

Ink Matters: Comparative Analysis of Black Fountain Pen Inks from Three Popular Brands

Nur Syazwani Rahmie Rahman¹, Nor Zakiah Nor Hashim^{2*}, Hussein Hanibah²,
Poppy Puspitasari³, Jamaluddin Mahmud⁴, Muhammad Aidil Tasnim Roslan⁴
and Rossuriati Dol Hamid¹

¹Faculty of Applied Science, Universiti Teknologi MARA, Shah Alam, 40450 Shah Alam, Selangor, Malaysia

²Center of Foundation Studies, Universiti Teknologi MARA, Cawangan Selangor, Kampus Dengkil, 43800 Dengkil, Selangor, Malaysia

³Department of Mechanical Engineering, Faculty of Engineering, Universitas Negeri Malang, Semarang 5, Malang 65145, Indonesia

⁴College of Engineering, Universiti Teknologi MARA, Shah Alam, 40450 Shah Alam, Selangor, Malaysia

*Corresponding author (e-mail: norzakiah@uitm.edu.my)

This study presents a comparative analysis of black fountain pen inks from three commercial brands—Pilot, Pelikan and Lamy—using thin-layer chromatography (TLC), gas chromatography–mass spectrometry (GC–MS), attenuated total reflectance–Fourier-transform infrared spectroscopy (ATR–FTIR), UV–visible spectroscopy (UV–Vis) and cyclic voltammetry (CV). TLC revealed multiple dye components with different polarities in each ink, consistent with complex commercial mixtures. GC–MS tentatively identified substituted phenolic compounds, notably 2,4-di-tert-butylphenol and its positional isomers, in the volatile fraction. These compounds are common antioxidants in plastics and coatings and may have originated from additives or packaging rather than being intentional major ink constituents. ATR–FTIR spectra contained bands consistent with phenolic and silicon-related functionalities, whereas UV–Vis analysis identified brand-specific absorption maxima (λ_{max}), with Lamy showing the highest absorbance. CV using screen-printed carbon electrodes with an Ag/AgCl pseudo-reference electrode provided distinct electrochemical profiles: the 0.1 M KCl blank was nearly featureless, whereas all inks displayed brand-dependent anodic responses and predominantly irreversible behaviour. Minor oxygen-reduction features near 0 to –0.2 V diminished during conditioning. Collectively, the chromatographic, spectroscopic and electrochemical results show that the inks share some stabilising agents and dye-related features while retaining distinguishable analytical profiles. This integrated approach provides a useful basis for forensic ink discrimination and quality control.

Keywords: Fountain pen ink, thin-layer chromatography, GC–MS, ATR–FTIR, UV–Vis spectroscopy, cyclic voltammetry, forensic chemistry

Received: February 2026; Accepted: August 2026

Fountain pen inks are complex liquid formulations containing colourants (dyes or pigments), solvents, surfactants, preservatives and stabilising agents. Their composition is designed to provide suitable flow, vivid colouration and long-term stability on paper. Despite their widespread use, fountain pen ink formulations remain less extensively characterised in the academic literature than other writing materials, such as ballpoint and gel inks [1]. Detailed compositional information is particularly important in forensic science because differences among ink sources can support document authentication, fraud investigation and the examination of historical manuscripts.

Ink components have been investigated using several analytical techniques, each with distinct advantages. Thin-layer chromatography (TLC) is widely used because it is simple, inexpensive and

effective for separating dye mixtures according to polarity. It enables preliminary profiling of dye components and can reveal similarities or differences among ink samples [2]. However, TLC is primarily qualitative and cannot identify chemical structures with high specificity.

Following preliminary dye separation by TLC, GC–MS provides more specific chemical information by separating and tentatively identifying volatile and semi-volatile organic compounds in ink extracts. This technique is particularly useful for detecting additives or degradation-related compounds that cannot be identified by TLC alone. For example, GC–MS can detect phenolic antioxidants such as 2,4-di-tert-butylphenol, which are used in plastics and coatings and may leach into inks from packaging or additives. Their detection in an ink extract therefore

does not necessarily demonstrate intentional addition to the formulation [3, 4]. Although such compounds may contribute to stability, evidence for their deliberate use in fountain pen inks remains limited.

The compound-level information obtained by GC–MS can be complemented by Fourier-transform infrared spectroscopy (FTIR), which provides functional-group information. In attenuated total reflectance (ATR) mode, FTIR can detect bands associated with hydroxyl (O–H), carbonyl (C=O), aromatic (C=C) and silicon-related (Si–O–Si) groups with minimal sample preparation [4, 5]. These functional signatures can support or refine GC–MS interpretations concerning phenolic compounds, aromatic dye structures and silicon-containing species such as siloxanes. Nevertheless, silicon-related signals must be interpreted cautiously because they may also originate from column bleed or silicone-containing laboratory materials.

UV–visible spectroscopy (UV–Vis) provides complementary information about the chromophoric properties of dye molecules. A dye absorbs light at wavelengths determined by its conjugated structure, producing characteristic absorption maxima (λ_{max}). UV–Vis can therefore support TLC-based comparisons of dye composition and provide information about relative light absorption among ink brands [6]. Bathochromic or hypsochromic shifts may reflect differences in dye structure, formulation or interactions between dyes and stabilisers.

Electrochemical techniques such as cyclic voltammetry (CV) extend this analysis by providing a redox-based fingerprint of fountain pen inks. CV probes the oxidation and reduction behaviour of electroactive dyes and additives by recording current across a selected potential window [7]. Current magnitude, oxidation onset and the overall voltammetric profile may reveal differences in the identity, concentration and stability of electroactive components. CV can thus complement GC–MS, ATR–FTIR and UV–Vis by indicating whether dye or additive components contribute to measurable electrochemical responses.

The novelty of this study lies in the integrated use of TLC, GC–MS, ATR–FTIR, UV–Vis and CV to establish complementary analytical profiles of commercial black fountain pen inks. Previous ink studies have often focused on ballpoint or gel inks, whereas fountain pen inks remain comparatively underexplored despite their continued use in hand-writing, official documents and archival materials. By combining chromatographic, spectroscopic and electrochemical techniques, this study relates dye-migration behaviour, volatile and semi-volatile compounds, functional-group signatures, chromophoric absorption and redox responses within a single analytical framework. This multi-technique approach provides a more comprehensive basis for differentiating

Pilot, Pelikan and Lamy fountain pen inks than any single method alone.

EXPERIMENTAL

Materials

Black fountain pen inks from three commercial brands—Pilot, Pelikan and Lamy—were selected for analysis. Double A A4 paper was used as the substrate. All solvents and chemicals, including n-butanol, glacial acetic acid and distilled water, were of analytical grade and were purchased from Merck (Darmstadt, Germany).

Characterization Methods

Sample Preparation

For instrumental analysis, a 1 μL aliquot of each ink was deposited as a single drop on Double A A4 paper using a micropipette and was allowed to air-dry at room temperature unless otherwise specified.

Thin-Layer Chromatography (TLC)

TLC was used to separate the dye components in the ink samples. Each sample was applied to a silica gel 60 F₂₅₄ TLC plate on an aluminium backing. A mixture of n-butanol, glacial acetic acid and distilled water (4:1:5, v/v/v) was used as the mobile phase. The plate was placed in a covered developing chamber lined with filter paper and was developed until the solvent front had travelled 2.8 cm, which required approximately 10–15 min. The plate was then removed, air-dried and examined under visible light. Retention-factor (R_f) values were calculated from the distance travelled by each spot relative to the solvent-front distance.

Gas Chromatography–Mass Spectrometry (GC–MS)

GC–MS was used to investigate volatile and semi-volatile organic compounds in the ink extracts. Ink was extracted from the stained paper with distilled water and the extract was filtered. An aliquot (1 μL) was injected into an Agilent Technologies 7890B gas chromatograph coupled to a 5977A mass-selective detector. The injector temperature was maintained at 260 °C. The oven was initially held at 50 °C for 1 min and was then heated to 200 °C at 10 °C min^{−1}. Compounds were tentatively identified by matching their mass spectra against the NIST library.

Attenuated Total Reflectance–Fourier Transform Infrared (ATR–FTIR) Spectroscopy

ATR–FTIR was used to characterise functional groups in the ink residues. After drying, the ink-stained paper was placed directly on the diamond ATR crystal of a PerkinElmer Spectrum One FTIR spectrometer.

Spectra were recorded from 4000 to 650 cm^{-1} at a resolution of 8 cm^{-1} using four scans per sample. A background spectrum was collected before each measurement, and the resulting spectra were interpreted by comparison with reference spectra and published data.

UV-Visible Spectroscopy (UV-Vis)

The dried ink-stained paper was cut into 1 cm $\times$ 1 cm pieces and soaked in 10 mL of distilled water at room temperature. The extract was diluted with distilled water to a final dilution factor of 1:350 and transferred to a quartz cuvette with a 1 cm optical path length. Absorbance was measured from 230 to 800 nm using a PerkinElmer UV-Vis spectrophotometer, with distilled water as the blank. All measurements were performed at room temperature under ambient conditions.

Electrochemical Measurements (Cyclic Voltammetry)

Cyclic voltammetry was performed using a Metrohm Autolab potentiostat and disposable screen-printed carbon electrodes comprising carbon working and counter electrodes and an on-chip Ag/AgCl pseudo-reference electrode. A 0.1 μL aliquot of each ink (Pilot, Pelikan or Lamy) was drop-cast onto the working-electrode area, gently dried and allowed to cool to room temperature. A droplet of 0.1 M

KCl supporting electrolyte was then applied to cover the working, reference and counter electrodes. Cyclic voltammograms were recorded from -0.2 to $+0.8$ V versus Ag/AgCl. Consecutive cycles were collected until a reproducible response was obtained, and a fresh screen-printed electrode was used for each ink to prevent cross-contamination.

RESULTS AND DISCUSSION

Thin Layer Chromatography (TLC) Analysis

Thin-layer chromatography (TLC) was used to compare the dye compositions of black fountain pen inks from Pilot, Pelikan and Lamy. Silica gel 60 F₂₅₄ plates on aluminium backing (5.4 cm $\times$ 4.2 cm) were used. The samples were applied 1.0 cm from the bottom of each plate, and the n-butanol–glacial acetic acid–water mobile phase (4:1:5, v/v/v) was allowed to travel 2.8 cm before the plate was removed, dried and examined (Figure 1). The calculated retention-factor (R_f) values are summarised in Table 1.

Distinct separation patterns were observed for the three inks, indicating that each black ink contained multiple dye components. The R_f value of each spot was calculated as follows:

$$\text{Retention Factor } (R_f) = \frac{\text{Distance Travelled by Spot (cm)}}{\text{Distance Travelled by Solvent Front (cm)}}$$

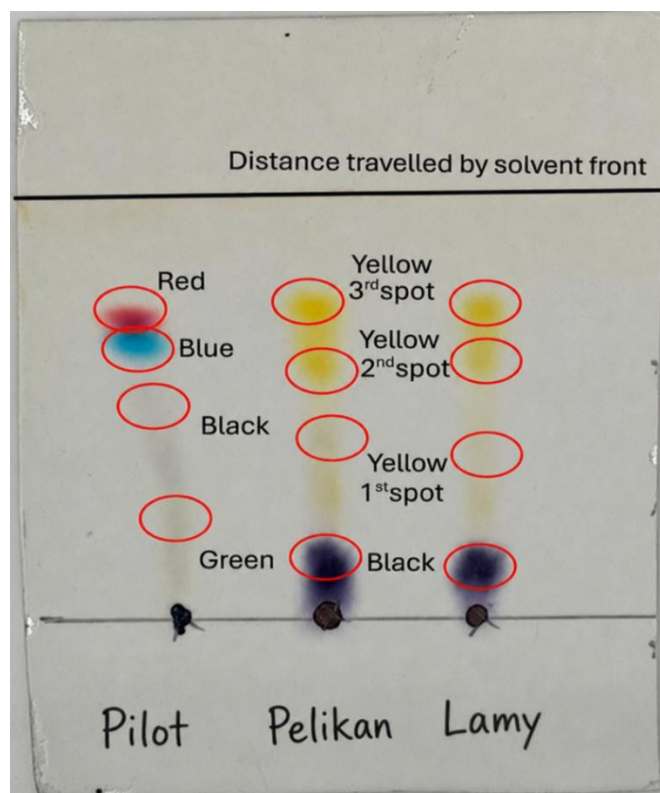


Figure 1. TLC plate developed for Pilot, Pelikan and Lamy fountain pen inks.

Table 1. TLC data for Pilot, Pelikan and Lamy fountain pen inks.

Ink brand	Spot colour	Distance from baseline (cm)	Solvent front (cm)	R _f value
Pilot	Green	0.8	2.8	0.29
Pilot	Black	1.7	2.8	0.61
Pilot	Blue	2.0	2.8	0.71
Pilot	Red	2.2	2.8	0.79
Pelikan	Black	0.5	2.8	0.19
Pelikan	Yellow (spot 1)	1.5	2.8	0.54
Pelikan	Yellow (spot 2)	1.8	2.8	0.64
Pelikan	Yellow (spot 3)	2.2	2.8	0.79
Lamy	Black	0.5	2.8	0.19
Lamy	Yellow (spot 1)	1.4	2.8	0.50
Lamy	Yellow (spot 2)	2.0	2.8	0.71
Lamy	Yellow (spot 3)	2.2	2.8	0.79

For a solvent-front distance of 2.8 cm, the chromatographic spots produced R_f values from 0.19 to 0.79, indicating dye components with a broad range of migration behaviours.

The Pilot ink produced four distinct spots with R_f values of 0.29 (green), 0.61 (black), 0.71 (blue) and 0.79 (red). This broad range suggests the presence of both relatively polar and less-polar dyes and indicates that the black colour may have been produced by blending several coloured components. Such multicomponent patterns are consistent with the complex colourant mixtures reported for commercial fountain pen inks [8].

The Pelikan ink also produced four spots: a dark, relatively polar component at R_f = 0.19 and three yellow components at R_f = 0.54, 0.64 and 0.79. The shared R_f value of 0.79 with the Pilot sample indicates similar migration under the selected conditions but does not establish that the two spots contain the same compound. Optical libraries of commercial pen inks likewise demonstrate that inks from different brands can share some analytical features while retaining distinguishable overall profiles [9].

The Lamy ink produced a dark spot at R_f = 0.19 and three yellow-toned spots at R_f = 0.50, 0.71 and 0.79. The values shared with Pelikan indicate similar migration behaviour and polarity under the selected solvent conditions. However, identical R_f values in a single solvent system cannot confirm chemical

identity because different compounds may co-elute or migrate similarly. The TLC results should therefore be regarded as preliminary comparative evidence; confirmation would require additional solvent systems, dye standards or complementary instrumental methods. Commercial inks commonly use a limited range of stable colourants, which may account for partially overlapping migration patterns [10].

Overall, the TLC results demonstrate the complexity of black fountain pen inks, which contained several dye components spanning a broad polarity range. The n-butanol–glacial acetic acid–water mobile phase (4:1:5, v/v/v) successfully separated these components on silica gel, supporting the use of TLC as an inexpensive and accessible method for preliminary comparative analysis of ink formulations [1].

GC–MS Analysis of Fountain Pen Ink Samples

GC–MS was performed on Pilot, Pelikan and Lamy fountain pen inks. A Double A A4 paper blank was analysed separately to identify background compounds originating from the substrate, although its chromatogram was not included in the overlaid figure.

Figure 2 presents the overlaid GC–MS total ion chromatograms (TICs) of the Pilot, Pelikan and Lamy ink samples. The overlay facilitates comparison of peak positions and intensities and highlights chemical features that are shared among or differ between the samples.

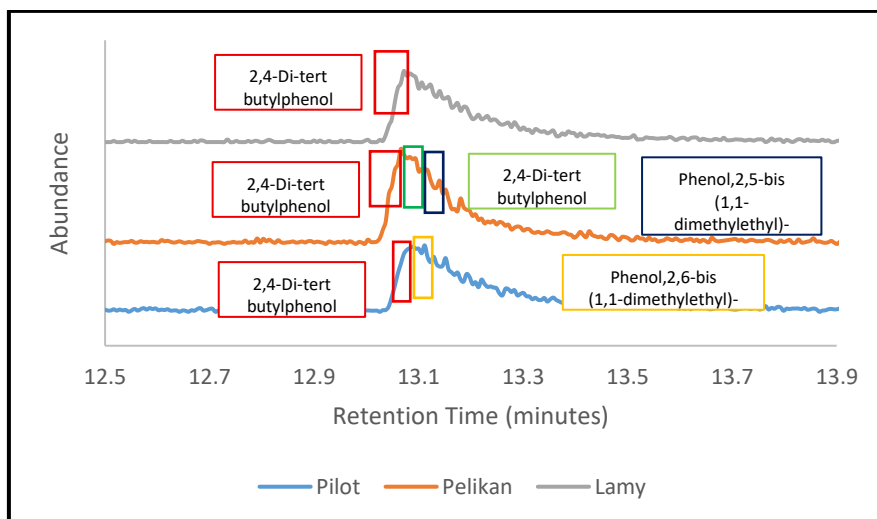


Figure 2. Overlay GC–MS chromatogram of Fountain Pen Ink Samples.

Because the A4 paper blank is not shown in the overlay, the chromatograms were interpreted with consideration of possible substrate-derived signals. Peaks observed in all samples were not treated as exclusive ink markers; instead, emphasis was placed on differences among the Pilot, Pelikan and Lamy profiles. Presenting the blank trace alongside the ink chromatograms in future work would enable paper-derived and ink-derived contributions to be distinguished more clearly.

Pilot Ink

The Pilot chromatogram contained two dominant peaks at retention times of 13.091 and 13.154 min. NIST-library matching tentatively assigned these peaks to 2,4-di-tert-butylphenol and 2,6-di-tert-butylphenol, respectively. Both compounds are phenolic antioxidants used in polymer and coating formulations [11]. Their presence in the extracts may reflect ink additives, packaging materials or other formulation-related sources rather than deliberate use as major constituents. Although the peaks dominated the detected volatile fraction, their relative areas do not represent the overall composition of the ink. No substantial signal was observed in this retention region in the separately analysed paper blank, supporting—but not conclusively proving—their attribution to the ink sample.

Pelikan Ink

The Pelikan TIC contained three peaks at retention times of 13.070, 13.110 and 13.184 min. These peaks were tentatively assigned to 2,4-di-tert-butylphenol and positional isomers. Their occurrence may indicate stabilising additives, but contributions from packaging materials or processing contaminants cannot be

excluded without confirmation using authentic standards.

The Pelikan peaks were less intense than those in the Pilot chromatogram, and their NIST-library match qualities ranged from 78 to 87. The corresponding signals were not detected in the separately analysed paper blank, supporting their attribution to the ink. Tert-butyl-substituted phenols are widely reported as antioxidants that inhibit the oxidative degradation of organic materials [3, 12].

Lamy Ink

The Lamy chromatogram contained an intense peak at 13.075 min, tentatively identified as 2,4-di-tert-butylphenol. This peak represented 40.76% of the detected GC–MS peak area but should not be interpreted as 40.76% of the total ink formulation. Because phenolic antioxidants are common in plastics and coatings, the compound may have originated from an additive, packaging material or another formulation-related source [3, 12]. Two smaller peaks at 24.012 and 24.147 min (Figure 3) were tentatively assigned to octasiloxane and 1,2-bis(trimethylsilyl) benzene, respectively. These signals may indicate silicone-based additives such as surfactants, flow modifiers or defoamers; however, similar compounds can also arise as artefacts from column bleed or silicone-containing laboratory materials. The assignments were therefore treated cautiously [4].

A separate chromatogram of the later-eluting region was plotted to improve visual clarity and prevent the dominant phenolic peak from obscuring the smaller signals. This presentation enabled the minor peaks to be assessed more clearly.

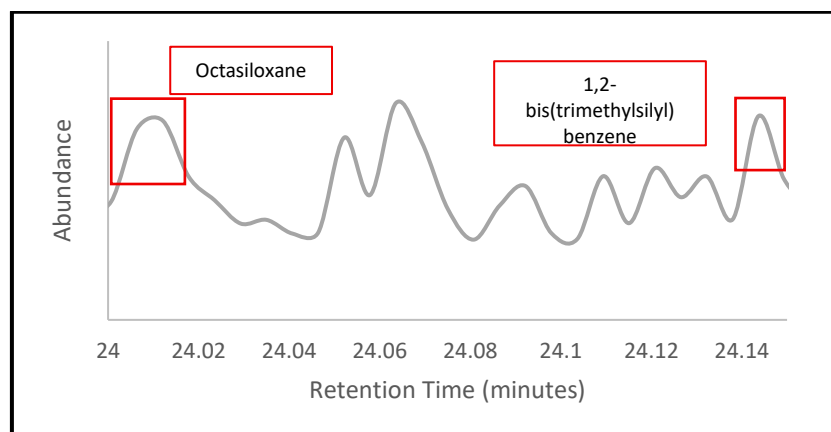


Figure 3. GC–MS TICs of Lamy Fountain Pen Ink Sample.

Table 2. Major compounds tentatively identified in the ink extracts by GC–MS.

Sample	RT (min)	Compound	CAS No.	Area (%)	Match quality	Supporting reference(s)
Pilot	13.09	2,4-di-tert-butylphenol	96-76-4	8.44	80	[11]
	13.15	2,6-di-tert-butylphenol	128-39-2	4.47	80	[11]
Pelikan	13.07	2,4-di-tert-butylphenol	96-76-4	3.38	87	[3, 12]
	13.11	2,4-di-tert-butylphenol	96-76-4	2.27	80	[3, 12]
	13.18	2,5-di-tert-butylphenol	5875-45-6	0.67	78	[3, 12]
Lamy	13.08	2,4-di-tert-butylphenol	96-76-4	40.76	50	[3, 4]
	24.01	Octasiloxane	19095-24-0	4.31	50	[3, 4]
	24.15	1,2-bis(trimethylsilyl)benzene	17151-09-6	6.85	53	[3, 4]

The major GC–MS peaks are summarised in Table 2. The repeated detection of 2,4-di-tert-butylphenol in all three extracts is consistent with a shared formulation-related or packaging-related source, but confirmation with an authentic standard would be required. Pilot and Pelikan also contained peaks tentatively assigned to 2,6-di-tert-butylphenol and 2,5-di-tert-butylphenol, respectively. Lamy showed the largest relative peak area for 2,4-di-tert-butylphenol (40.76%) and additional silicon-related signals. Because the paper blank was analysed separately but was not displayed in the overlay, interpretation focused on differences in peak patterns and relative areas rather than treating the detected compounds as exclusive markers or major constituents of the inks.

Overall, the GC–MS results indicate that the ink extracts contained phenolic compounds that may reflect stabilising additives or other formulation-related sources. Analysis of authentic standards

and presentation of the paper-blank chromatogram alongside the samples would be required to confirm the compound identities and sources more definitively.

ATR-FTIR Analysis

ATR–FTIR was used to examine the functional-group characteristics of the ink-stained paper samples. Because each sample was analysed directly on the ATR diamond crystal, the spectra may contain contributions from both the ink and the paper substrate. The comparative ATR–FTIR spectra of the fountain pen inks are shown in Figure 4. The bands were therefore interpreted as complementary evidence rather than definitive confirmation of individual compounds, consistent with the comparative use of FTIR in previous ink studies [1, 5]. The GC–MS identified compounds used to support the FTIR band assignments are summarised in Table 3, while the ATR–FTIR peak assignments and functional-group interpretations are presented in Table 4.

Table 3. GC–MS Identified Compounds Used to Support FTIR Band Assignments.

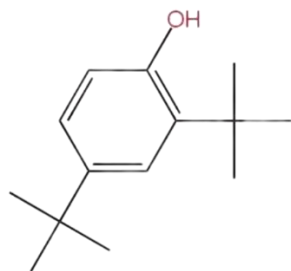
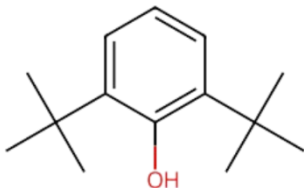
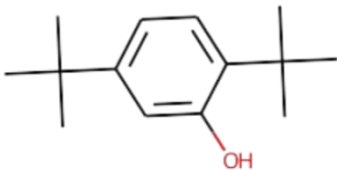
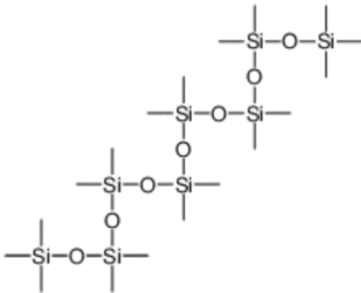
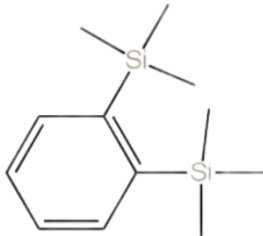
No	Compound Name	Formula	Chemical Structure
1.	2,4-di-tert-butylphenol	C ₁₄ H ₂₂ O	
2.	2,6-di-tert-butylphenol	C ₁₄ H ₂₂ O	
3.	2,5-di-tert-butylphenol	C ₁₄ H ₂₂ O	
4.	Octasiloxane	O ₇ Si ₈	
5.	Bis(trimethylsilyl) benzene	C ₁₂ H ₂₂ Si ₂	

Table 4. ATR–FTIR peak assignments and functional-group interpretation for fountain pen ink samples.

Brand	Wavenumber (cm ⁻¹)	Peak Intensity	Functional Group	Possible chemical origin of the functional group
Pilot	3300–3400	Broad	O–H stretching	Overlapping contribution from cellulose/moisture and possible phenolic components
	1600	Medium	Aromatic C=C stretching	Benzene ring structures
	1200–1250	Medium	C–O stretching	Phenolic ether or alcohol group
Pelikan	3300	Broad	O–H stretching	Overlapping contribution from cellulose/moisture and possible phenolic components
	1580–1600	Medium	Aromatic C=C stretching	Aromatic ring system
	1260–1210	Medium	C–O stretching	Substituted phenols
Lamy	3300	Weak/broad	O–H stretching	Cellulose/moisture and possible trace phenolic contribution
	1000–1100	Strong	Si–O–Si stretching	Cellulose/paper substrate and possible siloxane-related component supported by GC–MS
	750–850	Sharp	Aromatic C–H bending	Aromatic benzene ring

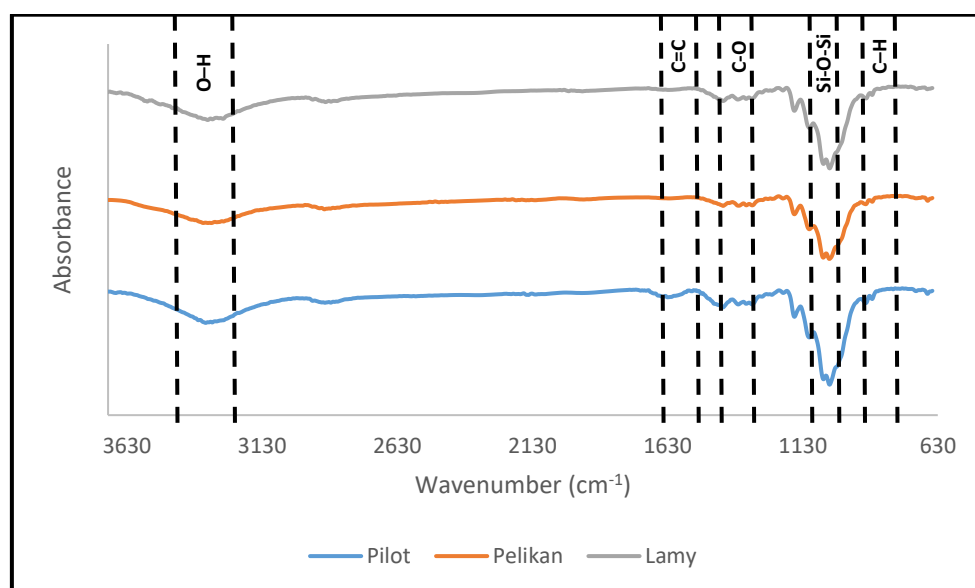


Figure 4. Comparative ATR–FTIR spectra of Pilot, Pelikan and Lamy fountain pen inks.

The broad band at approximately 3300–3400 cm⁻¹ was assigned to O–H stretching. Because the ink was analysed on paper, this band cannot be attributed solely to phenolic O–H groups: cellulose contains abundant hydroxyl groups and produces strong absorption in the same

region. The band was therefore interpreted as an overlapping contribution from cellulose, moisture and possible phenolic components. GC–MS supported a possible phenolic contribution, but ATR–FTIR alone could not establish its source [1, 5].

The band at approximately $1000\text{--}1100\text{ cm}^{-1}$, which was more pronounced for Lamy, was also interpreted cautiously. This region may contain C–O and C–O–C stretching from cellulose and other paper-derived components, as well as a possible Si–O–Si contribution. The band was not treated as exclusive evidence of siloxanes; instead, it was considered together with the tentative GC–MS identification of octasiloxane and 1,2-bis(trimethylsilyl) benzene. Combining the two techniques is useful because GC–MS provides tentative compound-level assignments, whereas ATR–FTIR supplies complementary functional-group information [1, 4].

Overall, ATR–FTIR provided complementary functional-group information that supported the GC–MS interpretation. Because the analysis was performed directly on ink-stained paper, the assignments remain tentative and may include

substrate contributions. The spectra were therefore used for comparative ink profiling rather than as stand-alone confirmation of specific compounds.

UV–Vis Analysis

The UV–Vis absorption spectra of the Pilot, Pelikan and Lamy inks were recorded to determine their absorption maxima (λ_{max}) and absorbance intensities. Figure 5 presents the three spectra on a common axis to facilitate comparison.

The combined UV–Vis spectra (Table 5 and Figure 5) showed clear differences among the inks. Pilot exhibited a λ_{max} of 566.96 nm and an absorbance of 0.055384, whereas Pelikan and Lamy showed maxima at 576.16 and 576.31 nm, respectively. Lamy had the highest absorbance (0.071191), while Pelikan had the lowest (0.042718).

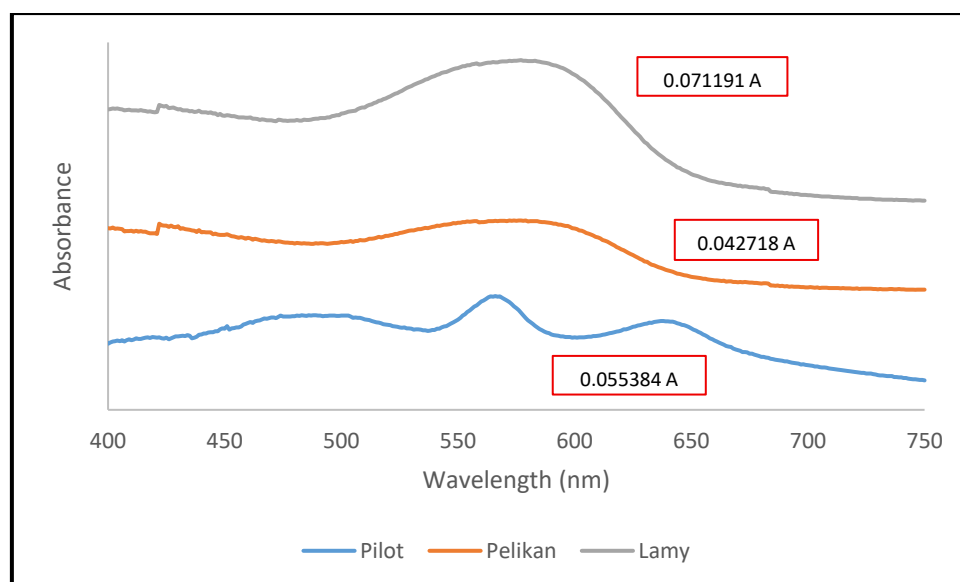


Figure 5. UV–Vis absorption spectra of Pilot, Pelikan and Lamy fountain pen inks.

Table 5. Absorption maxima (λ_{max}) and corresponding absorbance values for Pilot, Pelikan and Lamy fountain pen inks.

Sample (Brand)	λ_{max} (nm)	Absorbance (A)
Pilot	566.96	0.055384
Pelikan	576.16	0.042718
Lamy	576.31	0.071191

The approximately 9 nm difference between the Pilot maximum and those of Pelikan and Lamy suggests differences in their chromophores or local molecular environments. The hypsochromic shift for Pilot may reflect a less extended conjugated system or another structural difference, whereas the bathochromic positions of Pelikan and Lamy may reflect greater conjugation or stronger intermolecular interactions [6]. These interpretations remain tentative because λ_{max} can also be affected by concentration, solvent and matrix effects.

Differences in absorbance intensity may arise from dye concentration, molar absorptivity or formulation effects [9]. The higher absorbance of Lamy therefore indicates stronger light absorption under the tested dilution and measurement conditions, but it does not by itself establish a higher total dye concentration.

Spectral features, including shifts in absorption maxima and differences in intensity patterns, can support forensic discrimination among inks from different manufacturers [8]. UV–Vis is therefore a rapid and comparatively simple technique for ink comparison, particularly when its results are evaluated alongside ATR–FTIR and TLC data.

Overall, the spectra demonstrate compositional variability among the three inks and support the use of UV–Vis as a comparative tool in forensic and analytical chemistry.

Cyclic Voltammetry of Fountain Pen Inks

The screen-printed carbon electrode contained a carbon working electrode, a carbon counter electrode and an on-chip Ag/AgCl pseudo-reference electrode. A 0.1 M KCl solution was first tested as the supporting-electrolyte blank and as a source of chloride ions for the Ag/AgCl reference. The blank produced a nearly featureless CV trace (purple line in Figure 6), with only a small non-faradaic current and no distinct redox peaks between -0.2 and $+0.8$ V. Under the same experimental conditions, the additional current observed for the ink-coated electrodes was therefore attributed primarily to electroactive ink components.

The voltammograms comprise complete forward and reverse scans and were compared in terms of current magnitude, oxidation onset and overall profile.

Unlike the supporting-electrolyte blank, all three inks exhibited clear faradaic responses. Pilot showed the strongest response, with anodic current increasing above the baseline at approximately $+0.2$ to $+0.3$ V versus Ag/AgCl and developing into a broad oxidation wave. Pelikan and Lamy exhibited weaker oxidation currents with later onsets, approximately $+0.4$ to $+0.5$ V. At the upper end of the scan, the Lamy response was slightly greater than that of Pelikan. These differences in onset potential and current magnitude indicate different types and/or amounts of oxidisable species and provide brand-specific voltammetric profiles [13].

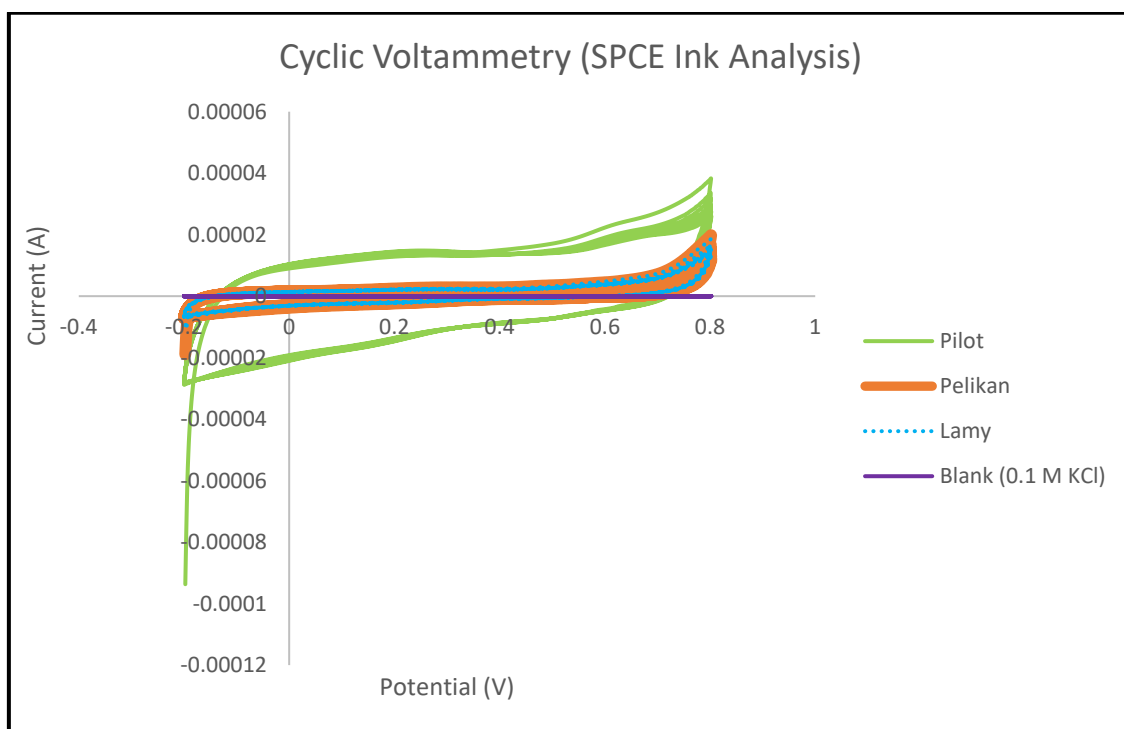


Figure 6. Cyclic voltammograms of the 0.1 M KCl blank and Pilot, Pelikan and Lamy inks on screen-printed carbon electrodes.

The oxidation processes were predominantly irreversible. A reversible redox couple would normally produce corresponding anodic and cathodic peaks, but no well-defined reduction peak mirrored the observed anodic waves [4]. On the reverse scan, the currents returned close to the baseline with only a small, broad cathodic deflection. The oxidised species therefore did not readily return to their reduced forms on the experimental timescale. Possible explanations include follow-up reactions, such as dimerisation or decomposition, and partial passivation of the carbon surface. This interpretation is consistent with the electrochemical oxidation behaviour reported for hindered phenolic antioxidants [13].

The initial scans also showed a cathodic current between approximately 0 and -0.2 V, most prominently for Pilot. This feature was attributed to the reduction of dissolved oxygen at the carbon-electrode surface, which can occur in this potential region in aerated aqueous systems [4, 13]. The current decreased during successive conditioning scans and eventually disappeared, supporting its

assignment to dissolved oxygen rather than an intrinsic ink component.

After conditioning, the CV responses of all three inks were stable and repeatable over multiple cycles. The shapes and magnitudes of the anodic waves remained largely unchanged, suggesting that the electroactive components were not rapidly depleted and that severe electrode fouling did not occur under the applied conditions. The stable onset potentials also indicate that the screen-printed Ag/AgCl pseudo-reference electrode performed consistently in the supporting electrolyte. Pilot exhibited the strongest and earliest oxidation response, whereas Pelikan and Lamy showed weaker, later-onset responses. These brand-specific electrochemical profiles complement chromatographic and spectroscopic approaches to forensic ink discrimination [13].

To provide a clearer overall comparison of the three fountain pen inks, the main findings obtained from TLC, GC–MS, ATR–FTIR, UV–Vis and cyclic voltammetry are summarised in Table 6.

Table 6. Multi-technique comparison of Pilot, Pelikan and Lamy fountain pen inks.

Analysis	Pilot	Pelikan	Lamy	Overall comparison
TLC	Four spots: green, black, blue and red.	Four spots: black and three yellow spots.	Four spots: black and three yellow spots.	Multiple dye components were detected. Similar R_f values indicate comparable migration but not necessarily identical dyes.
GC–MS	2,4-DTBP; 2,6-DTBP detected.	2,4-DTBP; 2,5-DTBP detected.	2,4-DTBP and silicon-related compounds tentatively detected.	Substituted phenols were detected in all extracts; Lamy also showed silicon-related signals. All assignments were tentative.
ATR–FTIR	O–H, aromatic C=C and C–O bands.	O–H, aromatic C=C and C–O bands.	O–H band and stronger absorption at $1000\text{--}1100\text{ cm}^{-1}$.	The spectra provided complementary functional-group information but included possible contributions from the paper substrate.
UV–Vis	$\lambda_{\text{max}} = 566.96\text{ nm}$; absorbance = 0.055384.	$\lambda_{\text{max}} = 576.16\text{ nm}$; absorbance = 0.042718.	$\lambda_{\text{max}} = 576.31\text{ nm}$; absorbance = 0.071191.	Lamy showed the highest absorbance and Pelikan the lowest under the tested conditions.
Cyclic voltammetry	Strongest current response and earlier oxidation behaviour.	Lower current response and later oxidation onset.	Moderate current response, slightly higher than Pelikan at higher potential.	CV provided an additional electrochemical fingerprint for differentiating the inks.
Overall	Diverse dye profile and the strongest electrochemical response.	Lowest absorbance and the weakest electrochemical response.	Highest UV–Vis absorbance and additional silicon-related signals.	The combined methods provided stronger discrimination than any single technique.

CONCLUSION

This study demonstrates the value of combining TLC, GC–MS, ATR–FTIR, UV–Vis and CV to characterise and differentiate black fountain pen inks from Pilot, Pelikan and Lamy. TLC showed that each ink contained multiple dye components spanning a broad range of migration behaviours. GC–MS tentatively identified substituted phenols in all extracts; however, these compounds may have originated from additives, packaging or other formulation-related sources. ATR–FTIR provided complementary evidence of O–H, C–O and possible Si–O–Si functionalities, although contributions from the paper substrate could not be excluded. UV–Vis revealed brand-specific absorption maxima and intensities, with Lamy showing the highest absorbance under the tested conditions.

CV provided additional electrochemical fingerprints that complemented the chromatographic and spectroscopic results. The 0.1 M KCl blank produced only a small capacitive response, whereas all inks showed brand-dependent anodic waves and predominantly irreversible behaviour. Pilot exhibited the strongest and earliest oxidation response, while the smaller oxygen-reduction feature near 0 to –0.2 V diminished during conditioning. Repeated cycling produced stable profiles. Collectively, the results show that the three inks share some chemical features but retain distinguishable chromatographic, spectroscopic and electrochemical profiles. The integrated approach strengthens forensic ink discrimination and may also support quality-control and formulation studies.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support provided by Universiti Teknologi MARA through grant 600-UiTMSEL (PI.5/4/11) (031/2025). The authors also thank the laboratory staff and analytical technicians for their technical assistance and the supervisor and co-supervisor for providing access to the equipment and materials used in this study.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest related to this study or its publication.

REFERENCES

- Sharif, M., Chand, S., Tirmazi, S. A. A. S., Farooq, U., Athar, M. M. and Batool, M. (2022) Investigation and discrimination of ballpoint pen inks by analytical techniques and chemometrics. *International Journal of Analytical Chemistry*, **2022**, 7450539.
- Kravchenko, A. V., Makeeva, D. V., Tumkin, I. and Kalinichev, A. V. (2024) Rapid analysis and classification of blue ballpoint pen inks using high-performance thin-layer chromatography and digital colour analysis. *Talanta*, **275**, 126117.
- Hoang, N. M. H. and Park, K. (2024) Applications of tert-butyl-phenolic antioxidants in consumer products and their potential toxicities in humans. *Toxics*, **12**(12), 869.
- Sharif, M., Jalees, M. I., Tirmazi, S. A. A. S., Athar, M. M., Durrani, A. I. and Batool, M. (2022) Discrimination of Pakistani fountain pen inks by gas chromatography–mass spectrometry (GC–MS). *International Journal of Analytical Chemistry*, **2022**, 7186625.
- Panda, S. S., Singh, N. and Singh, M. R. (2021) Development and characterisation of traditional inks for restoration of ancient manuscripts and application on various substrates to understand stability. *Vibrational Spectroscopy*, **114**, 103232.
- Patel, S., Raulji, A., Chu, D., Panchal, D., Dalwadi, M. and Upadhyay, U. (2022) A review on UV–visible spectroscopy. *International Journal of Pharmaceutical Research and Applications*, **7**(5), 1144–1151.
- Navashree, N. and Parthasarathy, P. (2023) A comparative study on electrochemical behaviour of various electrolytes by cyclic voltammetry: GCE as electrode material. *Materials Today: Proceedings*, *in Press*.
- Simsek, O. and Seker, S. S. (2024) RGB analysis for forensic discrimination of blue fountain pen inks. *International Journal of Forensic Research*, **5**(2), 1–5.
- Luňáková, M., Dorazil, J., Jonák, M., Ježek, Š. and Burget, R. (2025) Pen ink library: An interactive database of writing instruments based on Vis–NIR reflection spectra and optical properties of inks. *Forensic Science International*, **373**, 112508.
- Christie, R. and Abel, A. (2021) Organic pigments: General principles. *Physical Sciences Reviews*, **6**(12), 807–834.
- Li, C., Feng, C., Zhang, L., Zhang, L. and Wang, L. (2025) Direct ink writing of polymer-based materials—A review. *Polymer Engineering & Science*, **65**(2), 431–454.
- Liu, R. and Mabury, S. A. (2020) Synthetic phenolic antioxidants: A review of environmental occurrence, fate, human exposure and toxicity. *Environmental Science & Technology*, **54**(19), 11706–11719.

13. Zabik, N. L., Virca, C. N., McCormick, T. M. and Martic-Milne, S. (2016) Selective electrochemical versus chemical oxidation of bulky phenol. *The Journal of Physical Chemistry B*, **120**(34), 8914–8924.
14. Churinsky, C. R. (2013) Characterization of Carbon Electrode Surfaces: Development of Biosensors for Forensic DNA Applications M.S. Thesis. *Boston University, Boston, Massachusetts, USA*.