Mini-Review:

Trends of Forensic Analysis of Pen Ink Using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy

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Abstract: *Many articles have been published on ink analysis to assist Forensic Document Examiner (FDE) in examining questioned documents. Ink analysis encountered about 45% of ballpoint and 24% of gel pen in forensic cases. Typically, ink samples found on the documents are limited to small quantities, requiring non-destructive techniques to preserve the evidence. Previous studies on ink analysis cover about 80% of spectroscopy techniques, including the Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR). FDE prefers ATR-FTIR to retain the legibility of evidence since ATR-FTIR is known as non-destructive, fast, reliable, and precise instrumentation. Various modifications and developments to this technique have been published. Therefore, this work reviews the trend of analysis performed on samples of the document and evaluates the current approaches to the capacity of using ATR-FTIR on such samples. Remarks on the comparison studies are also included.*

Keywords: *document examination; Fourier Transform Infrared Spectroscopy; ink analysis; pen ink; spectroscopy technique*

■ INTRODUCTION

The forensic document examiner (FDE) is responsible for performing designated scientific methods on questioned documents. Questioned documents that are commonly investigated include cheques, passports, birth certificates, wills, and ransom or threat notes [1]. Document examination has various analyses such as ink, paper, handwriting, and security features. Ink analysis is usually performed by examining the physical and chemical characteristics of inks from the questioned document. According to Calcerrada and García-Ruiz [2], 72% of ink analyses were performed on ink differentiation, while the remaining included ink intersecting, ink dating, and ink composition analysis. Generally, pen inks are classified based on their formulations. For example, a gel pen contains dispersed pigments in a water-based solution, whereas a ballpoint pen traditionally consists of dyes in an oil-based solution as its colorants [3]. Numerous manufacturers are involved in the production of various inks, with each generating its own identity. Eventually, this complex composition would be a key point for FDE to narrow down and distinguish the inks. However, the differentiation process is limited to the type or brand of inks as their production would be made in the bulk formulation [4].

Depending on the analysis selected, some might ruin the natural state of the samples, as seen in chromatographic techniques. Most chromatography techniques (thin-layer chromatography; TLC, gas chromatography; GC and high-performance liquid chromatography; HPLC) involve the extraction of inks from the document using solvent by a process known as dissolution. Despite these techniques offering detailed chemical constituents, the consumption of samples during the analysis could destroy the integrity of the evidence. FDE needs an alternative non-destructive technique, fast analysis, accurate, and reliable to be presented to the court of law. Thus, this leads to FDE opting for spectroscopy techniques for ink analysis. Spectroscopic techniques utilize electromagnetic radiation interaction with matter and probe different molecular features of a sample to learn about its consistency or structure [5]. These methods require little to no sample preparation and sample and solvent consumption depending on the instrumentation used. Fourier transform infrared (FTIR) is one of the prominent spectroscopy techniques, especially in ink analysis. Trends of utilizing FTIR for ink analysis continue to increase yearly with multiple variations of a pen of ink used. Fig. 1 shows the percentage of types and colors of pen inks used in ink analysis of FTIR.

Based on Fig. 1, ink analysis involving FTIR instrument has led to about 45% use of ballpoint pens as the sample subject, followed by gel pens (24%) and fountain pens (10%). Rollerball, felt-tip, and marker pens have only 5% preferences, while only 3% of the analysis was conducted on the erasable pen. In terms of color, most studies included blue and black ink colors with a preference of 37% and 28%, respectively. On the other hand, 12% of the reviewed studies had preferences for red color, 6% for green color, while 15% did not mention the inks' color. These statistics are based on collecting several research papers [4,6-33]. These preference trends were made in consideration to simulate real FDE cases as close as possible to provide data that FDE can refer.

■ METHODOLOGY

The strategy for the research was done by exploring Google Scholar and Science Direct online databases with the keywords "ATR-FTIR". Inclusion criteria cover articles based on writing ink analysis, focusing on samples that include ballpoint and gel pen inks. Articles dated from the previous 10–15 years that fulfilled the criteria were reviewed to note any development or modifications performed by the authors to this particular technique.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. In addition, FTIR offers quantitative and qualitative analysis for organic and inorganic samples. FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information [34]. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for different components. Attenuated total reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) is an example of non-destructive analysis, which allows the examination without the need for prior sample preparation. ATR-FTIR analysis provided information on the ink's specific characteristics from its "fingerprint region" of the spectrum and proved to be an effective tool for characterizing complex ink formulation [27].

Theoretically, ATR-FTIR is a reflectance FTIR. The IR source reflects internally inside the ATR crystal and produces an evanescence wave. This incident wave can only extend around 0.5 to 5µm, which can only be

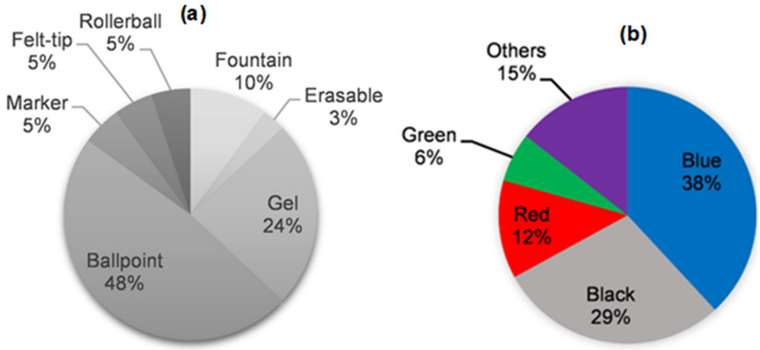

Fig 1. (a) Percentage of the preferred types and (b) Percentage of the preferred color of pen inks

directed onto the surface of the sample. For the transmission of FTIR, the sample is mixed with potassium bromide (KBr) powder to facilitate homogenization and produce a transparent film. KBr is inert to the IR region allowing the IR source to pass through the sample and collect its complete information. However, the thickness of the pressed sample of the transmission technique affects the path length of the FTIR signal; therefore, the reproducibility relies entirely on the sampling technique. In contrast, the ATR-FTIR technique has a higher reproducibility rate since it only requires the sample to be in contact with the ATR crystal. However, the overall FTIR technique has its drawbacks based on the difficulty of detecting nonpolar compounds. The similarity of functional groups in a compound could pose a problem, where their broad peaks may overlap [27].

Spectral absorption of FTIR

Through the spectrum range, 4000 to 675 cm^{-1} used in the study by Lee et al. [12], the region ranging from 4000 to 2000 cm^{-1} was disregarded as it was mainly contributed by the atmosphere's moisture and carbon dioxide as well as some weak yet broad bands from the inks. Some peaks around 3600 to 3000 cm^{-1} are usually the absorption of the NH_2 group from the ink. The wide OH band occasionally overlaps the peaks at regions 3600 to 3200 cm^{-1}, which may arise from the ink or atmospheric moisture [11,25]. Of six different types of black ballpoint pen inks studied by Lee et al. [12], each showed similar spectral patterns with the prominent peak at 1584 cm^{-1}; however, the peak's height and shapes exhibited some dissimilarities. According to Wang et al. [35], the skeletal vibration of triarylmethane dye of black ink and the C=C stretch vibration of epoxy resin is at about 1581 cm^{-1}, corresponding to the peak of 1584 cm^{-1}. Furthermore, CH_3 and CH_2 stretching bond vibrations were observed in 2900 to 2857 cm^{-1}, whereas N–O group was detected at 1380 cm^{-1} [25]. In the 1100 to 1000 cm^{-1} region, most peaks were sourced from the paper substrate [11,36]. The range between 1800 to 700 cm^{-1} is the fingerprint region of many inks constituents [20]. For example, the intense peak of ink samples is observed for carbonyl (C=O) in region 1725–1720 cm^{-1}, asymmetrical C–O–C vibrations at 940 cm^{-1}, and symmetrical C–O–C at 1170 cm^{-1} [25]. Fig. 2 shows the illustration of FTIR spectra.

Halim et al. [15] mentioned that based on the spectra of FTIR, the elemental analysis of inks could be performed by observing the position of peaks at a specific wavelength, which indicates the present functional group. However, it is difficult to manually discriminate the source of inks as most would have similar constituent functional groups. Gazy et al. [20] observed that the spectra between blue ballpoint and blue erasable pen inks had different peak patterns that

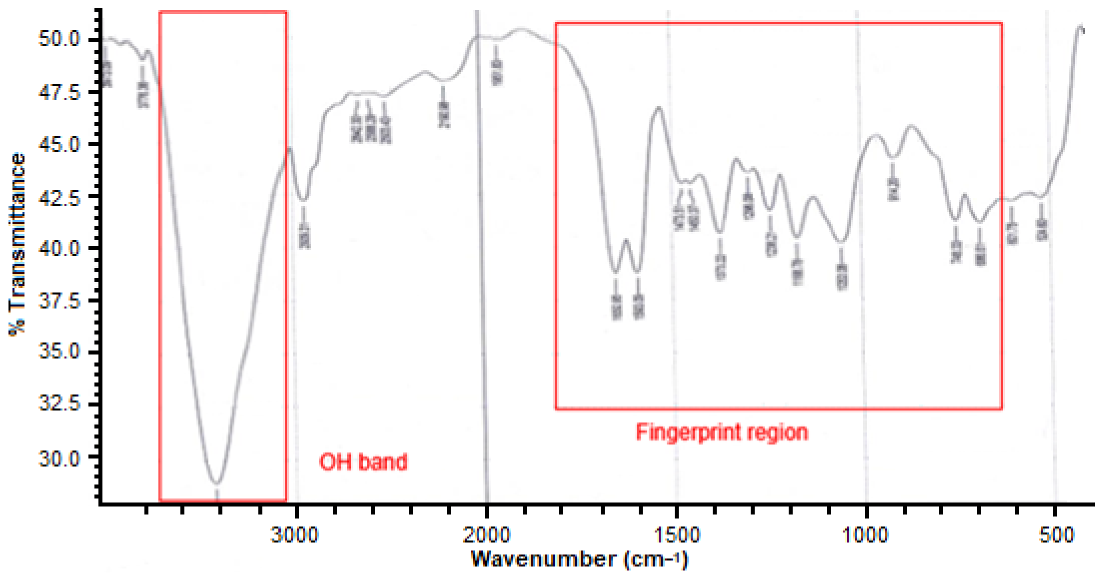

Fig 2. Example of FTIR spectra of blue ballpoint pen ink [20]

could be easily discriminated manually, it is challenging to discriminate ink samples of unbranded sources as some of the samples may arise from similar ink formulations of certain manufacturers, thereby producing similar spectra [22]. Therefore, the chemometric analysis would help eliminate irrelevant peaks for discrimination purposes.

Ink Analysis by ATR-FTIR

Analysis done on written document samples using ATR-FTIR does not involve separating or extracting inks from the paper. Thus, analysis is usually performed directly onto the specified area in which the ink is shaded or written on paper. Most researchers will shade a section to ensure the contact area of the crystal is fully covered with the ink sample surface [11-12,16-17,22,25,29-30]. Enhancing ATR-FTIR with microscopic sampling, which is Micro-ATR FTIR, allows a smaller area of sample acquisition. A thinner line of written ink, such as a signature, could be analyzed using this improved technique [10]. However, a spectrum of ATR-FTIR shows an overlapping of bands originating from the ink with the strong absorption bands of the paper [1]. Therefore, it is crucial to identify the ink spectrum collected either directly from the pen or deposited on the paper, as well as the spectrum of the substrate, such as paper. Characterization of ink based on the spectrum should mention the sampling manners to avoid missed interpretation of data.

Various ink analyses can be executed using ATR-FTIR development, such as characterization, discrimination, classification, line intersecting, and ink dating analysis. Characterization analysis is carried out to identify the characteristic ink formulation based on the information obtained from the spectra. To individualize the inks, the researcher performs discrimination analysis, whereas classification analysis is conducted to group the inks based on desired characteristics. On the other hand, line intersecting involves multiple analyses, including the sequence of intersecting and discriminant analysis. Ink dating analysis studies the aging of the ink, but this technique has not been explored much using ATR-FTIR spectroscopy. Table 1 shows the research findings involving ATR-FTIR spectroscopy.

The research by Silva et al. [16] mentioned the use of the Universal ATR crystal (UATR) accessory, which is also known as diamond crystal. Considering this information, about 46% of crystal used for ATR is Diamond crystal, which is more favored than Germanium with 30% usage (Table 1). These crystals are more utilized as they have a higher refractive index [19]. Without considering those lacking specified parameters, the prominent resolution was 4 cm^{-1}, while the number of scans was 16. Although, there is no justification for why why those mentioned conditions were chosen, these studies also incorporate chemometric data to support

Table 1. Research findings involving ATR-FTIR spectroscopy

No	Instrumentation Specification	Analysis involves	Findings	Year
1	Micro-ATR-FTIR Analysis Thermo Scientific Nicolet iN10 MX FT-IR microscope with mercury cadmium telluride (MCT) detector, Germanium (Ge) crystal tip ATR Resolution: 4 cm^{-1}, No of scan: 16 Chemometric analysis	Discrimination analysis Classification analysis	The pens were grouped into three clusters based on brands using discriminant analysis (DA). The discrimination power from the analysis was 86.67%	2012 [12]
2	Micro-ATR-FTIR Analysis Thermo Scientific Nicolet iN10 MX FT-IR microscope with MCT detector, Ge crystal tip ATR Resolution: 4 cm^{-1}, No of scan: 16 Chemometric analysis	Discrimination analysis Classification analysis	The pens of nine brands were grouped into three clusters through the statistical method of discriminant analysis (DA). Using one-way Analysis of Variance (ANOVA), only two pairs out of nine brands could not be differentiated at a 95% confidence interval.	2012 [11]

Table 1. Research findings involving ATR-FTIR spectroscopy (*Continued*)

No	Instrumentation Specification	Analysis involves	Findings	Year
3	ATR-FTIR spectroscopy Spectrum400 (Perkin Elmer) equipment with a universal attenuated total reflectance (UATR) accessory Resolution: 4 cm^{-1}, No of scan: 16 Chemometric analysis Linear discriminant analysis (LDA), Successive projections algorithm (SPA), Genetic algorithm (GA), Stepwise formulation (SW)	Discrimination analysis Classification analysis	Based on IR spectra, the linear discriminant analysis results paired with SPA, GA, and SW algorithms for variable selection were successfully employed to classify blue ink pens by types and brands. In general, LDA-SPA and LDA-GA showed a better performance than LDA-SW models	2013 [16]
5	Micro-ATR FTIR (Thermo Mattson, Infinity Gold FT-IR, Waltham, MA) equipped with an IR microscope (SpectraTech, Inspect IR plus, Franklin Lakes, NJ), MCT detector, Ge ATR crystal Spectral range: 4000 cm–600 cm^{-1} Resolution: 8 cm^{-1}, No of scan: 64	Discrimination analysis Intersecting line analysis	The micro-ATR FTIR can differentiate the black ballpoint pen inks and their sequence of intersecting.	2014 [10]
6	Micro-ATR FTIR spectroscopy Thermo Scientific Nicolet iN10 MX FT-IR microscope with MCT detector, Ge crystal tip ATR Spectral range: 4000–675 cm^{-1} Resolution: 4 cm^{-1}, No of scan: 16 Chemometric analysis	Discrimination analysis	The clustering of PCA-DA was able to group the similar model's name with a variation of pen tip sizes. Therefore, if pen tip sizes were disregarded, it was possible to differentiate this particular brand's variation of pen models.	2014 [17]
7	ATR-FTIR spectroscopy Brand: Bruker FTIR spectrometer (USA) Diamond crystal ATR Resolution: 4 cm^{-1} Chemometric analysis	Discrimination analysis	Similar IR spectra do not necessarily indicate an origin from the same pen, especially for unbranded pen inks. The researcher proposed to pair with other analyses, such as HPLC or GC, for definitive confirmation of the identification of inks.	2016 [22]
8	ATR-FTIR IR Tracer–100 FTIR spectrometer (Shimadzu, Japan), Diamond crystal ATR, Zinc selenide, ZnSe (focusing element) Resolution: 16 cm^{-1}, No of scan: 45 Chemometric analysis	Characterization analysis Discrimination analysis	Complex ink formulations were characterized using the ATR-FTIR approach. Discrimination of ink analysis based on visual inspection of ATR-FTIR spectra was 97.93%, while the discriminant power increased to 99.69% after pairing with multivariate analysis,	2017 [27]
9	FTIR spectroscopy Brand: Bruker Model & specification parameters not stated	Discrimination analysis	Black pen ink comprised fewer absorption peaks than blue pen inks. It was not possible to clearly distinguish between all brands of pen inks.	2018 [25]
10	ATR-FTIR spectroscopy Bruker Tensor 27 (Bruker Optics, UK) FTIR spectrometer equipped with a diamond ATR sampling attachment. Spectral range: 4000–600 cm^{-1}, Resolution: 4 cm^{-1}	Ink dating analysis	No significant changes for results of ink aging based on visual examination of spectra. Paired test-test performed using the frequency region (3700–3000 cm^{-1}) revealed significant changes between aged inks and their fresh counterparts.	2018 [30]

Table 1. Research findings involving ATR-FTIR spectroscopy (*Continued*)

No	Instrumentation Specification	Analysis involves	Findings	Year
11	ATR-FTIR spectroscopy Perkin Elmer Frontier FT-IR spectroscopy equipped with a deuterated triglycine sulfate (DTGS) detector, single bounce Diamond/ZnSe ATR crystal accessory Spectral range: 2000–650 cm^{-1}, Resolution: 2 cm^{-1}	Classification analysis	ATR-FTIR spectra of pen inks have signal interferences (or overlaps) with paper substrates. Data processing improves the results, especially using a spectral window that contains lesser background interferences, and the slope was corrected via the Asymmetric least squares (AsLS) algorithm.	2018 [29]
12	FTIR spectroscopy Bruker Alfa FTIR spectrometer ZnSe crystal tip ATR objective Resolution: 4 cm^{-1}, No of scan: 16	Discrimination analysis	Although FTIR is a well-established and non-destructive technique for comparing inks, it is not easy to discriminate between them since all the samples have the same formulations.	2019 [31]
13	ATR-FTIR spectroscopy Perkin Elmer 'Spectrum Two' FTIR spectrometer Diamond crystal ATR, Zinc selenide, ZnSe (focusing element) Spectral range: 4000–400 cm^{-1}, Resolution: 4 cm^{-1}, No of scan: 16	Classification analysis	Based on the spectral result of ATR-FTIR, PLS-DA provides 100% classification among ballpoint and gel ink samples with zero balance error rates. The model also shows 100% classification for its class prediction and the source prediction for a blind test of the black ink samples.	2021 [37]

the analysis, especially for the classification and discrimination analysis of inks.

Incorporation of Multiple Analysis and Statistical Data

Most researchers would not rely solely on FTIR results as the spectra are based on functional groups. To increase the credibility of the FTIR spectrum, some researchers compared and contrasted the results with other methodologies, including chromatography and spectroscopy techniques. Specifically, some of these techniques include Thin Layer Chromatography (TLC), High-Performance Thin Layer Chromatography (HPTLC), UV-Vis Spectroscopy, Raman Spectroscopy, X-Ray Fluorescence Spectrometer (XRF), Video Spectral Comparator (VSC), and Filtered Light Examination (FLE). Recent studies also incorporated statistical support better to comprehend the results [32,38-40]. The statistical analysis involving chemical data is called chemometric analysis. These statistical data are crucial supports to justify the standard method credentials. Furthermore, these results increase the discriminant power (DP) or provide in-depth information in distinguishing the inks. The research findings incorporating several FTIR techniques are summarized in Table 2.

According to Kamil et al. [22], their research only focused on region 1800–1200 cm^{-1} for chemometric analysis as it was reported to possess predominant variability from each sample. However, the agglomerative hierarchical clustering (AHC) and principal component analysis (PCA) clustering of unbranded black ballpoint ink samples were not homogenous. Thus unable to cluster the pens accordingly. This phenomenon was also due to the limited wavelength provided. Although chemometric analysis can analyze multiple variables, the analysis's limits are between 5 to 300 variables [15,42]. From the peaks of the spectra, there is an elimination process that removes the peaks commonly present in most pen inks. This removal of peaks or variables is necessary as the presence of outliers might affect the results of the AHC through an overestimation of the within-sample variance, thereby reducing the effectiveness of the discriminate model. In multivariate systems, PCA assists the observation of outliers by projecting the data on a

Table 2. Research findings of techniques used along with FTIR

Sample	Analysis and Techniques	Findings	Year
Blue ballpoint pen ink	Characterization of ink by ATR–FTIR spectroscopy Discrimination of ink by HPTLC & ATR–FTIR spectroscopy coupled with multivariate analysis	ATR-FTIR was able to characterize complex ink formulation Visual spectral inspection discrimination of ATR-FTIR and HPTLC results was 97.93% and 93.80% DP, respectively. Multivariate analysis of ATR-FTIR resulted in 99.69% DP.	2017 [27]
Blue and Black ballpoint and gel pen ink	Discrimination of ink by micro-FTIR spectroscopy, Raman spectroscopy, and XRF method	95% of blue and black inks could be distinguished from the collective method. Gel inks were differentiated up to 90% depending on the color.	2006 [6]
Blue and black ballpoint pen	The discrimination of ink by UV-Vis, TLC, and FTIR methods	Samples that UV-VIS and TLC could not differentiate were distinguished based on the FTIR spectra. These facts corresponded to an overall DP of the techniques' sequence, equal to 100% and 98% for black and blue inks, respectively.	2008 [8]
Blue and black ballpoint pen	Discrimination of ink using VSC 6000 & FTIR	Most brands can be discriminated by VSC filtered light examination. IR analysis revealed that each brand could be differentiated by observing its spectra.	2018 [25]
Blue, black, red, and green ballpoint pen	Discrimination of ink using FLE, TLC, FTIR, and Raman	FLE was a better discriminating tool for the analysis of black, red, and green ballpoint pen inks compared to other methods. TLC was the best for blue ballpoint pen inks (DP = 0.99). By combining the results from the 3 methods of analysis, namely FLE, TLC, and FTIR spectroscopy, all the inks, including those from the same brand/manufacturer, were successfully discriminated.	2016 [24]
Blue ballpoint and erasable pen inks	Discrimination between blue ballpoint pen inks and blue erasable pen inks using TLC, UV-Vis, IR & Raman	Raman analysis revealed that each brand for blue ballpoint pen ink and erasable pen ink samples could be discriminated by examining the pattern of each spectrum. TLC could discriminate all samples based on the retention factor (Rf).	2015 [20]
Blue ballpoint and gel pens	Classification of type of ink using TLC, Microscope, VSC 6000 & ATR-FTIR	ATR-FTIR showed that ink samples from the same types tend to locate closer in the score plot, as they could have contained similar compositional profiles. 2 gel ink samples were clustered into the ballpoint group. 3 gel pen inks exhibited hybrid characteristics through microscopic examination, TLC, and luminescence tests such as: • Dissolved in methanol • Luminesced under 485-610 nm and 605-730 nm light sources	2021 [41]

plane after the Varimax rotation of the first two extracted components. The next step in the study is to determine the quality of the discriminant model calculated in the AHC.

From Halim et al. [15], after the elimination process of variables, 18 wavelengths were selected for the classification of the blue gel pen inks. The classifications of blue gel pen inks were studied individually at each of the 18 wavelengths and the simultaneous combination of all the wavelengths with two chemometric algorithms, PCA and AHC. The classification relied on the presence of peaks, a distance of peak base to its baseline, followed by the ratio of peaks' distance. 74.67% of the blue gel pen inks were discriminated, with six of the 15 blue gel pen inks successfully classified. In contrast, the remaining nine pen inks were classified into a single group. However, each pen did not target the same point, indicating the possibility that they could still be discriminated.

To discriminate inks based on a single brand of variation model, Lee [17] introduced the results from ATR-FTIR to chemometric analysis. The author labeled its reduction techniques of principal component analysis – discriminant analysis as ZCA-PCA-DA. This approach was performed using clustering analysis (on standardized raw variables and eight different clusters) and PCA sequential as the eight resultant clusters underwent separate PCA. This method is more effective in extracting important IR spectrum information than conducting PCA on whole spectrum data points. This approach proves running more minor data points in PCA results is a more stable matrix. From the 688 data points of the IR spectra matrix, it was reduced to 37 principal components using the ZCA-PCA-DA approach. In addition, the stepwise DA could discriminate 85.70% of the variation in the data. However, it was noted that the samples used were also included in a similar model with a variation of pen tip sizes. Without considering the pen tip sizes, the discrimination percent could be increased.

■ CONCLUDING REMARKS

This review assessed the trends and approaches of using FTIR spectroscopy in writing ink analysis, emphasizing ATR-FTIR spectroscopy. With the advantages of the non-destructive and direct sampling technique, ATR-FTIR spectroscopy is more preferred, especially for forensic analysis. Although direct sampling of written ink has drawbacks of overlapping bands from paper with the inks, it does not necessarily affect line intersecting, ink dating, discrimination, and classification analysis. The chemometric analysis is a good extension for ATR-FTIR data of ink discrimination and classification. Most studies rely on chemometric analysis, whereas those that did not apply the technique faced difficulties observing and extracting the information from IR spectra. More research on ink dating using ATR-FTIR should be considered since it has not been explored compared to other analyses. However, with mixed remarks on the FTIR spectroscopy approach, further developments of this technique would be very important in the future.

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■ AUTHOR CONTRIBUTIONS

Putri Nabihah Abdul Khofar, Umi Kalsum Abdul Karim, Ezlan Elias, Muhd Fauzi Safian, and Mohamed Izzharif Abdul Halim evaluate and interpret the appropriate writing data process of the manuscript. Putri Nabihah Abdul Khofar and Mohamed Izzharif Abdul Halim collected the data and constructed the manuscript structure. All authors wrote and revised the manuscript, and the definitive version of this manuscript has reached a mutual agreement of all authors.

■ REFERENCES

[1] Braz, A., López-López, M., and García-Ruiz, C., 2013, Raman spectroscopy for forensic analysis of inks in questioned documents, *Forensic Sci. Int.*, 232 (1-3), 206–212.

[2] Calcerrada, M., and García-Ruiz, C., 2015, Analysis of questioned documents: A review, *Anal. Chim. Acta*, 853, 143–166.

[3] Alamilla, F., Calcerrada, M., García-Ruiz, C., and Torre, M., 2013, Forensic discrimination of blue ballpoint pens on documents by laser ablation inductively coupled plasma mass spectrometry and multivariate analysis, *Forensic Sci. Int.*, 228 (1-3), 1–7.

[4] Lee, L.C., Liong, C.Y., and Jemain, A.A., 2018, Validity of the best practice in splitting data for hold-out validation strategy as performed on the ink strokes in the context of forensic science, *Microchem. J.*, 139, 125–133.

[5] Hofmann, A., 2010, "Spectroscopic Techniques: I Spectrophotometric Techniques" in *Principles and Techniques of Biochemistry and Molecular Biology*, 7th Ed., Eds. Wilson, K., and Walker, J., Cambridge University Press, Cambridge, UK, 477–521.

[6] Zięba-Palus, J., and Kunicki, M., 2006, Application of the micro-FTIR spectroscopy, Raman

spectroscopy and XRF method examination of inks, *Forensic Sci. Int.*, 158 (2-3), 164–172.
[7] Lee, J., Kim, S.H., Cho, Y.J., Nam, Y.S., Lee, K.B., and Lee, Y., 2014, Characterization and sequence determination of pen inks, red sealing inks, and laser toners by TOF-SIMS and ATR FTIR, *Surf. Interface Anal.*, 46 (S1), 317–321.
[8] Causin, V., Casamassima, R., Marega, C., Maida, P., Schiavone, S., Marigo, A., and Villari, A., 2008, The discrimination potential of ultraviolet-visible spectrophotometry, thin layer chromatography, and Fourier transform infrared spectroscopy for the forensic analysis of black and blue ballpoint inks, *J. Forensic Sci.*, 53 (6), 1468–1473.
[9] Halim, M.I.A., Aziz, N.S.A., Saim, N., Osman, R., and Jasmani, H., 2012, Statistical discrimination of blue ballpoint pen inks by infrared (IR) spectroscopy, *Malays. J. Fundam. Appl. Sci.*, 8 (3), 155–161.
[10] Nam, Y.S., Park, J.S., Lee, Y., and Lee, K.B., 2014, Application of micro-attenuated total reflectance Fourier transform infrared spectroscopy to ink examination in signatures written with ballpoint pen on questioned documents, *J. Forensic Sci.*, 59 (3), 800–805.
[11] Lee, L.C., Othman, M.R., and Pua, H., 2012, Systematic assessment of attenuated total reflectance-Fourier transforms infrared spectroscopy coupled with multivariate analysis for forensic analysis of black ballpoint pen inks, *Malays. J. Anal. Sci.*, 16 (3), 262–272.
[12] Lee, L.C., Othman, M.R., Pua, H., and Ishak, A.A., 2012, Application of multivariate chemometry for discrimination of black ballpoint pen inks based on the IR spectrum, *Malays. J. Forensic Sci.*, 3 (1), 5–10.
[13] Senior, S., Hamed, E., Masoud, M., and Shehata, E., 2012, Characterization and dating of blue ballpoint pen inks using principal component analysis of UV-Vis absorption spectra, IR spectroscopy, and HPTLC, *J. Forensic Sci.*, 57 (4), 1087–1093.
[14] Feraru, D.L., Meghea, A., and Badea, N., 2013, Forensic discrimination of ballpoint pen inks based on correlation of data obtained by optical and spectral methods, *Rev. Chim.*, 64 (1), 74–80.
[15] Halim, M.I.A., Saim, N., Osman, R., Jasmani, H., and Aziz, N.S.A., 2013, Multivariate chemometric discrimination of blue gel-pen inks by Fourier transform infrared spectroscopy, *2013 IEEE Symposium on Computers & Informatics (ISCI)*, Langkawi, Malaysia, 236–240.
[16] Silva, C.S., Borba, F.D.S.L., Pimentel, M.F., Pontes, M.J.C., Honorato, R.S., and Pasquini, C., 2013, Classification of blue pen ink using infrared spectroscopy and linear discriminant analysis, *Microchem. J.*, 109, 122–127.
[17] Lee, L.C., 2014, Investigating Between-model variation of the PaperMate® pen using infrared spectrum and multivariate statistical techniques, *Forensic Sci. J.*, 13 (1), 15–22.
[18] Sharma, N., and Agarwal, A., 2014, Analysis of blue fountain pen inks, *Pharma Chem.*, 6 (1), 448–452.
[19] Durney, L., 2015, Using Vibrational Spectroscopy to Analyse the Effect of Environmental Aging on Gel Pen Inks, *Thesis*, University of Central Lancashire.
[20] Gazy, M., Eldebss, T., El-Zawawy, W., Helal, M., and Rashed, K., 2015, Comparative study between blue ballpoint pen inks and blue erasable pen inks by using spectroscopic analysis and chromatography method, *Nat. Sci.*, 13 (12), 16–27.
[21] Garrappa, S., Germinario, G., Van Der Werf, I.D., Mirabile, A., and Sabbatini, L., 2016, Multi-analytical study of artist felt-tip pen inks, *IMEKO International Conference on Metrology for Archaeology and Cultural Heritage*, October 19–21, 2016, Torino, Italy, 136–139.
[22] Kamil, M., Mohamad Asri, M.N., Mat Desa, W.N.S., and Ismail, D., 2015, Fourier transform infrared (FTIR) spectroscopy and principal component analysis (PCA) of unbranded black ballpoint pen inks, *Malays. J. Forensic Sci.*, 6 (1), 48–53.
[23] Sharma, V., Kumar, R., Devgan, K., Mishra, P. K., Ekielski, A., Kumar, V., and Kumar, V., 2018, Multivariate analysis for forensic characterization, discrimination, and classification of marker pen inks, *Spectrosc. Lett.*, 51 (5), 205–215.

[24] Nunkoo, M.I., Saib-Sunassy, M.B., Li Kam Wah, H., and Jhaumeer Laulloo, S., 2016, "Forensic Analysis of Black, Blue, Red, and Green Ballpoint Pen Inks" in *Crystallizing Ideas – The Role of Chemistry*, Eds. Ramasami, P., Gupta Bhowon, M., Jhaumeer Laulloo, S., and Li Kam Wah, H., Springer International Publishing, Cham, Switzerland, 323–339.

[25] Yadav, J., and Yadav, L., 2018, Characterization of ballpoint pen ink by using non-destructive methods, *Res. J. Forensic Sci.*, 6 (6), 1–6.

[26] e Brito, L.R., Martins, A.R., Braz, A., Chaves, A.B., Braga, J.W., and Pimentel, M.F., 2017, Critical review and trends in forensic investigations of crossing ink lines, *TrAC, Trends Anal. Chem.*, 94, 54–69.

[27] Sharma, V., and Kumar, R., 2017, Fourier transform infrared spectroscopy and high performance thin layer chromatography for characterization and multivariate discrimination of blue ballpoint pen ink for forensic applications, *Vib. Spectrosc.*, 92, 96–104.

[28] Zaffino, C., Passaretti, A., Poldi, G., Fratelli, M., Tibiletti, A., Bestetti, R., Saccani, I., Guglielmi, V., and Bruni, S., 2017, A multi-technique approach to the chemical characterization of colored inks in contemporary art: The materials of Lucio Fontana, *J. Cult. Heritage*, 23, 87–97.

[29] Lee, L.C., Liong, C.Y., and Jemain, A.A., 2018, Effects of data pre-processing methods on classification of ATR-FTIR spectra of pen inks using partial least squares-discriminant analysis (PLS-DA), *Chemom. Intell. Lab. Syst.*, 182, 90–100.

[30] Said, H.M., and Ismail, D., 2018, Study on the effect of ageing to gel pen ink on papers using attenuated reflectant mode Fourier transform infrared (ATR-FTIR) spectroscopy, *TIJMS*, 3 (1), 38–43.

[31] Bansinge, M.D., Tekade, P.V., Bajaj, S.D., Mahodaya, O.A., and Barwat, N.A., 2019, Analysis of different ball point pen inks using thin layer chromatography and comparison with FTIR spectrometer, *Chem. Sci. Trans.*, 8 (2), 160–171.

[32] Lee, L.C., and Jemain, A.A., 2019, Predictive modelling of colossal ATR-FTIR spectral data using PLS-DA: Empirical differences between PLS1-DA and PLS2-DA algorithms, *Analyst*, 144 (8), 2670–2678.

[33] Sharif, M., Batool, M., Chand, S., Farooqi, Z.H., Tirmazi, S.A.A.S., and Athar, M., 2019, 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.*, 2019, 5980967.

[34] Kivioja, A., Hartus, T., Vuorinen, T., Gane, P., and Jaaskelainen, A.S., 2013, Use of total internal reflection Raman (TIR) and attenuated total reflection infrared (ATR-IR) spectroscopy to analyze component separation in thin offset ink films after setting on coated paper surfaces, *Appl. Spectrosc.*, 67 (6), 661–671.

[35] Wang, J., Luo, G., Sun, S., Wang, Z., and Wang, Y., 2001, Systematic analysis of bulk blue ballpoint pen ink by FTIR spectrometry, *J. Forensic Sci.*, 46 (5), 1093–1097.

[36] Causin, V., Marega, C., Marigo, A., Casamassima, R., Peluso, G., and Ripani, L., 2010, Forensic differentiation of paper by X-ray diffraction and infrared spectroscopy, *Forensic Sci. Int.*, 197 (1-3), 70–74.

[37] Gautam, R., Chauhan, R., Kumar, R., and Sharma, V., 2021, PLS-DA and infrared spectroscopy based rapid and non-destructive discrimination of black ball and gel pen inks for forensic application, *Forensic Sci. Int.: Rep.*, 3, 100162.

[38] Lee, L.C., Liong, C.Y., and Jemain, A.A., 2016, Applying fourier-transform infrared spectroscopy and self- organizing maps for forensic classification of white-copy papers, *Int. J. Adv. Sci. Eng. Inf. Technol.*, 6 (6), 1033–1039.

[39] Kumar, R., and Sharma, V., 2018, Chemometrics in forensic science, *TrAC, Trends Anal. Chem.*, 105, 191–201.

[40] Sauzier, G., McGinn, J., Trubshoe, T., and Lewis, S.W., 2019, In situ examination of handwritten blue ballpoint inks using video spectral comparison with chemometrics, *Forensic Sci. Int.: Rep.*, 1, 100021.

[41] Gannetion, L., Noor, S.N.M.M., Lim, P.Y., Chang, K.H., and Abdullah, A.F.L., 2021, Forensic discrimination of blue pen inks: Emergence of hybrid pen inks, *Malays. J. Anal. Sci.*, 25 (4), 584–595.
[42] Halim, M.I.A., Saim, N., Osman, R., Jasmani, H., and Aziz, N.S.A., 2012, Multivariate Chemometric Discrimination of Black Ballpoint Pen Inks Based on Infrared Spectra, *2012 IEEE Symposium, Business, Engineering and Industrial Application*, Bandung, Indonesia, 834–837.