5 | 0.46 | - | 0.60 |
| S6 | 0.45 | - | 0.63 |
| S7 | - | 0.88 | 0.688 |
| S14 | - | - | 0.682 |
| S17 | - | 0.67 | 0.73 |
| S19 | 0.82 | 0.86 | 0.93 |

The nine distinctive clusters suggest that the blue roller-ball pen inks considered in this study are of different formulations.

**Table 6** shows results of ultraviolet-visible spectra of blue fountain pen analyzed. The spectra band were 276nm, 369nm and 592nm. Since only one type of ink was available, discrimination power cannot be done as it can serve as a database for examination of document written with fountain pens.

**Thin layer chromatography**

TLC has been comprehensively used for regular forensic assessment due to its ease of use and low cost [8, 47]. TLC is used to discover ink extract differences, as it has proved to aid comparison of ink.

**Table 7** shows the TLC results of blue ballpoint pen. Thin Layer Chromatogram of blue ballpoint pen ink samples developed by ethyl acetate/ethanol/distilled water (70:35:30 v/v) solvent resolved better compared to other solvents producing bands of blue, sky blue, and violet colors with different Rf values. All samples had violet colour band with varying Rf values. Sample S19 showed the three colours which are blue, sky blue and violet as compared to other samples which had minimum of two colours respectively.

Discrimination power (DP) results produced discriminating pairs of 44, while non-discriminating pair of one (1) were prevalent for S5, S6 as shown in **Table 8**, which was significant at 97.77%. TLC values were higher than Lee *et al.* [48] having 89.90% in 12 blue ballpoint of various brands.

**Figure 3** displays PCA conducted on TLC, Rf results obtained for ballpoint pen produced 10 clusters suggesting that the pen inks were of different formulations. Cluster A, B, C, D, E, F, G, H, I and J constitute blue ballpoint pen ink of S7 S17, S1, S14, S3, S19, S2, S6, S5 and S4 respectively.

**Table 9** depicts TLC analyzed on rollerball pen. The chromatogram of blue rollerball pen showed that ethyl acetate/ethanol/distilled water (70:35:30 v/v) solvent produced good colour bands of blue, sky blue, and violet colors with different Rf values. No Sample showed the three colours bands which are blue, sky blue and violet, as light blue was prevalent across all samples except for S9 and S12. DP conducted on TLC results as reproduced in **Table 10** showed that discriminating pairs and non-discriminating pairs were 35 and 1 pairs that is significant at 97.22%.

**Figure 4** shows PCA applied to thin layer chromatographic, Rf results attained rollerball pen, which gave three clusters. Cluster A constitutes blue rollerball pen ink of S10, S11, S13, S15, S16 and S18, as cluster B for S8 and cluster C gave S9 and S12. The three distinctive clusters suggest that the blue roller-ball pen inks considered in this study are of different formulations except cluster A, which had similar homogeneous clusters respectively.

**Table 11** shows TLC analyzed on fountain pen. Chromatogram of blue fountain pen sample showed that butanol/acetic acid/distilled water (60:25:25 v/v) solvent combination produced two colour band (blue and sky blue). Discrimination power and principal component analysis cannot be conducted due to limited sample size, but will serve as a database for forensic investigation.

**Fourier Transform Infrared Spectroscopy**

Fourier Transform Infrared (FTIR) Spectroscopy is the instrument used to characterize the functional group of the extracted inks, which forms discrimination due to position, number and intensities of peaks [41, 49]. The IR spectrum of inks give an entire composition of the mixture that makes it easy for compound identification through fingerprint region (less than 1500 cm$^{-1}$) and functional group (greater than 1500 cm$^{-1}$) [32, 34, 50].

**Table 8**: Discrimination Power of ballpoint pen using TLC

| n = total number of samples | Total number of sample pairs = n(n-1)/2 | Discriminating Pairs = total number | Non Discriminating pairs = total number | DP |
|---|---|---|---|---|
| 10 | (10×9)/2 = 45 | S1,S2; S1,S3; S1,S4; S1,S5; S1,S6; S1,S7; S1,S14; S1,S17; S1,S19; S2,S3; S2,S4; S2,S5; S2,S6; S2,S7; S2,S14; S2,S17; S2,S19; S3,S4; S3,S5; S3,S6; S3,S7; S3,S14; S3,S17; S3,S19; S4,S5; S4,S6; S4,S7; S4,S14; S4,S17; S4,S19; S5,S7; S5,S14; S5,S17; S5;S19; S6,S7; S6,S14; S6,S17; S6,S19; S7,S14; S7,S17; S7,S19; S14,S17; S14,S19; S17,S19 = 44 | S5,S6 = 1 | 44/45 = 0.9777 |

DP: Discriminating Power
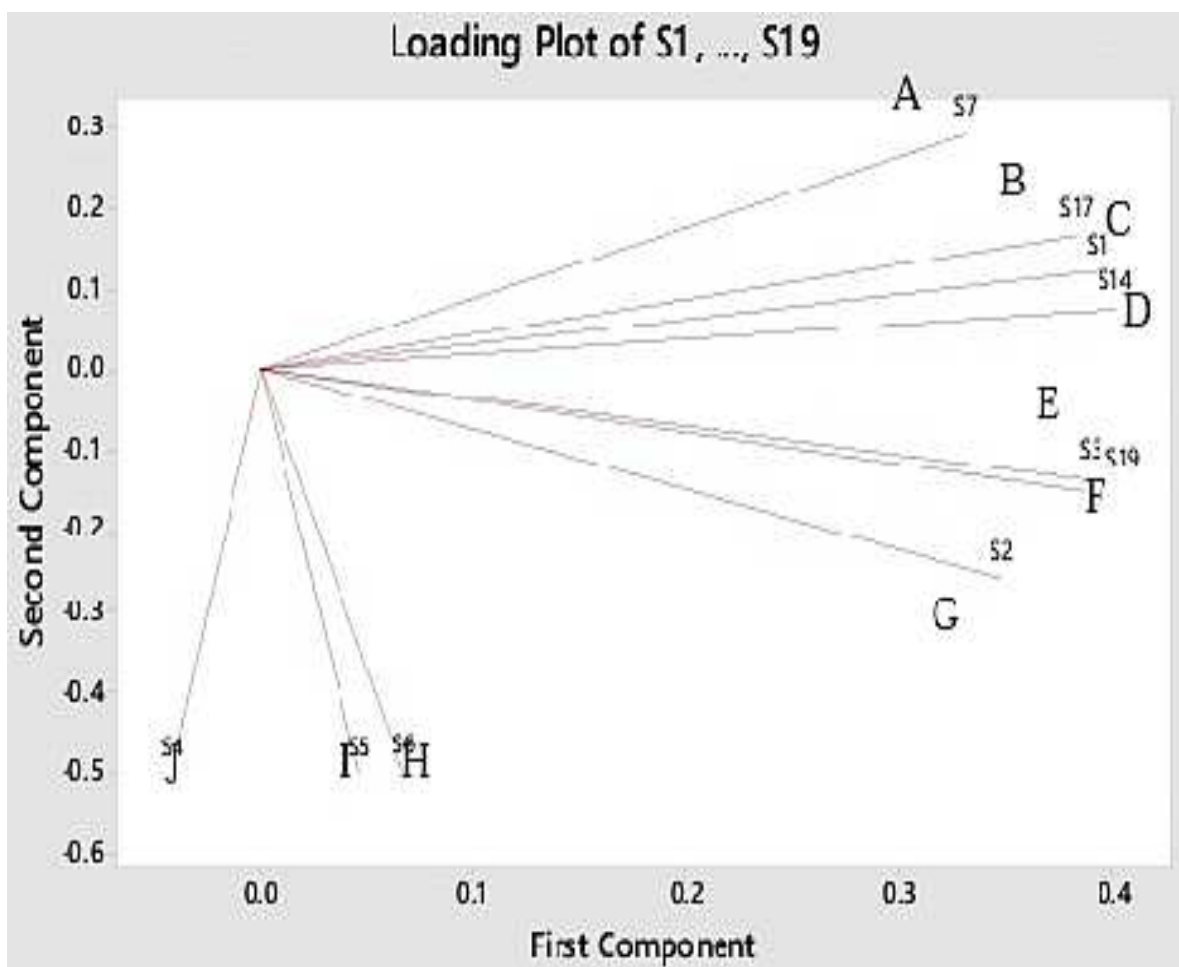


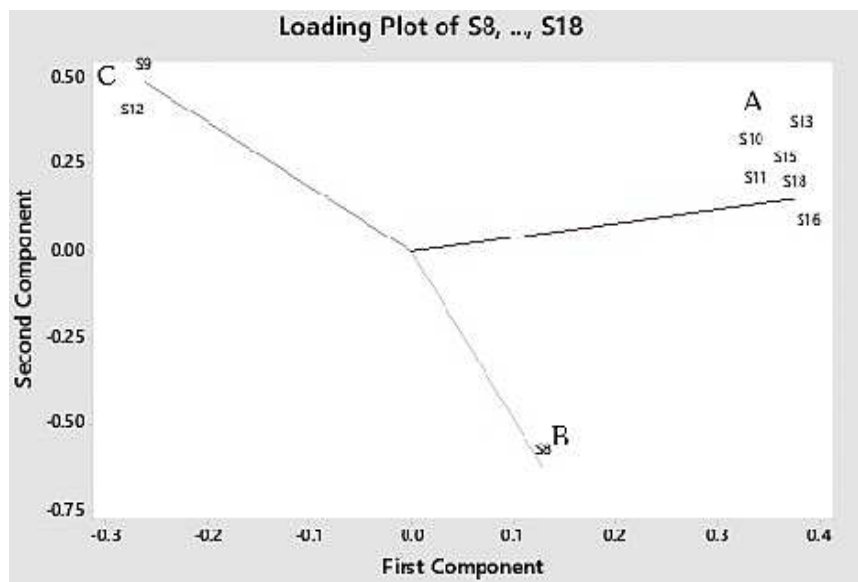**Figure 3**: Principal component analysis of TLC ballpoint pen

**Table 9**: TLC Rf results for rollerball pen samples

| Sample ID | Blue (Rf) | Light blue (Rf) | Violet (Rf) |
|---|---|---|---|
| S8 | - | 0.25 | 0.42 |
| S9 | 0.6 | - | - |
| S10 | - | 0.1 | - |
| S11 | - | 0.2 | - |
| S12 | 0.48 | - | - |
| S13 | - | 0.29 | - |
| S15 | - | 0.44 | - |
| S16 | - | 0.25 | - |
| S18 | - | 0.33 | - |

**Table 10**: Discrimination Power of rollerball pen using TLC

| n = total number of samples | Total number of sample pairs = n(n-1)/2 | Discriminating Pairs = total number | Non Discriminating pairs = total number | DP |
|---|---|---|---|---|
| 9 | (9×8)/2 = 36 | S8,S9; S8,S10; S8,S11; S8,S12; S8,S13; S8,S15; S8,S16; S8,S18; S9,S10; S9,S11; S9.S12; S9,S13; S9,S15; S9,S16; S9,S18; S10,S11; S10,S12; S10,S13; S10,S15; S10,S16; S10,S18; S11,S12; S11,S13; S11,S15; S11,S16; S11,S18; S12,S13; S12,S15; S12,S16; S12,S18; S13,S15; S13,S18; S15,S16; S15, S18; S16,S18 = 35 | S13,S16 = 1 | 35/36 = 0.9722 |

DP: Discriminating Power


Loading Plot of S8, .., S18

**Figure 4**: Principal component analysis of TLC rollerball pen

**Table 11**: TLC Rf results for rollerball pen samples

| Sample ID | Blue (Rf) | Light blue (Rf) | Violet (Rf) |
|---|---|---|---|
| S20 | 0.69 | 0.92 | - |

**Table 12**: FTIR results for ballpoint pen samples

| Peak | S1 (cm$^{-1}$) | S2 (cm$^{-1}$) | S3 (cm$^{-1}$) | S4 (cm$^{-1}$) | S5 (cm$^{-1}$) | S6 (cm$^{-1}$) | S7 (cm$^{-1}$) | S14 (cm$^{-1}$) | S17 (cm$^{-1}$) | S19 (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3313.6 | 3313.6 | 3317.3 | 3328.5 | 3317.3 | 3313.6 | 3317.3 | 3317.3 | 3313.6 | 3328.5 |
| 2 | 2940.9 | 2940.9 | 2940.9 | 2940.9 | 2940.9 | 2937.1 | 2940.9 | 2937.1 | 2940.9 | 2940.9 |
| 3 | 2829.0 | 2829.0 | 2829.0 | 2829.0 | 2829.0 | 2825.3 | 2829.0 | 2829.0 | 2829.0 | 2829.0 |
| 4 | 0.0 | 2516.0 | 2527.1 | 0.0 | 0.0 | 0.0 | 2005.3 | 0.0 | 0.0 | 2523.4 |
| 5 | 0.0 | 1736.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 6 | 1654.9 | 1654.9 | 0.0 | 0.0 | 0.0 | 0.0 | 1654.9 | 0.0 | 0.0 | 1654.9 |
| 7 | 1446.2 | 1446.2 | 1446.2 | 1446.2 | 1446.2 | 1446.2 | 1446.2 | 1446.2 | 1446.2 | 1446.2 |
| 8 | 1408.9 | 1408.9 | 1416.4 | 1416.4 | 1416.4 | 1408.9 | 1416.4 | 1416.4 | 1416.4 | 1412.7 |
| 9 | 0.0 | 1215.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 10 | 1110.7 | 1110.7 | 1114.5 | 1114.5 | 1114.5 | 1110.7 | 1114.5 | 1114.5 | 1114.5 | 1110.7 |
| 11 | 1021.3 | 1021.3 | 1021.3 | 1021.3 | 1021.3 | 1021.3 | 1021.3 | 1021.3 | 1021.3 | 1021.3 |

**Table 13**: Discrimination Power of ballpoint pen using FTIR

| n = total number of samples | Total number of sample pairs = n(n-1)/2 | Discriminating Pairs = total number | Non Discriminating pairs = total number | DP |
|---|---|---|---|---|
| 10 | (10×9)/2 = 45 | S1,S2; S1,S3; S1,S4; S1,S5; S1,S6; S1,S7; S1,S14; S1,S17; S1,S19; S2,S3; S2,S4; S2,S5; S2,S6; S2,S7; S2,S14; S2,S17; S2,S19; S3,S4; S3,S5; S3,S6; S3,S7; S3,S14; S3,S17; S3,S19; S4,S7; S4,S19; S5,S7; S5;S19; S6,S7; S6,S19; S7,S14; S7,S17; S7,S19; S14,S19; S17,S19 = 35 | S4,S5; S4,S14; S4,S17; S4,S6; S5,S6; S5,S14; S5,S17; S6,S14; S6,S17; S14,S17; = 10 | 35/45 = 0.7777 |

DP: Discriminating Power



Loading Plot of S1, ..., S19

31
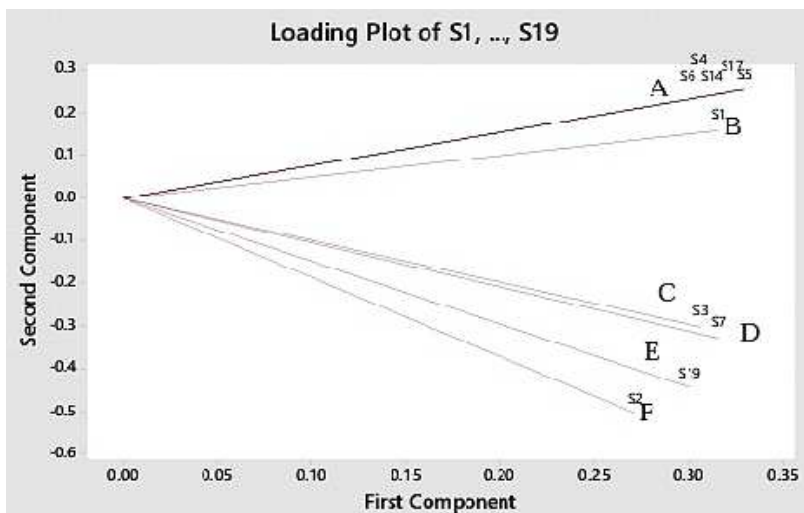
**Figure 5**: Principal component analysis of FTIR ballpoint pen

FTIR absorption peak for blue ballpoint pen inks shown in **Table 12** were compared with infrared standard [51, 52]. Peak 1 produced medium broad band attributed to N-H group in amines [52]. Peak 2 and 3 is due to C–H stretch around range of (2829 – 2825.3 cm$^{-1}$) and (2940.9 – 2937.1 cm$^{-1}$) across all samples [51]. Peak 4 were noticeable in S2, S3, S7 and S19 having 2516.0 cm$^{-1}$, 2527.1 cm$^{-1}$, 2005.3 cm$^{-1}$ and 2523.4 cm$^{-1}$, due to presence of weak –OH stretch in carboxylic acid and its derivatives or C≡N in inorganic form of cyanide, thiocyanates and cyanates [51, 52]. S2 in Peak 5 showed =C=O stretch at 1736.9 cm$^{-1}$ due to carbonyl group in aldehydes, ketones and carboxylic acid [51] Peak 6 (S1, S2, S7, S19) is due to N-H group or carboxylic acid derivatives [51]. Peak 7 for all samples were similar at 1446.2 cm$^{-1}$ and dissimilar in Peak 8 can be associated to C-C stretch or C-H bending or =CO stretch in carbonates (CO$_3^{2-}$), esters (RCOO$^-$) and secondary alcohol (R$_2$–COH) [51]. Peak 10 and 11 can be attributed to Carbonyl compounds (alcohol, aldehydes, ketones, carboxylic, ester) or Sulphur compounds (sulphoxides, sulphones, sulphites, sulphates, sulphonamides) or organophosphates or organosilicates [51].

**Table 13** shows discrimination power conducted on ballpoint pen ink. Discrimination pairs and non-discrimination pairs formed 35 and 10 pairs, which was significant at 77.77%. Similar FTIR study by Lee *et al.* [49] produced higher DP value of 86.67% in black ballpoint pen ink.

Principal Component Analysis applied to FTIR results were distinguish between the pen inks according to their brands as shown in **Figure 5**. PCA were grouped into 6 clusters; cluster A produced homogeneous group of S4, S5, S6, S14 and S17, which were similar [53]. Cluster B, C, D, E and F constitute blue ballpoint pen ink of S1, S3, S7, S19 and S2 that were heterogeneous in form [53].

**Table 14** shows FTIR results of rollerball pens in 9 brands using literature standard [51, 52]. Peak 1 formed very broad band with range of 3257.7 – 3332.2 cm$^{-1}$ that is ascribed to –OH group (carboxylic acid) for S8, S10, S11, S13, S15, S16

and S17 only, while S9 and S12 were due to N-H group (amines and imines) [52]. Peak 2 were associated to carboxylic acid (OH stretch) or imines (N-H stretch) [52]. Peak 3 band were noticeable in S9, S12 and S18 only as Peak 4 were evident in S8, S9, S10 and S18 that can be associated to the presence of C-H stretch [51]. Peak 5 were visible in all samples except S9 and S12, which is connected to N-H bend or C=N stretch [51]. Peak 6 ranged between 1423.8 – 1449.9 cm$^{-1}$ in S8, S9, S10, S12 and S18 due to C=O stretch, which is in close connection to Peak 7 [51]. Peak 8, 9 and 10 showed absorption peaks at S8 and S10 only due to N-O stretch, N≡N stretch or C=S stretch [52]. Peak 11 were evident in S8, S9, S10, S12 and S18 due to fluoroalkanes (C-F stretch) [51]. Peak 12 is associated to aliphatic amines (≡C-N≡ vibration) in S8 and S12 at 1051.1 cm$^{-1}$ [51]. Peak 13 were present in S8, S9, S11, S12, S13 and S18 due to S=O stretch (sulphoxides, sulphonic acid). Peak 14 were visible in S8 and S12 is associated to aromatic compound via –CH deformation of 1 free hydrogen atom [51]. Peak 15 were present in S8 (872.2 cm$^{-1}$), which is due to aromatic compound (-CH deformation of 2 adjacent free hydrogen atoms) or carbonyl group (carboxylic acid) or alkene (-CH deformation out –of–phase) [51].

Discrimination power (DP) were applied on IR spectra for rollerball pen inks as shown in **Table 15**. DP produced discriminating pairs and non-discriminating pair having 31 and 5 pairs, which were significant at 86.11%.

Principal Component Analysis (PCA) conducted on FTIR results of rollerball pen ink as shown in **Figure 6** to distinguish between the pen inks according to their brands. PCA were successfully aggregated into six (6) clusters, having two homogeneous clusters (A and B) and four heterogeneous clusters (C, D, E and F). Cluster A constitute were similar to S8 and S10, as cluster B were similar to S11, S15 and S16, which suggest that pen inks formulation is of similar composition. Cluster C, D, E and F constitute blue roller-ball pen inks of S13, S12, S18 and S9, which mean that pen inks formulations were of different composition respectively [41, 54].

**Table 14**: FTIR results for rollerball pen samples

| Peak | S8 (cm⁻¹) | S9 (cm⁻¹) | S10 (cm⁻¹) | S11 (cm⁻¹) | S12 (cm⁻¹) | S13 (cm⁻¹) | S15 (cm⁻¹) | S16 (cm⁻¹) | S18 (cm⁻¹) |
|------|-----------|-----------|------------|------------|------------|------------|------------|------------|------------|
| 1 | 3328.5 | 3317.3 | 3332.2 | 3261.4 | 3313.6 | 3265.1 | 3283.8 | 3287.5 | 3257.7 |
| 2 | 3283.8 | 0.0 | 3291.2 | 0.0 | 2940.9 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3 | 0.0 | 2937.1 | 0.0 | 0.0 | 2829.0 | 0.0 | 0.0 | 0.0 | 2948.3 |
| 4 | 2899.9 | 2829.0 | 2896.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2840.2 |
| 5 | 1636.3 | 0.0 | 1636.3 | 1636.3 | 0.0 | 1632.6 | 1632.6 | 1636.3 | 1640.0 |
| 6 | 1423.8 | 1446.2 | 1423.8 | 0.0 | 1446.2 | 0.0 | 0.0 | 0.0 | 1449.9 |
| 7 | 0.0 | 1416.4 | 0.0 | 0.0 | 1416.4 | 0.0 | 0.0 | 0.0 | 1405.2 |
| 8 | 1367.9 | 0.0 | 1371.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 9 | 1244.9 | 0.0 | 1200.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 10 | 1159.2 | 0.0 | 1159.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 11 | 1107.0 | 1114.5 | 1103.3 | 0.0 | 1114.5 | 0.0 | 0.0 | 0.0 | 1110.7 |
| 12 | 1051.1 | 0.0 | 1051.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 13 | 1025.0 | 1021.3 | 0.0 | 1013.8 | 1021.3 | 1031.8 | 0.0 | 0.0 | 1013.8 |
| 14 | 894.6 | 0.0 | 898.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 15 | 872.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

**Table 15**: Discrimination Power of rollerball pen using FTIR

| n = total number of samples | Total number of sample pairs = n(n-1)/2 | Discriminating Pairs = total number | Non Discriminating pairs = total number | DP |
|------|------|------|------|------|
| 9 | (9×8)/2 = 36 | S8,S9; S8,S11; S8,S12; S8,S13; S8,S15; S8,S16; S8,S18; S9,S10; S9,S11; S9,S13; S9,S15; S9,S16; S9,S18; S10,S11; S10,S12; S10,S13; S10,S15; S10,S16; S10,S18; S11,S12; S11,S15; S11,S16; S11,S18; S12,S13; S12,S15; S12,S16; S13,S15; S13,S16; S13,S18; S15, S18; S16,S18 = 31 | S8,S10; S9.S12; S11,S13; S12,S18; S15,S16 = 5 | 31/36 = 0.8611 |

DP: Discriminating Power

**Table 16**: FTIR results for fountain pen sample

| Peak | S20 (cm⁻¹) |
|------|-----------|
| 1 | 3313.6 |
| 2 | 2940.9 |
| 3 | 2829.4 |
| 4 | 1662.4 |
| 5 | 1446.2 |

| 6 | 1416.0 |
|---|--------|
| 7 | 1114.5 |
| 8 | 1021.3 |
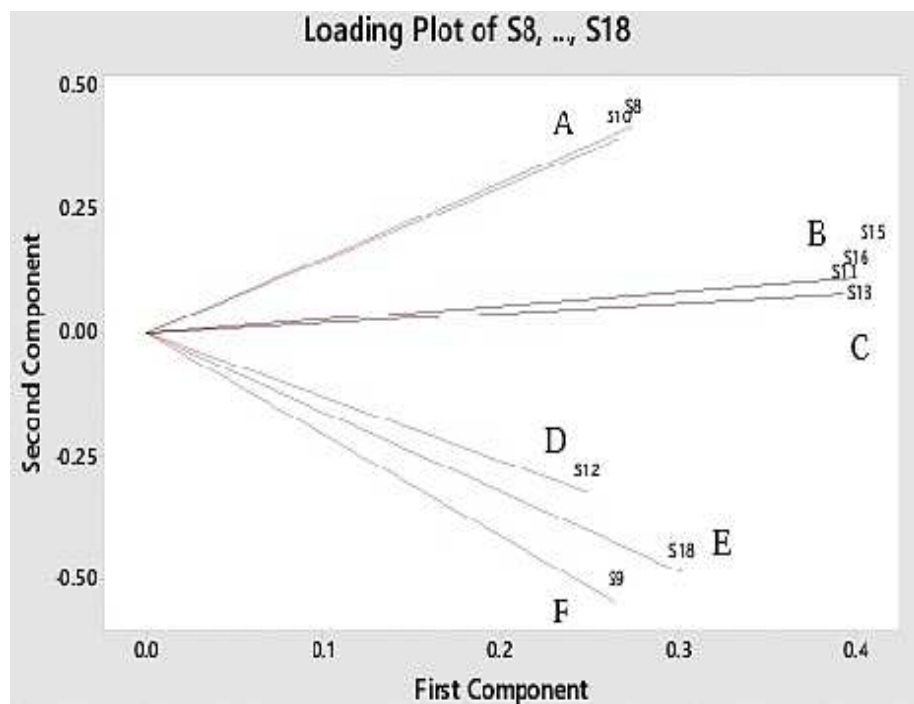


**Figure 6**: Principal component analysis of FTIR rollerball pen

**Table 16** shows FTIR results of fountain pen analyzed that produced 7 peaks. Peak 1 showed medium broad band of N-H stretch (amines) at $3313.6$ cm$^{-1}$, as peak 2 and 3 gave medium C-H stretch (alkyl group) and weak C-H stretch (CH$_3$, CH$_2$ and CH) respectively [51]. Peak 4 displayed weak amino acid (NH$_3^+$ deformation) or unsaturated nitrogen compounds (-O-NO$_2$, nitrates) [51]. Peak 5 and 6 revealed medium C-H stretch (CH) [51]. Peak 7 produced weak alkyl group (CH$_3$, CH$_2$ and CH) or ester (C-O stretch) as peak 8 displayed sharp band attributed to organophosphates or organosilicates at $1021.3$ cm$^{-1}$ [51, 52].

Discrimination power and principal component analysis were not conducted due to low sample size as these can serve as reference in forensic examination of fountain pens.

**CONCLUSION**

Blue colored ballpoint, rollerball and fountain ink extracts were analyzed using ultraviolet – visible spectroscopy (UV-Vis), thin layer chromatography (TLC) and Fourier transformed infrared spectroscopy (FTIR). The results were evaluated for relationship and deviations using discrimination power (DP) and principal component analysis (PCA). UV-Vis results showed that DP were significant at 93.33% and 100% for blue ballpoint and rollerball pens, as PCA produced 6 and 9 clusters. For TLC, DP were significant at 97.77% and 97.22% with PCA having 10 and 3 clusters for blue ballpoint and roller ball pens. For FTIR, DP were 77.77% and 86.11%, while PCA had 6 clusters for both blue ballpoint and roller ball pens. Three pairs of blue ballpoint pen inks S1, S4; S1, S14; and S14, S17 were not discriminated by UV/Vis. and FTIR, but by applying TLC it was discriminated accordingly. Five pairs of blue roller-ball pen inks S8, S10; S9, S12; S11, S13; S12, S18; and S15, S16 were not discriminated by FTIR but

was discriminated by applying UV/Vis. and TLC. PCA conducted showed that UV/Vis. spectra for blue ballpoint pen inks, S1, S14 and S17 had similar formulation that while the UV/Vis. spectra for roller-ball pen inks showed no similarity in formulation. TLC for ballpoint had no similar formulation as compared to rollerball, which had higher similarity between S10, S11, S15, S16, and S18, and little similarity with S9 and S12. The FTIR spectra for ballpoint pens revealed similarity between S4, S5, S6, S14 and S17, while rollerball pens were similar for S11, S15 and S16. Due to limited sample size of fountain pen, DP and PCA were not conducted but will serve as a reference guide for forensic evaluation. Having assessed these analytical methods, one can draw salient points:

1. The chemical composition of any pen can be attained through functional group
2. The colour spectra can be determined using TLC, an inexpensive and efficient tool in the absence of spectroscopic tools
3. Discrepancies and deviations can be determined using discrimination power and principal component analysis to get pen significance and cluster arrangement
4. Scientific database can be created to accelerate forensic audits and examinations.

We recommend that future research should be conducted on black, red and green colored pens sold in Nigeria, and evaluate ink dating and degradation, as it will aid better forensic evaluation of any scenario.

**Funding:** None

**Data Availability**: Raw data from all laboratory procedures are available in supplementary material

**Declarations of interest:** The authors declare no conflict of interest regarding this article

**Reference**
1. The Tide News, Nigeria, Offense of Forgery. https://www.thetidenewsonline.com/2018/07/04/ offense-of-forgery-2/, 2018 (accessed 24 April 2021).
2. Infoguide, Nigeria, Punishment for Forgery under Nigerian Law. Infoguide Nigeria https://infoguidenigeria.com/punishment-forgery-nigerian-law, 2019 (accessed 24 April 2021).
3. Nigeria's Criminal Code Act of 2004, Nigeria, Criminal Code - Laws of the Federal Republic of Nigeria. https://www.lawyard.ng/wp-content/uploads/2015/11/CRIMINAL-CODE-ACT-2014.pdf, 2004 (accessed 24 April 2021).
4. Canada Immigration and Refugee Board of Canada, Nigeria: False documents available in Nigeria and from Nigeria, NGA104617.E, https://www.refworld.org/docid/52a82baf4.html, 2013 (Accessed 24 April 2021)
5. M. Sharif, M. Batool, S. Chand, S.H. Farooqi, S.A.A.S. Tirmazi, M. Athar, Forensic Discrimination Potential of Blue, Black, Green, and Red Colored Fountain Pen Inks Commercially Used in Pakistan, by UV/Visible Spectroscopy, Thin Layer Chromatography, and Fourier Transform Infrared Spectroscopy, Int. J. Anal. Chem. 5980967 (2019) 1-10. https://doi.org/10.1155/2019/5980967.
6. V. Sharma, R. Kumar, Fourier transform infrared spectroscopy and high performance thin layer chromatography for characterization and multivariate discrimination of blue ballpoint pen ink for forensic applications, Vib. Spec. 92 (2017) 96-104. https://doi.org/10.1016/j.vibspec.2017.05.006.
7. L.C. Lee, I.S.M. Yunus, W.N.S.W. Fuad, A.A. Ishak, K. Osman. Statistical Discrimination of Black Ballpoint Pen Inks Using UltraPerformance Liquid Chromatography with Principal Component Analysis, J. Anal. Chem. 70(3) (2015) 374-379. https://doi.org/10.1134/S1061934815030119.
8. R.P. Gorziza, C.M. Bello de Carvalho, M. González, L.B. Leal, T. Korndörfer, R.S. Ortiz, T. Trejos, R.P. Limberger, Blue and Black Ballpoint Pen Inks: a Systematic Review for Ink Characterization and Dating Analysis, Brazil J. For. Sci., Med. Law Bioethics 8(3) (2019) 113-138. http://dx.doi.org/10.17063/bjfs8(3)y2019113.
9. K. Saini, R. Rathore, Differentiation of Red and Black Ballpoint Pen Inks using High Performanc Thin Layer Chromatography and Gas Chromatography-Mass Spectrometry, J. For. Sci. For. Med. 1(7) (2018) 829-841. https://doi.org/10.26735/16586794.2018.011.
10. V. Sharma, R. Kumar, Fourier transform infrared spectroscopy and high performance thin layer chromatography for characterization and multivariate discrimination of blue ballpoint pen ink for forensic applications, Vib. Spec. 92 (2017) 96–104. https://doi.org/10.1016/j.vibspec.2017.05.006.
11. L.C. Lee, M.A. Hakim, A.A Ishak, The Analysis of Dyes in Black Ballpoint Pen Inks using High Performance Thin Layer Chromatography, Malaysian J. For. Sci. 5(2) (2014) 22-26.
12. M. Calcerrada, M. González-Herráez, C.A. Garcia-Ruiz, A microdestructive capillary electrophoresis method for the analysis of blue-pen-ink strokes on office paper, J Chroma. A. 1400 (2015) 140–148. https://doi.org/10.1016/j.chroma.2015.04.036.
13. K. Saini, R. Rathore, Differentiation of Red and Black Ballpoint Pen Inks using High Performance Thin Layer

Chromatography and Gas Chromatography-Mass Spectrometry, Arab J For. Sci. & For Med. 1(7) (2018) 829-841. https://doi.org/10.26735/16586794.2018.011.

14. F. Alamilla, M. Calcerrada, C. García-Ruiz, M. Torre. Forensic discrimination of blue ballpoint pens on documents by laser ablation inductively coupled plasma mass spectrometry and multivariate analysis, For. Sci. Int. 249 (2013) 1–7. https://doi.org/10.1016/j.forsciint.2013.01.034.

15. O. Díaz-Santana, D. Vega-Moreno, F. Conde-Hardisson, Gas chromatography-mass spectrometry and high-performance liquid chromatography-diode array detection for dating of paper ink, J. Chroma A. 1515 (2017) 187–195. https://doi.org/10.1016/j.chroma.2017.07.093.

16. L.C. Lee, K.T.S. Shandu, N.S.M. Razi, A.A. Ishak, K. Osman, Forensic analysis of blue ballpoint pen inks using ultraviolet-visible spectrometer and ultra-performance liquid chromatograph, Malaysian J. Anal. Sci. 19(2), (2015) 397 – 401.

17. C. Neumann, R. Ramotowski, T. Genessay, Forensic examination of ink by high-performance thin layer chromatography — the United States Secret Service Digital Ink Library, J. Chroma. A., For. Sci. Int. 1218(19) (2011) 2793-2811.

18. D. Ismail, Z. Austad, W.N.S.M. Desa, Ultra-Violet and Visible (UV-VIS) Spectroscopy and Chemometrics Techniques for Forensic Analysis of Ballpoint Pen Inks: A Preliminary Study, Malaysian J. For. Sci. 5(1) (2014) 47-52.

19. D.L. Feraru, A. Meghea, Possibilities to Differentiate Ballpoint Pen Inks by Spectroscopic and Chromatographic Techniques. UPB Sci. Bull, 76(1) (2014) 113-126.

20. C.D. Adam. In situ luminescence spectroscopy with multivariate analysis for the discrimination of black ballpoint pen ink-lines on paper, For. Sci. Int. 182 (2008) 27–34. https://doi.org/10.1016/j.forsciint.2008.09.008.

21. R. Hofer, A.S.Y. Bako, Migration of luminescent ink components, a new approach for ink dating, For. Chem. 2 (2016) 75–81. https://doi.org/10.1016/j.forc.2016.10.006.

22. R. Kumar, V. Kumar, and V. Sharma, Fourier transform infrared spectroscopy and chemometrics for the characterization and discrimination of writing/photocopier paper types: Application in forensic document examinations, Spectrochimica Acta Part A: Mol. Biomol. Spec. 170 (2017) 1-19.

23. X.F. Wang, J. Yu, A.L. Zhang, D.W. Zhou, M.X. Xie, Nondestructive identification for red ink entries of seals by Raman and Fourier transform infrared spectrometry Spectrochimica Acta Part A: Mol. Biomol. Spec. 97 (2012) 986-995.

24. V. Causin, C. Marega, P. Carresi, S. Schiavone, A. Marigo, A quantitative differentiation method for plastic bags by wide angle X-ray diffraction for tracing the source of illegal drugs, For. Sci. Int. 168(1) (2007) 37–41.

25. H. Guo, B. Yin, J. Zhang, Y. Quan, G. Shi, Forensic classification of counterfeit banknote paper by X-ray fluorescence and multivariate statistical methods, For. Sci. Int. e43 (2016) 266–273.

26. N.J. Deitz, L. Quarino, Differentiation of Blue Gel Inks Using Adobe Photoshop, J. For. Sci. 60 (3) (2010) 291-307.

27. P. Dansena, R. Pal, S. Bag, Quantitative assessment of capabilities of colour models for pen ink discrimination in handwritten documents, IET Image Process. 14(8) (2020) 1594-1604 https://doi.org/10.1049/iet-ipr.2018.6616.

28. S.I. Sharaa, A.A. Aboul El-Magd, A.A. Bakr, Y.M. Moustafa, A.A Shabana, I.M. Abd El-Aziz, Some of the Physical and Chemical Characterizations Applied for the Laser Printers toner and Ballpoint Pen Inks to Determine the Sequence of their Intersections, Egypt. J. Chem. 62(11) (2019) 2047-2060. https://www.doi.org/10.21608/ejchem.2019.10960.1702.

29. A. Kula, R. Wietecha-Posłuszny, K. Pasionek, M. Król, M. Woźniakiewicz, P. Kościelniak, Application of laser induced breakdown spectroscopy to examination of writing inks for forensic purposes, Sci. Justice 54 (2014) 118–125.

30. S. Senior, H. Ezzat, M. Mamdouh, S. Eman, Characterization and Dating of Blue Ballpoint Pen Inks Using Principal Component Analysis of UV–Vis Absorption Spectra, IR Spectroscopy, and HPTLC, J. For. Sci. 57(4) (2012) 136-144.

31. M. Ezcurra M, J.G. Góngora, I. Maguregui, R. Alonso, Analytical methods for dating modern writing instrument inks on paper, For. Sci. Int. 197(1-3) (2010) 1-20.

32. C.S. Silva, S.L. Borba, M.F. Pimentel, M.J.C. Pontes, R.S. Honorato, C. Pasquini, Classification of blue pen ink using infrared spectroscopy and linear discriminant analysis, Microchemical J. 109, (2013) 122–127.

33. T.J. Wilkinson, D.L. Perry, M.C. Martin, W.R. McKinney, A.A. Cantu, Use of synchrotron reflectance infrared spectromicroscopy as a rapid, direct, nondestructive method for the study of inks on paper. Appl. Spec., 56 (2002) 800–803.

34. M. Sharif, M. Batool, S. Chand, S.H. Farooqi, S.A.A.S. Tirmazi, M. Athar, Forensic Discrimination Potential of Blue, Black, Green, and Red Colored Fountain Pen Inks Commercially Used in Pakistan, by UV/Visible Spectroscopy, Thin Layer Chromatography, and Fourier Transform Infrared Spectroscopy, Int. J. Anal. Chem. 5980967 (2019) 1-10. https://doi.org/10.1155/2019/5980967.

35. N.C. Thanasoulias, N.A. Parisis, N.P. Evmiridis, Multivariate chemometrics for the forensic discrimination of blue ball-point pen inks based on their Vis spectra, For. Sci. Int. 138(1-3) (2003) 75–84.

36. P. Devgan, V. Sharma, R. Kumar, K. Mishra, A. Ekielski, V. Kumar, Multivariate analysis for forensic characterization, discrimination, and classification of marker pen inks, Spec. Letters, 51(5) (2018) 205 - 211.

37. C.M. Bello de Carvalho, R.S. Ortiz, M. Reis, A. Zamboni, R.P. Limberger, M.F. Ferrão, G. Vaz Boniek, Characterization and Differentiation of Ballpoint Pen Ink Strokes on Paper Using Orbitrap Mass Spectrometry and Multivariate Statistic, For. Sci. Res. 2(2) (2018) 1-8. https://doi.org/10.31031/FSAR.2018.02.000537.

38. D. Akhmerova, A. Krylova, A. Stavrianidi, O. Shpigun O, Rodin I. Forensic Identification of Dyes in Ballpoint Pen Inks Using LC–ESI–MS. Chromatographia, 80 (2017) 1701–1709. https://doi.org/10.1007/s10337-017-3404-1.

39. D. Djozan, T. Baheri, G. Karimian, M. Shahidi, Forensic discrimination of blue ballpoint pen inks based on thin layer chromatography and image analysis, For. Sci. Int. 179 (2008) 199–205. https://doi.org/10.1016/j.forsciint.2008.05.013.

40. D.L. Feraru, A. Meghea, Possibilities to Differentiate Ballpoint Pen Inks By Spectroscopic and Chromatographic Techniques. UPB Sci. Bull. 76 (1) (2014) 113-126.

41. D.L. Feraru, A. Meghea, N. Badea, Forensic Discrimination of Ballpoint Pen Inks Based on Correlation of Data Obtained by Optical and Spectral Methods. Revista de Chimie. 64(1) (2013) 74-80.

42. M.N.M. Asri, W.N.S.M. Desa, D. Ismail, Fourier Transform Infrared (FTIR) Spectroscopy with Chemometric Techniques for the Classification of Ballpoint Pen Inks. Arab J. For. Sci. and For. Med., 1(2) (2015) 194-200.

43. Y.S. Nam, J.S. Park, Y. Lee, K.B. Lee, Application of Micro-Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy to Ink Examination in Signatures Written with Ballpoint Pen on Questioned Documents. J. For. Sci. 59(3) (2014) 800-805. https://doi.org/10.1111/1556-4029.12405.

44. L.C. Lee, S.M. Nunurung, A.A. Ishak, Forensic Analysis Of Blue Ballpoint Pen Inks On Questioned Documents By High Performance Thin Layer Chromatography Technique (HPTLC), Malaysian J. Anal. Sci. 18 (2) (2014) 226 – 233.

45. S. Senior, H. Ezzat, M. Mamdouh, S. Eman, Characterization and Dating of Blue Ballpoint Pen Inks Using Principal Component Analysis of UV–Vis Absorption Spectra, IR Spectroscopy, and HPTLC, J. For. Sci. 57(4) (2012) 136-144.

46. N. Muhammad, A. Mohamad, N. Wan, M.D. Syuhaila, I. Dzulkiflee, Fourier Transform Infrared (FTIR) Spectroscopy with Chemometric Techniques for the Classification of Ballpoint Pen Inks, Arab J. For. Sci. and For. Med. 1(2) (2015) 194-200.

47. C. Roux, M. Novotny, I. Evans, C. Lennard, A study to investigate the evidential value of blue and black ballpoint pen inks in Australia, For. Sci. Int. 101(3) (1999) 167–176.

48. L.C. Lee, S.M. Nunurung, A.A. Ishak, Forensic Analysis of Blue Ballpoint Pen Inks On Questioned Documents by High Performance Thin Layer Chromatography Technique (HPTLC). Malaysian J. Anal. Sci. 18 (2) (2014) 226 – 233.

49. L.C. Lee, M.R. Othman, H. Pua, Systematic assessment of attenuated total reflectance fourier transforms infrared spectroscopy coupled with multivariate analysis for forensic analysis of black ballpoint pen inks, Malaysian J. Anal. Sci. 16 (3) (2012) 262 – 272.

50. C.S. Silva, F.D.S.L. Borba, M.F. Pimentel, M.J.C. Pontes, R.S. Honorato, C. Pasquini, Classification of blue pen ink using infrared spectroscopy and linear discriminant analysis, Microchemical J. 109 (2013) 122–127.

51. A.K. Srivastava and P.C. Jain, Instrumental Approach to Chemical Analysis forth ed., S. Chand Publication New Delhi, 2013. ISBN: 81-219-1659-3.

52. P.Y. Bruice, Organic Chemistry. fifth ed., Pearson International Edition, New Jersey, United States, 2007. ISBN: 0-13-199631-2.

53. M. Kamil, M.N.B. Asrib, W.S.N.M. Desab, D. Ismail, Fourier Transform Infrared (FTIR) Spectroscopy and Principal Component Analysis (PCA) of Unbranded Black Ballpoint Pen Inks, Malaysian J. For. Sci. 6(1) (2015) 48-53.

54. H. Zou, Z. Wang, Z. Yee, R. Xu, R. Zhu, B. Wang, X. Gu, NACE Discrimination of Black Ballpoint Pen Inks, Chromatographia, 67(5-6) (2008) 483-486. https://doi.org/10.1365/s10337-008-0528-3