Brazilian Journal of Analytical Chemistry
Pre-publication – Accepted after peer review
doi: 10.30744/brjac.2179-3425.AR-19-2026

BrJAC

ARTICLE

Chemical Fingerprinting and Analytical Characterization of Writing Inks in Questioned Document Examination

Malavika Panicker, Sandheep Ponnampully*

Department of Life Sciences, Christ University, Bengaluru, Karnataka, India

A document can be questioned on various grounds to prove its authenticity. It is a diverse field in forensic science dealing with the analysis of different types of documents, including printed, typewritten and handwritten. Forgery can be of different types, and the analytical method depends on the type of forgery and the document involved. The identification and authentication of the questioned documents are fundamental aspects of the forensic document examination, as documents may be forged or altered using a variety of techniques. This study utilizes attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) to analyze the various ink samples in questioned documents. ATR-FTIR could reveal the distinct functional groups, such as aromatic, hydroxyl, and carbonyl groups, while SEM-EDS provided elemental profiles, including oxygen, carbon, sulfur and other elements which were useful for the comparative characterization. This study suggests the combined use of both techniques which allows the detection of chemical profiles enabling precise differentiation between inks of similar appearance. The total number of samples collected was 66, and the number of samples analyzed was 18 for ATR-FTIR and 6 for SEM-EDS. The types of inks used were ballpoint, gel, fountain; blue and black and the key methodological parameters used were ATR mode for FTIR and SEM-EDS coating and analysis approach. The identification of functional groups and elemental compounds contributes to the development of reliable chemical fingerprints. This study provides a comparative characterization of the selected inks which were commercially available rather than previously known fingerprints, which helps in improving the accuracy of forgery detection and validation of the document. Analysis of these documents can be both destructive techniques and nondestructive such as ATR-FTIR and SEM-EDS which provides the preservation of the sample as well as providing the elemental and chemical profiling. The combined use of the techniques enhances the differentiation of ink and detection

Cite: Panicker, M.; Ponnampully, S. Chemical Fingerprinting and Analytical Characterization of Writing Inks in Questioned Document Examination. *Braz. J. Anal. Chem.* (Forthcoming). https://doi.org/10.30744/brjac.2179-3425.AR-19-2026

Submitted: March 4, 2026; **Revised:** May 9, 2026; June 19, 2026; **Accepted:** August 21, 2026; **Published online:** September 2026.

This article was submitted to the BrJAC Special Issue dedicated to the 8th EspeQBrasil & 17th RSAS.

of forgery which improves the accuracy and reliability. This study should be regarded as a preliminary analytical feasibility study which intends to evaluate the utility of ATR-FTIR and SEM-EDS for the comparative characterization of the inks.

Keywords: Forensic science, analytical examination, ink analysis, ATR-FTIR, SEM-EDS, questioned documents

INTRODUCTION

Documents are an important part of an individual's life, from birth certificates to financial and legal records. The documents encountered in daily life include personal diaries, wills, receipts, bank cheques, identity documents, loans, testimonies, tax returns, etc. It is necessary to prove their validity during legal proceedings.[1] The field of forensic document evaluation comprises the analysis and assessment of writing ink in addition to the examination of handwriting. Examining and identifying ink in papers became a task for forensic document examiners in the past. An essential factor in establishing the legitimacy of the disputed document is the ink analysis.[2] Analysis of documents is complex in the field of forensic questioned document examination. The analysis helps to identify the types of components present in a document.[3] Crimes involving documents, such as threatening notes, suicide notes, forgery, and counterfeit banknotes, can be investigated using chemical or physical methods.[4] Various destructive and nondestructive methods can be employed for this purpose. Researchers mostly prefer non-destructive techniques over destructive ones in order to preserve the authenticity of documents during the final stage of examination. ASTM standards have made some consideration for the analysis of ink patterns present in the document.[5] The examination of ink was performed to compare the writing materials, support forensic interpretation and assess the possible sources in the investigations of questioned documents.[6]

The recent literature has focused on analyzing the documents, with particular emphasis on the pen inks. Half of the studies were focused on dating, while the others were based on comparisons between different inks used.[3] Ink comprises various components, including pigments, solvents, dyes, lubricants, resins, surfactants, solubilizers, and other compounds.[7] For an ink to be used as a writing ink, two things are taken into consideration. Firstly, its composition should be specific to meet certain requirements, and the second thing is that it should have certain tinctorial capability, while the solvents should be of low volatility to prevent evaporation and clogging while writing. They should also have a proper pH and should not be corrosive. The inks can be divided into two types: non-ballpoint and ballpoint. These inks vary in terms of their writing mechanisms as well as the types of components present in them. Ballpoint pens contain glycols and other solvents, which make the ink more viscous compared to non-ballpoint pens. Non-ballpoint pens are more aqueous based and contain more fluid components.[8]

Various methods can be used for the analysis of the questioned documents. Physical examination of documents mostly relies on nondestructive techniques such as visual examination under proper light sources to identify macroscopic features and the use of microscopes such as stereomicroscopes for microscopic features.[9] There is always a question of when the pen entry was made in the document.[10–12] The identification of morphological features of the document by analyzing the variation in the flow of ink was done using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS). It is the most effective tool used for the analysis of questioned documents, which gives elemental profile, multivariate analysis, and morphological features.[13] The elemental profiles of the ink present in the document help to analyze the source of the document. The obtained result will be compared with peaks from attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).[14] Previous literature shows that characterization studies of the toners present in the ink were conducted by some researchers.[15] Studies have been previously reported on analyzing the set of toners to determine their discrimination capacities. The results were then analyzed using statistical software. It was concluded that SEM-EDS helps in image characterization and elemental analysis, and it also helps to discriminate between the toners with the help of laser-assisted methods such as LIBS and LA-ICP-MS.[16] All these features of SEM-EDS made it attractive for the experimentation process.

This study is focused on the identification of functional groups and elemental analysis of questioned documents. The analysis involving identification of the source of ink samples can be done by comparing the samples with already known or specific writing instruments involved. The results will be compared with inks having similar characteristics, and interpretations can be made.[17,18] It is possible to interpret when the ink was made to be written on the questioned document due to the technologies evolved. The entire process of analysis can be categorized into two steps, which involve the optical and visual examination of the ink samples using ultraviolet (UV), infrared (IR), or visible (VIS) spectra. This can be possible due to their composition of elements such as solvents, resins, colorants, etc.[1]

Examination of ink

Analysis of ink present in the document is an important part of questioned document examination, especially in cases involving documents such as criminal or murder cases.[1] Alterations in these documents play a vital role in solving these types of cases. Alterations can be of additions or subtractions that can happen in a single digit, a sentence, or an entire paragraph. For the analysis of ink samples, only a small or minute amount of ink from the document will be taken into consideration. Therefore, it is important to have an expert in this field for the careful examination of the samples, as there is a chance that these samples can be damaged.[19] For the analysis of ink samples, a thorough understanding of the inks, their elemental composition, etc., has to be developed. Inks are mainly composed of organic compounds. The key components of an ink are dyes, colorants, or pigments, which are used for color. Lubricants, solvents, resins, surfactants, corrosion inhibitors, biocides, etc., are the other components used for the preparation of inks. These inks can be classified based on the type of pen used, such as powder or paste, and aqueous, liquid, etc. They can also be categorized as printing or writing inks.[20]

Novelty and aim of the study

The present study aims to (i) establish comparative chemical fingerprints of commonly used blue and black writing inks from ballpoint, gel, and fountain pens commonly used in India, and (ii) evaluate the combined use of ATR-FTIR and SEM-EDS as a practical forensic workflow for ink discrimination. The study emphasizes forensic relevance, methodological feasibility, and comparative characterization rather than the identification of previously unreported chemical compounds.

In addition, the study evaluates the effectiveness of combining the analysis of functional groups with elemental profiling to enhance the characteristic discrimination between visually similar inks.

MATERIALS AND METHODS

Sample collection

A total of 66 handwritten samples were prepared using the commercially available inks of ballpoint, gel, and fountain pens in blue and black colors from different manufacturers. The samples were written on 80-gsm A4 paper under similar conditions to ensure consistency. The brands of pen used for the analysis were Cello, Rorito, Parker, Pilot, Luxor, Flair, Reynolds and Hauser in black and blue color (Tables I–III).

Table I. Samples of blue and black ballpoint pens of different brands

Sample No.	Ink Type	Brand	Ink Color	Sample Type
1	**Ballpoint (Standard)**	Rorito Fanta Glide	**Blue**	**Control**
2	Ballpoint	Cello Butterflow	Blue	Sample
3	Ballpoint	Cello Finegrip	Blue	
4	Ballpoint	Reynolds 045	Blue	
5	Ballpoint	Rorito Flymax	Blue	

(continued on next page)

Table I. Samples of blue and black ballpoint pens of different brands (continued)

Sample No.	Ink Type	Brand	Ink Color	Sample Type
6	Ballpoint	Rorito Racer	Blue	Sample
7	Ballpoint	Hauser XO	Blue	
8	Ballpoint	Hauser Auto Click	Blue	
9	Ballpoint	Luxor Pilot	Blue	
10	Ballpoint	Flair Marathon	Blue	
11	Ballpoint	Cello Techno Tip	Blue	
12	**Ballpoint (Standard)**	Rorito Fanta Glide	**Black**	**Control**
13	Ballpoint	Cello Butterflow	Black	Sample
14	Ballpoint	Cello Finegrip	Black	
15	Ballpoint	Reynolds 045	Black	
16	Ballpoint	Rorito Flymax	Black	
17	Ballpoint	Rorito Racer	Black	
18	Ballpoint	Hauser XO	Black	
19	Ballpoint	Hauser Auto Click	Black	
20	Ballpoint	Luxor Pilot	Black	
21	Ballpoint	Flair Marathon	Black	
22	Ballpoint	Cello Techno Tip	Black	

Table II. Samples of blue and black gel pens of different brands

Sample No.	Pen Type	Brand	Ink Color	Category
1	**Gel Pen**	**Rorito Flymax Gel**	**Blue**	**Standard**
2	Gel Pen	Rorito Jelly Gel	Blue	Sample
3	Gel Pen	Pilot G2	Blue	
4	Gel Pen	Cello Geltech	Blue	
5	Gel Pen	Cello Gripper Gel	Blue	
6	Gel Pen	Hauser Sonic Gel	Blue	
7	Gel Pen	Hauser Germany Gel	Blue	
8	Gel Pen	Luxor Glitter Gel	Blue	
9	Gel Pen	Flair Writo Gel	Blue	
10	Gel Pen	Uni-ball Signo	Blue	
11	Gel Pen	Reynolds Trimax Gel	Blue	
12	**Gel Pen**	**Rorito Flymax Gel**	**Black**	**Standard**

(continued on next page)

Table II. Samples of blue and black gel pens of different brands (continued)

Sample No.	Pen Type	Brand	Ink Color	Category
13	Gel Pen	Rorito Jelly Gel	Black	Sample
14	Gel Pen	Pilot G2	Black	
15	Gel Pen	Cello Geltech	Black	
16	Gel Pen	Cello Gripper Gel	Black	
17	Gel Pen	Hauser Sonic Gel	Black	
18	Gel Pen	Hauser Germany Gel	Black	
19	Gel Pen	Luxor Glitter Gel	Black	
20	Gel Pen	Flair Writo Gel	Black	
21	Gel Pen	Uni-ball Signo	Black	
22	Gel Pen	Reynolds Trimax Gel	Black	

Table III. Samples of blue and black fountain pens of different brands

Sample No.	Pen Type	Brand	Ink Color	Category
1	**Fountain Pen**	**Flair Ink CEO**	**Blue**	**Standard**
2	Fountain Pen	Camlin Trinity	Blue	Sample
3	Fountain Pen	Cello Fountain Pen	Blue	
4	Fountain Pen	Reynolds Fountain Pen	Blue	
5	Fountain Pen	Hero Fountain Pen	Blue	
6	Fountain Pen	Luxor Fountain Pen	Blue	
7	Fountain Pen	Parker Vector	Blue	
8	Fountain Pen	Rorito Fountain Pen	Blue	
9	Fountain Pen	Pierre Cardin Fountain Pen	Blue	
10	Fountain Pen	Lamy Safari	Blue	
11	Fountain Pen	Pilot Metropolitan	Blue	
12	**Fountain Pen**	**Flair Ink CEO**	**Black**	**Standard**
13	Fountain Pen	Camlin Trinity	Black	Sample
14	Fountain Pen	Cello Fountain Pen	Black	
15	Fountain Pen	Reynolds Fountain Pen	Black	
16	Fountain Pen	Hero Fountain Pen	Black	
17	Fountain Pen	Luxor Fountain Pen	Black	
18	Fountain Pen	Parker Vector	Black	
19	Fountain Pen	Rorito Fountain Pen	Black	
20	Fountain Pen	Pierre Cardin Fountain Pen	Black	
21	Fountain Pen	Lamy Safari	Black	
22	Fountain Pen	Pilot Metropolitan	Black	

Although we collected 66 samples to study natural writing differences, only a representative subset was selected for analysis using factorial sampling technique. Eighteen samples were taken for ATR-FTIR analysis, having the combination of pen types, ink color and brands. This method reduced the analytical redundancy while ensuring the adequate comparative coverage of different categories of ink. A representative subset of 18 samples was selected for the analysis by ATR-FTIR, which ensures the balanced coverage across the pen types (ballpoint, gel and fountain), colors of ink (blue and black), and the manufacturers while avoiding the redundant analysis of the chemically similar formulations. For the analysis by SEM-EDS, the six representative samples were further selected from the subset based on their balanced representation of different categories of ink and the presence of distinguishable features of spectrum observed during the preliminary analysis. The subset selection strategy was performed to provide a meaningful comparative coverage while remaining compatible with the practical constraints of the detailed instrumental examination.

For the SEM-EDS analysis, six representative samples were chosen based on their unique characteristics of the spectra and balanced representation of the classes of the ink. Since the SEM-EDS is comparatively surface sensitive and time intensive, the subset technique was used to guarantee analytical viability while preserving the forensic relevance.

The present study was designed as a preliminary pilot study aiming to evaluate the feasibility of the technique combining ATR-FTIR and SEM-EDS for comparative characterization of the ink samples. Therefore, the study has focused primarily on the qualitative comparison rather than the extensive statistical validation. Triplicate analysis and larger sample validation studies will be incorporated in future to improve the reproducibility, statistical reliability and robustness of the analytical workflow.

Sample preparation

The sample preparation was done for all the samples. A 3×7 cm portion of the paper was marked and given for the direct analysis using ATR-FTIR. Tiny portion of that area was cut and analyzed using the SEM-EDS. Six representative samples were analyzed using SEM-EDS. Since the paper was nonconductive, sputtering of the paper was done using chromium. The coated stubs were analyzed using the SEM-EDS.

Instrumental techniques

Fourier transform infrared spectroscopy (FTIR) was used to identify the functional group of samples present in the document. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) also helps to identify the specific characteristics of the ink present in the sample from the spectrum by analyzing the fingerprint region. It is helpful in the field of forensic document examination.[21] ATR-FTIR was selected for forensic examination because it requires little or no sample preparation, provides rapid analysis, and is cost-effective.[22]

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) was used for the analysis of variation in the ink present in the sample. In order to avoid charging, or the collection of electrons on the sample surface, the spot should also be positioned as low as feasible. The characteristics of the sample are diminished as a result of electron aggregation on its surface. To stop charging, a conductive substance must be applied to the sample that will be examined if it is not conductive. Gold, palladium, graphite, and other electrically conducting materials can be applied to the sample using sputter coaters. It helps with enhancing the contrast as well. The sample's topographical features will be improved by the proper adjustments to contrast and brightness. Using an EDX detector, additional analysis can be performed after the image has been viewed on the monitor. This detector can be used to determine the sample's elemental composition.[2,23,24]

Sample analysis

The samples were analyzed using the ATR-FTIR and SEM-EDS at Christ University, Bengaluru, India. ATR-FTIR analysis was performed over a spectral range of 4000–400 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans. SEM-EDS was carried out with an accelerating voltage of 15–20 kV and a working distance of

approximately 10 mm, and sputter coating with chromium was performed. Before ink examination, spectra of blank paper were obtained to assess possible substrate contributions. The only purpose of applying chromium sputter coating during SEM analysis was to lessen charging effects, and elemental interpretations took potential coating-related interferences into account. An EDS detector was used to obtain the spectra under standard acquisition conditions. The samples were kept in the sputter coater for 45 min, and the stubs were then placed for analysis. The spectrum was first obtained for the blank paper, followed by the original samples.

RESULTS AND DISCUSSION

FTIR spectroscopy was used to identify the functional groups present in the ink samples (Figures 1–3), while SEM-EDS provided information on elemental composition. Carbon and oxygen were identified as most dominant elements in most of the samples while additional elements such as Silicon (Si) and Magnesium (Mg) are the most abundant components that are present in the ink samples. All spectra were acquired under identical instrumental conditions to maintain analytical consistency.

ATR-FTIR analysis of ballpoint pen inks

The peaks in the ATR-FTIR spectra common to all three blue ballpoint pen ink samples (BUBS, BUBC, and BUBH) were those of O–H stretching, CH_2 bending, and C–O stretching (Figure 1). Additionally, there were peaks due to vibrations in C–Br and C–Cl bonds.

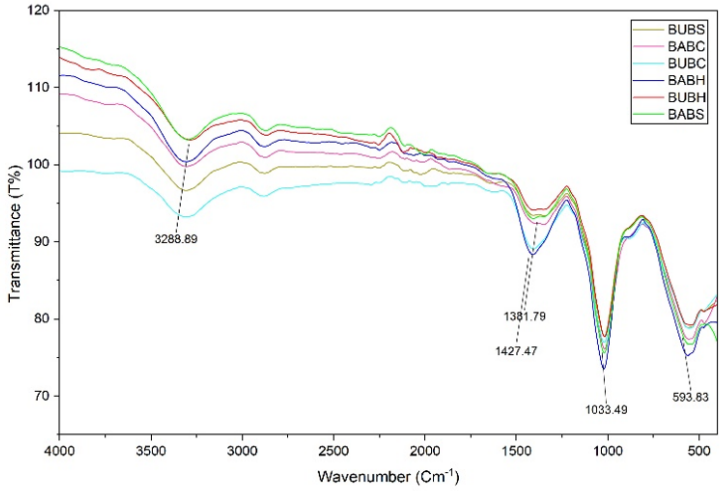

Figure 1. ATR-FTIR spectra of ballpoint inks.

The observed peaks were consistent with the presence of the functional groups which were commonly associated with the glycol-based solvents, additives and polymeric binders which were reported in formulations of ballpoint inks. However, the individual chemical ingredients cannot be definitely identified using ATR-FTIR alone. These assignments should be viewed as an indicative rather than definitive due to intricacy of the ink matrices. In addition, there were common peaks in the ATR-FTIR spectra of all three black ballpoint pen inks (BABS, BABC, and BABH) that were those of O–H stretching, CH_2 bending, and C–O stretching. These differences aside, the ATR-FTIR bands of the various inks showed distinguishing spectral differences. For example, the extra absorption of the blue Hauser Ballpoint Ink (BUBH) at ~2140 cm^{-1} can be ascribed to species containing nitrile or triple bonds in a chain of carbon atoms. This would apparently make for a distinguishing criterion. By contrast, the ATR-FTIR spectra of Cello blue Ballpoint Ink (BUBC) showed enhanced absorption in the aliphatic C–H stretching vibrations. Once again, in black Ballpoint inks, BABC showed an absorption band in the carbonyl-stretching band at ~1700 cm^{-1}, whilst in the case of BABH, enhanced absorption occurred in the aliphatic C–H stretches. Because the writing inks

have chemically complex matrices, the functional group assignments described should be considered as the tentative interpretations based on the characteristic absorption regions and not as a definitive identification of the individual compounds.

ATR-FTIR analysis of gel pen inks

The FTIR spectrum of blue gel ink (B.G.I. / Figure 2) shows a broad peak at approximately 3340 cm^{-1} corresponding to O–H / N–H stretching vibrations. The peak that appears at ~1992 cm^{-1} indicates a combination of the stretched bands. The bands between 1416 and 1307 cm^{-1} may be due to C–N stretching or C–C vibrations in the aromatic ring. The bands at 1027 cm^{-1} and 559 cm^{-1} may indicate C–O–C or S–O vibrations. The FTIR spectrum of Flair blue gel (Figure 2) also shows an O–H stretching band at ~3328 cm^{-1}, with an additional peak at ~2175 cm^{-1} and at ~1741 cm^{-1} corresponding to C≡N and C=O stretching vibrations, respectively, which suggests the presence of possible binder or resin related functional groups, although the definitive identification of the compound cannot be solely identified from the spectrum of ATR-FTIR.

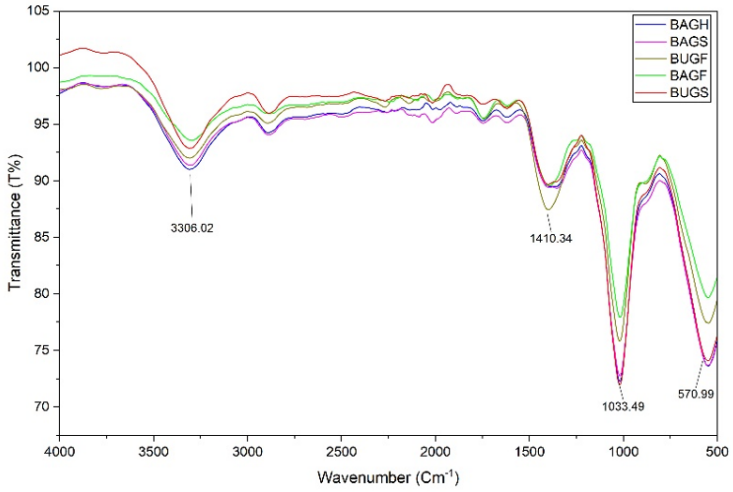

Figure 2. ATR-FTIR spectra of gel inks.

Similarly, the FTIR spectrum of Hauser Blue Gel (B.G.H. / Figure 2) contains a broad peak at approximately 3351 cm^{-1} corresponding to O–H / N–H stretching and a peak at 2175 cm^{-1} ascribed to nitrile (C≡N) and possibly C=C bonds from synthetic dyes. The bands at ~1416 cm^{-1} and ~522 cm^{-1} correspond to aromatic C=C (stretching) and C–O–C (stretching) as well as a possible halide/sulfonyl. It can be noted that all blue gel inks obtained exhibited the same frequency bands approximately 3300 cm^{-1} to 3350 cm^{-1} and approximately 1020 cm^{-1} indicating a similarity in the matrix of the dye and binders used.

ATR-FTIR analysis of fountain pen inks

All of the spectra had a large absorption peak around 3300–3340 cm^{-1}, indicating that each ink contains alcohol, an amine, water, or some type of resin binder (Figure 3). In addition, several weak-to-moderate bands in the 2900 cm^{-1} range were likely C–H stretching vibrations indicating that these pens most likely contain organic solvents or polymeric binders. Another type of aromatic absorption is clearly shown in the spectrum in the area of 1580–1600 cm^{-1}, where the most intense absorption peaks are caused by the stretching C=C of dye molecules. The aromatic C=C are also found in both types of blue and black inks at around the same frequencies. There are absorption peaks at 1410-1450 cm^{-1} caused by C=N stretching and aromatic ring vibrational modes (Figure 3).

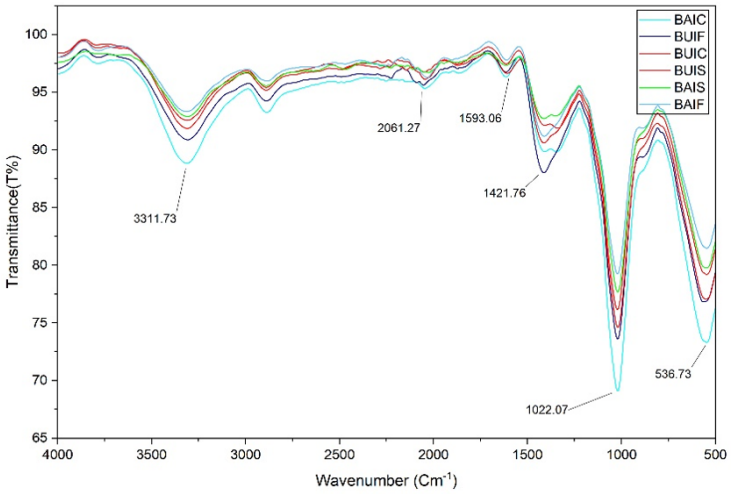

Figure 3. ATR-FTIR spectra of fountain inks.

A strong IR absorption was also found between 1020–1150 cm^{-1}, which results from the stretching modes of C–O bands in alcohols, ethers, and esters, where ink resins, plasticizers, and other ink modifiers are found. Other lower-frequency peaks at less than 900 cm^{-1} are due to bending vibrations associated with the out-of-plane C–H bending vibration of substituted aromatic rings, while lower-frequency bands at less than 600 cm^{-1} may represent inorganic compounds.

Comparative functional group analysis

The study was conducted to analyze the possible elements with the help of functional groups of ink present in the samples using analytical techniques. The initial process of analysis was conducted using FTIR where the functional group present in the sample was identified. The presence of triple bonds such as alkynes or cyanide groups (C≡C or C≡N), cyanates, or isocyanates may occur in the range 2300–2100 cm^{-1}. The presence of carbonyl compounds such as carbonyl-containing compounds or anhydrides was found to be in the range of 1900–1650 cm^{-1}. These bands of absorption may be associated with the carbonyl containing compounds which are commonly reported in the dyes, binders and pigment systems used in the commercial inks. The presence of alcohols such as primary, secondary and tertiary was found from the C–O stretching which represents the solvents that are used in the preparation of the ink.[25,26] The observed features of the spectra were consistent with the functional groups which were commonly reported in the writing inks which were associated with the resins, pigments, dyes, solvents and additives used. Two prominent peaks were obtained between 2900–3000 cm^{-1}, indicating the fundamental chemical bonds found in hydrocarbons, which serve as organic solvents or binders present in the ink. The common chemical bonds present in the ink samples were C–H, O–H, C=O, C=C, C–O, and N–H**,** bonds which indicate the presence of alkanes, alcohols, phenols, water, carbonyl groups, aldehydes, ketones.[27] All these are the functional groups identified through the study which was already reported by previous research studies and no new functional compounds could be identified.

It should be emphasized that, rather than definitively identifying specific chemical compounds, ATR-FTIR analysis mainly gives the information on the functional groups. The commercial writing inks were the intricate mixes of the pigments, resins, solvents, additives, polymers and plasticizers and many of these mixtures have resulted in the overlapping of the infrared absorption bands. Therefore, rather than giving the definitive proof of specific chemical components, the peak assignments in this study should be viewed as suggestive of likely functional groups based on the available literature and the spectral databases. Therefore, for the conclusive molecular characterization, complementary analytical techniques like chromatography, mass spectrometry or Raman spectroscopy would be needed.

Based on the results of the ATR-FTIR analysis, it was determined that there are both common and differentiating functional groups among the ballpoint and gel inks selected, as well as among each of the different types of pens—gel, ballpoint and fountain pens—as shown in Figures 1–3.

It can be noted that the absorption peaks (3300–3350 cm^{-1} for O–H/N–H stretching and 1400–1450 cm^{-1} for C–N/C–C/N–O vibrations) were found in several types of the inks, including BUBS, BABS, BUGS and BUIS, this can be due to presence of similar nature of some components including the solvents, resins and dyes. These bands are representative of the hydrocarbon backbone of the various ink formulations and are primarily made up of organic solvents, resin binders, and polymeric materials generally incorporated into the formulation for writing inks.[9-11]

Common and diagnostic peaks were identified from the data presented in Table IV. The presence of common peaks, such as C–H stretching in the range of approximately 2850–3000 cm^{-1}, in several of the ink samples suggests the presence of similar organic components across different ink types and/or brands.[10,28] Conversely, diagnostic features such as bands tentatively assigned to C≡N stretching in BUBH (~2140 cm^{-1}) and BUGF (~2175 cm^{-1}), and C=O stretching at approximately 1700 cm^{-1} in BABC, showed differences among the ink samples and may provide useful features for comparative discrimination. However, these functional-group assignments should be considered tentative because ATR-FTIR analysis of complex ink matrices may involve overlapping absorption bands. The presence of bands associated with N–H and C–N vibrations in several blue and black ballpoint inks may be related to nitrogen-containing dyes, binders, or other formulation additives.

Table IV. Characteristic FTIR absorption bands and functional group identification of writing ink samples

Sample Code	Ink Type	Ink Description	Wavenumber (cm^{-1})	Functional Group	Vibrational Mode	Remarks
BUBS	Ballpoint	Blue Ballpoint (Standard)	3300–3350	O–H / N–H	Stretching	Broad peak; hydrogen bonding
BUBS	Ballpoint	Blue Ballpoint (Standard)	2900–3000	C–H	Stretching	Aliphatic hydrocarbons
BUBS	Ballpoint	Blue Ballpoint (Standard)	1020–1150	C–O	Stretching	Solvents/ethers
BUBC	Ballpoint	Blue Ballpoint (Cello)	3300–3350	O–H / N–H	Stretching	Similar base composition
BUBC	Ballpoint	Blue Ballpoint (Cello)	1580–1600	C=C	Stretching	Aromatic dyes
BUBC	Ballpoint	Blue Ballpoint (Cello)	500–700	C–Cl	Stretching	Halogen additives
BUBH	Ballpoint	Blue Ballpoint (Hauser)	2100–2300	C≡N	Stretching	Nitrile (distinct marker)
BUBH	Ballpoint	Blue Ballpoint (Hauser)	2900–3000	C–H	Stretching	Organic backbone
BUBH	Ballpoint	Blue Ballpoint (Hauser)	1580–1600	C=C	Stretching	Aromatic compounds
BABS	Ballpoint	Black Ballpoint (Standard)	3300–3350	O–H / N–H	Stretching	Binder components
BABS	Ballpoint	Black Ballpoint (Standard)	2900–3000	C–H	Stretching	Hydrocarbon chains
BABC	Ballpoint	Black Ballpoint (Cello)	~1700	C=O	Stretching	Carbonyl (resins/ dyes)
BABC	Ballpoint	Black Ballpoint (Cello)	1400–1450	C–N	Stretching	Nitrogen compounds

(continued on next page)

Table IV. Characteristic FTIR absorption bands and functional group identification of writing ink samples (continued)

Sample Code	Ink Type	Ink Description	Wavenumber (cm^{-1})	Functional Group	Vibrational Mode	Remarks
BABH	Ballpoint	Black Ballpoint (Hauser)	1400–1450	N–O	Bending	Nitro compounds
BUGS	Gel Pen	Blue Gel (Standard)	3300–3350	O–H / N–H	Stretching	Aqueous ink
BUGS	Gel Pen	Blue Gel (Standard)	1020–1150	C–O–C	Stretching	Resin components
BUGF	Gel Pen	Blue Gel (Flair)	~2175	C≡N	Stretching	Nitrile groups
BUGF	Gel Pen	Blue Gel (Flair)	~1741	C=O	Stretching	Ester/carbonyl
BUGH	Gel Pen	Blue Gel (Hauser)	~3350	O–H / N–H	Stretching	Similar matrix
BUGH	Gel Pen	Blue Gel (Hauser)	~1416	C=C	Stretching	Aromatic ring
BAGS	Gel Pen	Black Gel (Standard)	2900–3000	C–H	Stretching	Organic solvents
BAGF	Gel Pen	Black Gel (Flair)	1020–1150	C–O	Stretching	Alcohol/ether
BAGH	Gel Pen	Black Gel (Hauser)	1300–1350	C–N	Stretching	Amines
BUIS	Fountain	Blue Ink (Standard)	3300–3340	O–H / N–H	Stretching	Water/resin
BUIS	Fountain	Blue Ink (Standard)	1580–1600	C=C	Stretching	Aromatic dyes
BUIF	Fountain	Blue Ink (Flair)	1410–1450	C–N	Stretching	Nitrogen compounds
BUIC	Fountain	Blue Ink (Cello)	1020–1150	C–O	Stretching	Solvents/resins
BAIS	Fountain	Black Ink (Standard)	~3300	O–H	Stretching	Moisture
BAIC	Fountain	Black Ink (Cello)	~1300	C–N	Stretching	Amines
BAIF	Fountain	Black Ink (Flair)	1400–1450	N–H	Bending	Dye-related

The sample analysis of black ballpoint and ink pens demonstrates the variation in chemical functional groups due to the presence of nitrogen–oxygen functional groups. A specific branding of black ballpoint pens may be indicative of the presence of nitro compounds or the pigment stabilisers commonly used in darker inks. The existence of these differing functional groups indicates that there is a distinct formulation for various ink types, based on brands, and that the composition is dependent on the ink type. Upon conducting an evaluation of the blue and black ink samples, it was found that all samples contain similar organic frameworks, however, the variations noticed in the functional groups containing heteroatoms (e.g., nitrogen and oxygen) can be used to differentiate between the pens. Such functional group variations are a result of the differences in dye chemistry, pigment loading, resin systems, as well as other auxiliary additives. The findings of this study coincide with other published studies that have demonstrated the utility of the ATR-FTIR spectroscopic technique in differentiating formulations of inks that are not visually distinguishable.[9-11]

SEM-EDS analysis

Figures 4 and 5 represent the data from SEM-EDS. Out of 18 samples, six were selected for the analysis using SEM-EDS. These pens were taken to ensure the balance between analytical feasibility and a representative coverage. Since SEM-EDS was a surface-sensitive and time-consuming method, it was used on a subset that could capture the differences in the formulation of inks among various brands, colors, and types, which also ensured the feasibility of the study. This method is related to forensic ink analysis through elemental profiling.

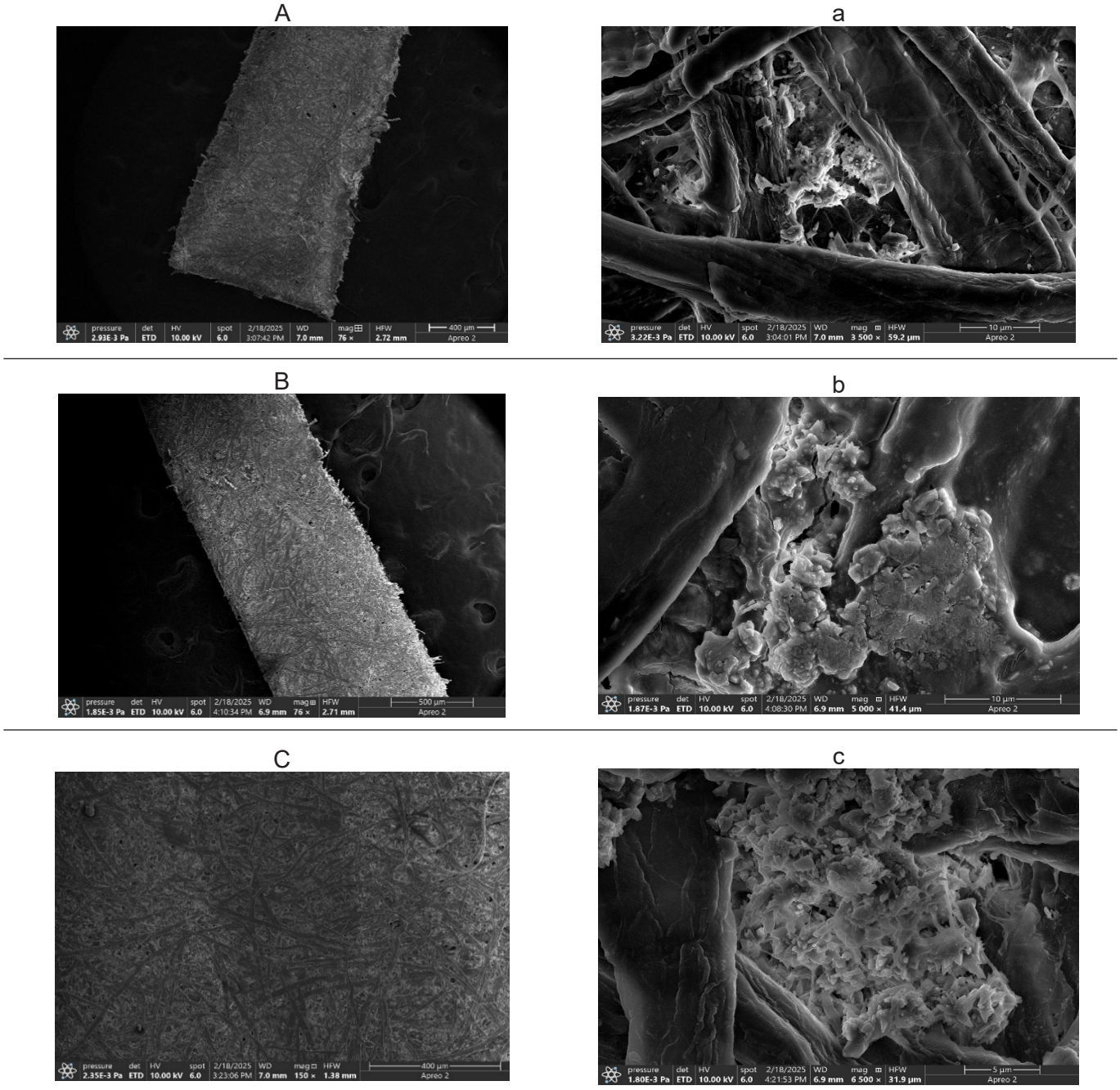

Figure 4. SEM images were obtained at magnifications ranging from ×500 to ×5000, depending on the morphology and surface characteristics of the samples (BUBC, BUBH, BUGH, BABS, BAGS, BUIS). (continued on next page)

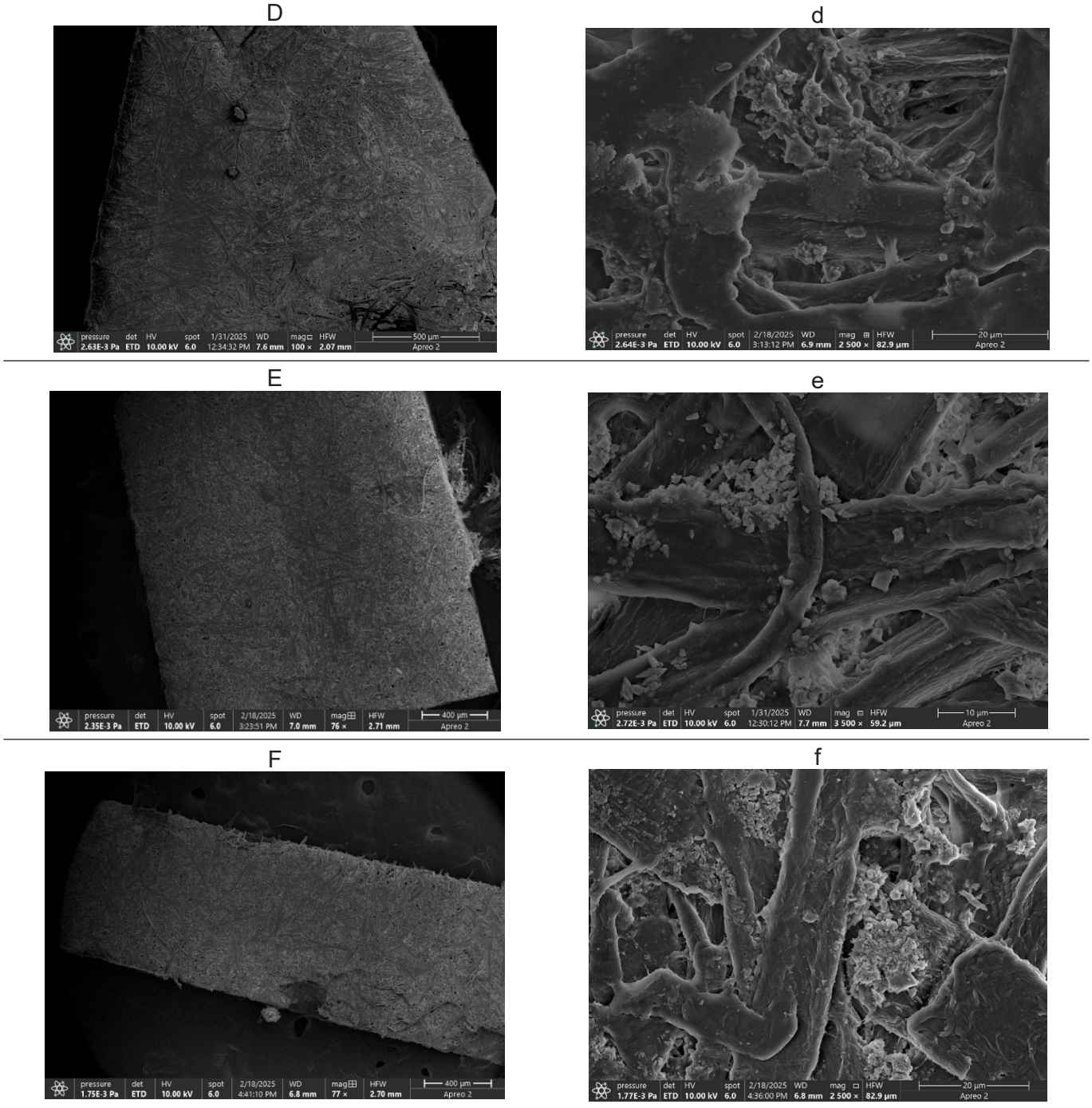

Figure 4. SEM images were obtained at magnifications ranging from ×500 to ×5000, depending on the morphology and surface characteristics of the samples (BUBC, BUBH, BUGH, BABS, BAGS, BUIS).

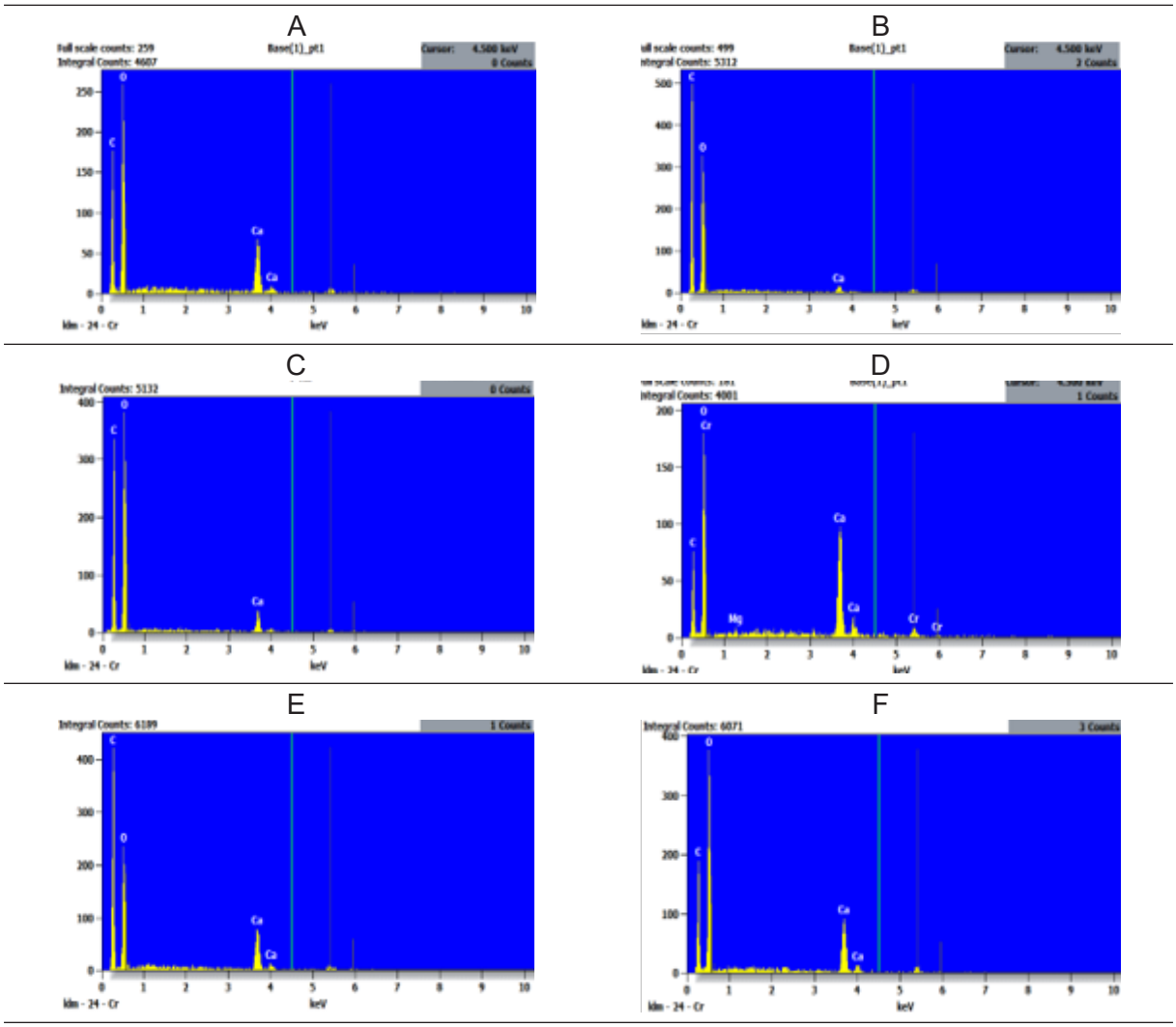

Figure 5. A–F represent the EDS images of the samples BUBC, BUBH, BUGH, BABS, BAGS, and BUIS.

From the current study, it can be taken into consideration that SEM-EDS can be used for the analysis of the elemental composition of the ink samples.[2] It was found that although the chemical composition of the ink samples is similar, there will be variations in their weight. The use of SEM-EDS helps in interpreting the variation in weight. By revealing the variations in the ink formulation, the elemental data from the SEM-EDS may aid in comparing forensic investigations. Nevertheless, the temporal variations and document aging or the temporal variations in the elemental composition were not intended to be validated by this investigation. Therefore, SEM-EDS is a rapid and efficient analytical tool in the field of questioned document examination.[10,21]

Differences in the elemental percentages were observed among the analyzed samples. These variations should be analyzed cautiously, as they may arise from substrate effects, formulation differences, environmental influences, and instrumental variability rather than aging alone. The present study primarily focused on preliminary qualitative forensic screening rather than a quantitative validation study; therefore, advanced chemometric modelling was beyond the scope of the current investigation.

Blank paper analysis was also conducted to reduce the substrate-related interferences during the interpretation.[10,21] Due to the exploratory nature of this pilot forensic study and limited instrument accessibility, replicate instrumental measurements were not performed.

Limitations and future aspects

In our present study, SEM-EDS was selected as the primary analytical method of analysis due to its suitability for surface characterization, elemental profiling, accessibility and rapid analysis, within routine laboratory conditions. The technique also provided valid and sufficient information about the elemental composition for the comparative examination of the ink. The complementary techniques such as Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) can further enhance the depth of analytical study, particularly for the detection of trace elements and enhanced discrimination of similar ink types. However, the LA-ICP-MS analysis was not accessible during our study and thus outside the scope of the current work.

Future studies may incorporate chemometric and multivariate statistical tools such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) to improve discrimination efficiency and objective classification of ink samples.

CONCLUSIONS

The present study demonstrates an exploratory analytical workflow rather than a proven technique of forensic identification. The results from the study demonstrate the potential ability of a combined ATR-FTIR and SEM-EDS, providing a comparative characterization of inks in questioned document examination, however the future studies which include large sample sets with replicate measurements, blind testing, and validation of the results using chemometrics will be required before routine forensic implementation. The ATR-FTIR spectra could identify the different chemical bonds that are present in all the ink samples, thereby analyzing the probable components used in their chemical composition. SEM-EDS is a quick, efficient, and semi-destructive method that may easily be included into the current ink analysis workflow. The ATR-FTIR based analyses reported in our study are intended for the comparative forensic characterization and be interpreted in the context of the inherent limitations of the peak assignments in the complex matrices of the ink. The present study establishes a preliminary analytical workflow for the comparative characterization of the ink and provides a foundation for the future validation studies which involve quantitative evaluation and expanded datasets. The elemental and chemical differences observed in this study should be interpreted as the comparative analytical features for the characterization of the ink and discrimination rather than the evidence of specific aging-related or compositional changes.

Acknowledgements

The authors gratefully acknowledge the participation of everyone that submitted their data for this research project.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Use of artificial intelligence tools

The authors acknowledge the use of ChatGPT (OpenAI) for language editing during the preparation of this article. The authors take full responsibility for the accuracy, integrity, and originality of the work and confirm that no AI tools were used to generate scientific ideas, independently analyze data, or replace the authors' critical role.

REFERENCES

(1) Fatima, F. F. Forensic examination and identification of writing inks on documents. *International Journal for Electronic Crime Investigation* **2020**, *4* (3), 9–31.

(2) Purba, M. K.; Gupta, S.; Gupta, R. R. Effectiveness and potential of SEM-EDX for analysis and differentiation of overlapped black pen inks. *Annals of the Romanian Society for Cell Biology* **2021**, *25* (6), 7332–7338. Retrieved from http://annalsofrscb.ro/index.php/journal/article/view/6883

(3) Calcerrada, M.; García-Ruiz, C. Analysis of questioned documents: A review. *Anal. Chim. Acta* **2015**, *853*, 143–166. https://doi.org/10.1016/j.aca.2014.10.057
(4) Dazzi, C.; Pedrabissi, L. Graphology and personality: An empirical study on validity of handwriting analysis. *Psychol. Rep.* **2009**, *105*, 1255–1268. https://doi.org/10.2466/PR0.105.F.1255-1268
(5) Neumann, C.; Margot, P. Considerations on the ASTM standards 1789-04 and 1422-05 on the forensic examination of ink. *J. Forensic Sci.* **2010**, *55*, 1304–1310. https://doi.org/10.1111/j.1556-4029.2010.01454.x
(6) Ellen, D.; Day, S.; Davies, C. *Scientific Examination of Documents: Methods and Techniques*. (4th Ed.). Taylor & Francis, London, 2018. https://doi.org/10.4324/9780429491917
(7) LaPorte, G. M. Chemical analysis for the scientific examination of questioned documents. In: Siegel, J. A. (Ed.). *Forensic Chemistry*. Wiley, Hoboken, 2015, pp 318–353. https://doi.org/10.1002/9781118897768.ch8
(8) Weyermann, C.; Kirsch, D.; Costa-Vera, C.; Spengler, B. A GC/MS study of the drying of ballpoint pen ink on paper. *Forensic Sci. Int.* **2007**, *168*, 119–127. https://doi.org/10.1016/j.forsciint.2006.06.076
(9) Brunelle, R. L.; Cantu, A. A. A critical evaluation of current ink dating techniques. *J. Forensic Sci.* **1987**, *32*, 1522–1536. https://doi.org/10.1520/JFS11212J
(10) Aginsky, V. Some new ideas for dating ballpoint inks—A feasibility study. *J. Forensic Sci.* **1993**, *38*, 1134–1150. https://doi.org/10.1520/JFS13517J
(11) Verma, N.; Sharma, V.; Kumar, R.; Sharma, R.; Joshi, M. C.; Umapathy, G. R.; Ohja, S.; Chopra, S. On the spectroscopic examination of printed documents by using a field emission scanning electron microscope with energy-dispersive X-ray spectroscopy (FE-SEM-EDS) and chemometric methods: application in forensic science. *Anal. Bioanal. Chem.* **2019**, *411*, 3477–3495. https://doi.org/10.1007/s00216-019-01824-z
(12) Trzcińska, B. M.; Brożek-Mucha, Z. The Possibilities of Identifying Photocopy Toners by Means of Infrared Spectroscopy (FT-IR) and Scanning Microscopy (SEM-EDX). In: Mink, J.; Keresztury, G.; Kellner, R. (Eds.). *Progress in Fourier Transform Spectroscopy*. *Mikrochim. Acta, Suppl.* **1997**, *14*, 235–237. https://doi.org/10.1007/978-3-7091-6840-0_43
(13) Gilmour, C. L. A comparison of laser printed and photocopied documents. Can they be Distinguished? *J. Can. Soc. Forensic Sci.* **1994**, *27* (4), 245–259. https://doi.org/10.1080/00085030.1994.10757038
(14) Trejos, T.; Corzo, R.; Subedi, K.; Almirall, J. Characterization of toners and inkjets by laser ablation spectrochemical methods and Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy. *Spectrochim. Acta B* **2014**, *92*, 9–22. https://doi.org/10.1016/j.sab.2013.11.004
(15) Burfield, R.; Neumann, C.; Saunders, C. P. Review and application of functional data analysis to chemical data—The example of the comparison, classification, and database search of forensic ink chromatograms. *Chemom. Intell. Lab. Syst.* **2015**, *149*, 97–106. https://doi.org/10.1016/j.chemolab.2015.07.006
(16) Neumann, C.; Margot, P. New perspectives in the use of ink evidence in forensic science: Part I. Development of a quality assurance process for forensic ink analysis by HPTLC. *Forensic Sci. Int.* **2009**, *185* (1-3), 29–37. https://doi.org/10.1016/j.forsciint.2008.11.016
(17) Sharma, V.; Kumar, R. 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.* **2017**, *92*, 96–104. https://doi.org/10.1016/j.vibspec.2017.05.006
(18) Placke, M.; Fischer, N.; Colditz, M.; Kunkel, E.; Bohne, K.-H. Drawing and writing materials. In *Ullmann's Encyclopedia of Industrial Chemistry.* Wiley-VCH, Weinheim, 2016, pp 1–12. https://doi.org/10.1002/14356007.a09_037.pub2
(19) Girão, A. V.; Caputo, G.; Ferro, M. C. Application of Scanning Electron Microscopy–Energy Dispersive X-Ray Spectroscopy (SEM-EDS). In: Rocha-Santos, T. A. P.; Duarte, A. C. (Eds.). *Comprehensive Analytical Chemistry*. Elsevier, 2017, vol. 75, Chapter 6, pp 153–168. https://doi.org/10.1016/bs.coac.2016.10.002

(20) Zięba-Palus, J.; Kunicki, M. Application of the micro-FTIR spectroscopy, Raman spectroscopy and XRF method examination of inks. *Forensic Sci. Int.* **2006**, *158* (2-3), 164–172. https://doi.org/10.1016/j.forsciint.2005.04.044

(21) Corzo, R.; Subedi, K.; Trejos, T.; Almirall, J. R. Evaluation of the Forensic Utility of Scanning Electron Microscopy-Energy Dispersive Spectroscopy and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry for Printing Ink Examinations. *J. Forensic Sci.* **2016**, *61* (3), 725–734. https://doi.org/10.1111/1556-4029.13110

(22) Ezcurra, M.; Góngora, J. M. G.; Maguregui, I.; Alonso, R. Analytical methods for dating modern writing instrument inks on paper. *Forensic Sci. Int.* **2010**, *197* (1-3), 1–20. https://doi.org/10.1016/j.forsciint.2009.11.013