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FORENSIC MULTI-TECHNIQUE PROFILING OF FOUNTAIN PEN INKS ON PAPER

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CONFIRMATION BY PANEL OF EXAMINERS

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ABSTRACT

Fountain pen inks are increasingly encountered in forensic document examination, yet they remain comparatively underexplored in ageing-focused studies. This research establishes baseline characterisation of three commercial fountain pen inks (Pilot, Pelikan and Lamy) deposited on Double A A4 paper and analysed at a single time point (fresh ink after 30 minutes drying at room temperature). A multi-technique analytical approach was applied, including Thin Layer Chromatography (TLC), Gas Chromatography-Mass Spectrometry (GC-MS), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), Ultraviolet-Visible Spectroscopy (UV-Vis), Polarised Optical Microscopy (POM), Field Emission Scanning Electron Microscopy with Energy-Dispersive X-ray analysis (FESEM-EDX) and cyclic voltammetry using Screen-Printed Carbon Electrodes (SPCE). TLC revealed that all inks contained multiple dye components, with distinct retention factor (R_f) patterns useful for discrimination. GC-MS identified formulation-related additives, including substituted phenolic antioxidants and siloxane-related compounds, supporting differences in stability-related composition between brands. ATR-FTIR and UV-Vis provided complementary functional group and chromophore information, while POM and FESEM-EDX highlighted differences in ink distribution and surface morphology on paper fibres. Cyclic voltammetry produced distinguishable redox profiles across the inks, demonstrating value as a rapid, low-volume complementary method for ink comparison. Overall, this work provides a baseline dataset for fountain pen ink discrimination and highlights chemical, optical, microscopic and electrochemical features that may be tracked in future controlled ageing studies. Long-term ageing trends were not measured in this thesis.

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LIST OF SYMBOLS

Symbols

pH	Measure of acidity or alkalinity of a solution
R_f	Retention factor in thin-layer chromatography
λ_{max}	Maximum absorption wavelength
O-H	Hydroxyl bond
C=C	Carbon–carbon double bond
C-O	Carbon–oxygen bond
Si-O-Si	Siloxane bond
Si-C	Silicon-carbon bond
C-H	Carbon-hydrogen bond
π	Pi bond / π-electron system
A	Absorbance, measure of light absorption
C	Carbon element
O	Oxygen element
Ca	Calcium element
Si	Silicon element

LIST OF ABBREVIATIONS

Abbreviations

AFM	Atomic Force Microscopy
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy
CAS	Chemical Abstracts Service
CV	Cyclic Voltammetry
EDX	Energy Dispersive X-ray
FDE	Forensic Document Examination
FESEM-EDX	Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray
GC-MS	Gas Chromatography-Mass Spectrometry
POM	Polarised Optical Microscopy
PTFE	Polytetrafluoroethylene
SEM-EDX	Scanning Electron Microscopy-Energy Dispersive X-ray
SPCE	Screen-Printed Carbon Electrode
TICs	Total Ion Chromatograms
TLC	Thin-Layer Chromatography
UV-Vis	Ultraviolet–Visible Spectroscopy

LIST OF NOMENCLATURE

Nomenclatures

$C_{12}H_{22}Si_2$	Molecular formula of an organosilicon compound
$C_{14}H_{22}O$	Molecular formula of an substituted phenolic compound
$C_4H_{10}O$	Butanol
$CaCO_3$	Calcium carbonate
CH_3COOH	Acetic acid
CH_3OH	Methanol
H_2O	Water
$K_4[Fe(CN)_6]$	Potassium ferrocyanide
KCl	Potassium chloride
O_7Si_8	Silica-based structural formula

CHAPTER 1
INTRODUCTION

1.1 Background of the Study

1.1.1 Forensic Document Examination and The Importance of Ink Analysis

Forensic document examination (FDE) is a specialised discipline within forensic science that focuses on the analysis of documents to determine authenticity, detect alterations and resolve disputes related to authorship or content. Documents frequently examined in forensic casework include contracts, wills, financial records, identification documents and handwritten notes. Writing inks play a critical role in such examinations, as they may provide information regarding document modification, sequence of writing and potential forgery (Calcerrada & García-Ruiz, 2015; Giles, 2016).

Ink analysis has long been recognised as a valuable tool in forensic investigations, particularly when questions arise concerning whether different entries were written at the same time or using the same writing instrument. Variations in ink composition, colour, or physical appearance can indicate the presence of alterations or additions to a document. As a result, analytical techniques capable of characterising ink composition and behaviour have become integral components of forensic document examination (Mirzanli et al., 2025).

Among the challenges faced by forensic examiners, the determination of ink age, commonly referred to as ink dating or ink ageing detection, remains one of the most complex and debated aspects of ink analysis. Unlike handwriting characteristics, which may remain relatively stable over time, inks undergo continuous physical and chemical changes after deposition onto paper. These changes complicate the interpretation of ink age and necessitate cautious, scientifically grounded approaches (Li et al., 2025).

1.1.2 Ink Ageing and Its Forensic Challenges

Ink ageing refers to the time-dependent changes that occur in writing inks following their deposition on a paper substrate. These changes involve both physical processes, such as solvent evaporation and ink diffusion into paper fibres, and chemical processes, including dye degradation, oxidation and additive transformation. The rate and extent of ink ageing are influenced by multiple factors, including ink formulation, paper composition, environmental exposure and storage conditions (Aydemir & Özsoy, 2020; Zhang et al., 2024).

Historically, many ink dating studies have focused on the loss of volatile components, particularly in ballpoint pen inks. Solvent-loss-based approaches typically monitor the decrease in specific organic solvents over time using gas chromatographic techniques. While such methods can demonstrate time-dependent trends under controlled conditions, their forensic applicability is limited. Environmental variability and the lack of information regarding the history of questioned documents often preclude reliable absolute dating in real casework (Devlin et al., 2024).

As a consequence, modern forensic practice increasingly emphasises relative and comparative ink ageing assessment rather than precise chronological dating. Relative ink ageing aims to determine whether one ink entry is older or newer than another, while comparative approaches assess whether multiple entries are contemporaneous. These interpretations align more closely with the evidential needs of forensic investigations and reduce the risk of overinterpretation (Ortiz-Herrero et al., 2020).

1.1.3 Fountain Pen Inks in Forensic Context

Despite extensive research on ballpoint pen inks, fountain pen inks have received comparatively limited attention in forensic ink ageing-related and discrimination studies. Fountain pen inks are predominantly water-based and consist mainly of dyes, humectants, preservatives, and other additives designed to ensure smooth ink flow and colour stability. Unlike ballpoint inks, they generally lack high concentrations of volatile organic solvents, which limits the applicability of solvent-loss dating models (Christie & Abel, 2021).

The ageing behaviour of fountain pen inks is therefore governed by alternative mechanisms, such as dye photodegradation, oxidation and ink–paper interaction effects. These processes may manifest as changes in colour intensity, chemical structure, or spatial distribution within paper fibres. Given the widespread use of fountain pen inks in signatures, official correspondence and archival documents, their underrepresentation in forensic ink baseline differences research represents a significant knowledge gap (Sharif, Jalees, et al., 2022).

Furthermore, fountain pen inks often exhibit deeper penetration into paper fibres compared to ballpoint inks, due to their lower viscosity and aqueous formulation. This characteristic complicates both sampling and analysis, reinforcing the need for analytical techniques capable of probing chemical, physical and electrochemical properties in a complementary manner.

1.2 Problem Statement

The increasing sophistication of document forgery presents significant challenges in forensic science, particularly in the authentication of questioned documents. Written documents are frequently used as critical evidence in criminal, civil and financial disputes, where the credibility of the case often depends on the authenticity and relative age of ink entries. However, determining ink baseline differences and ageing-related changes remains one of the most complex aspects of forensic document examination. Conventional methods, including visual inspection and chemical spot tests, are often subjective, poorly reproducible and insufficient for providing conclusive forensic evidence (Aginsky, 2019; Germinario et al., 2018).

Although various instrumental techniques have been applied to ink analysis, existing research predominantly focuses on ballpoint and gel pen inks. In contrast, fountain pen inks have received comparatively limited attention despite their continued use in personal, academic and formal documentation. Moreover, many studies investigate ink baseline differences from a single analytical perspective, such as solvent evaporation using GC-MS or dye composition using UV-Vis spectroscopy (Senior et al., 2012; Sharif, Jalees, et al., 2022). The lack of integration between chemical, morphological and electrochemical analyses restricts the reliability and forensic applicability of ink baseline differences and ageing-related changes.

Another critical challenge in forensic ink analysis is the balance between analytical sensitivity and preservation of original evidence. Advanced techniques such as GC-MS and FESEM-EDX can provide detailed chemical and morphological information, but they may require destructive or semi-destructive sampling, which may not always be permissible in real forensic casework. Morphological analysis is important because it helps observe ink deposition, spreading, penetration and interaction with paper fibres, while electrochemical analysis provides additional information on redox-active ink components that may change with formulation or ageing. In addition, ink ageing is strongly influenced by environmental factors including light exposure, humidity and temperature, further complicating reproducibility and interpretation of results across different forensic scenarios (Aydemir & Özsoy, 2020; Zhang et al., 2024).

In this context, combining chemical characterisation, physical examination, and emerging approaches such as electrochemical analysis provides a more holistic

understanding of the ink chemical fingerprint that may be related to ink ageing behaviour. Rather than attempting to assign an absolute age based on a single marker, integrated strategies aim to identify consistent trends and formulation-dependent characteristics that support relative age assessment and ink discrimination.

Therefore, there is a clear need for a comprehensive and integrated analytical approach that combines chemical, structural, morphological and electrochemical techniques to characterise the baseline differences and ageing behaviour of fountain pen inks. Such an approach has the potential to improve the reliability of forensic ink differentiation, support document authentication and contribute toward the development of more robust and standardised methodologies for forensic document examination.

1.3 Research Objectives

This research aspires to contribute to forensic document examination by enhancing the tools available for detecting forgery. Through the integration of advanced technologies, it aims to address the critical need for precision and reliability in forensic investigations. The specific objectives of this study are:

a) To establish baseline chemical profiles of selected fountain pen inks (Pilot, Pelikan and Lamy) at a single time point (fresh ink after drying) using Thin-Layer Chromatography (TLC), Gas Chromatography-Mass Spectrometry (GC-MS), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Ultraviolet-Visible Spectroscopy (UV-Vis).
b) To compare ink distribution, surface morphology and elemental characteristics of the inks on paper using Polarised Optical Microscopy (POM) and Field Emission Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (FESEM-EDX).
c) To evaluate Screen-Printed Carbon Electrodes (SPCE)-based cyclic voltammetry provides complementary electrochemical signatures for ink discrimination and formulation-dependent oxidative stability assessment, supporting future ink ageing studies.

1.4 Research Question

i) What baseline chemical features differentiate Pilot, Pelikan and Lamy fountain pen inks as measured by Thin-Layer Chromatography (TLC), Gas Chromatography-Mass Spectrometry (GC-MS), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Ultraviolet-Visible Spectroscopy (UV-Vis)?

ii) How do the inks differ in baseline physical distribution, morphology and elemental signals on paper as observed using Polarised Optical Microscopy (POM) and Field Emission Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (FESEM-EDX)?

iii) Can SPCE-based cyclic voltammetry provide reproducible electrochemical signatures that complement chemical and microscopic findings and may be tracked in future ageing studies?

1.5 Significance of Study

The detection of ink ageing in forensic documents is essential in forensic science, particularly for the authentication of questioned documents. Forged or altered documents often play a critical role in legal disputes, financial crimes and identity-related cases, where establishing relative ink characteristics can provide valuable evidence. Traditional examination methods, such as visual inspection and chemical spot tests, often lack the precision and reproducibility needed for conclusive results. Therefore, employing combined analytical techniques offers a more scientific, reproducible and legally defensible approach to document analysis.

This study applies an integrated analytical approach to investigate fountain pen inks from chemical, structural and electrochemical perspectives. Chemical characterisation using Thin-Layer Chromatography (TLC), Gas Chromatography-Mass Spectrometry (GC-MS), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Ultraviolet-Visible Spectroscopy (UV-Vis) provides insights into the chemical composition of inks. It identifies markers relevant to ink ageing detection and ink baseline differences.

Surface analysis using Polarised Optical Microscopy (POM) and Field Emission Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (FESEM-EDX) examines morphological features and elemental distributions associated with ink stability. These observations complement chemical data and enhance understanding of physical characteristics indicative of ink baseline differences.

Electrochemical analysis using Screen-Printed Carbon Electrodes (SPCE) introduces an additional dimension, enabling the detection of redox-active components and electrochemical signatures as indicators of ink chemical fingerprint while preserving the integrity of the original evidence.

Overall, this research provides a comprehensive, scientifically validated approach for detecting ink baseline differences that may be related to ink ageing, enhancing the reliability of forensic document examination and supporting the development of standardised methodologies applicable in forensic laboratories. The study bridges the gap between traditional examination methods and advanced instrumental analysis, equipping forensic scientists with robust tools to address complex document forgery cases.

1.6 Scope and Limitation

This study focuses on baseline characterisation of three commercial fountain pen inks (Pilot, Pelikan and Lamy) deposited on a single paper type (Double A A4) using multiple complementary analytical techniques. No systematic ageing time-series experiment was conducted. Therefore, the results are not used to claim time-dependent ageing trends. Any discussion related to ageing is limited to identifying candidate indicators reported in the literature and interpreting formulation-dependent stability-related differences observed at the baseline condition. Future work should include controlled ageing under defined environmental conditions (light, heat, humidity and oxygen) to validate the proposed indicators.

Despite the comprehensive analytical approach, several limitations are acknowledged. First, the restriction to only three commercial fountain pen ink brands may limit the generalisability of the findings, particularly when considering other ink types such as gel, ballpoint, or historical inks, which may exhibit distinct baseline characterisation (Luňáková et al., 2025; Mirzanli et al., 2025). Furthermore, although black inks were selected due to their high forensic relevance, the findings may not be directly applicable to inks of other colours, which often contain dyes and pigments with different chemical stability profiles.

Secondly, the study was conducted under controlled laboratory conditions that simulate, but do not fully replicate, real-world storage environments. Variations in environmental factors such as temperature, humidity and light exposure in actual forensic scenarios may result in different degradation pathways. Previous studies have shown that volatile components in inks decrease over time, a process that may be accelerated under environmental stress (Aydemir et al. 2020; Zhang et al. 2024).

Another limitation relates to the partially destructive nature of certain analytical techniques employed, including GC-MS and FESEM-EDX. These methods may not always be suitable in real forensic casework, where preservation of the original document is critical. Finally, this study does not aim to establish precise chronological dating of ink age. Instead, it focuses on identifying baseline compositional and structural characteristics that may be relevant to future ageing studies; therefore, absolute determination of the time since writing was beyond the scope of this research.

CHAPTER 2
LITERATURE REVIEW

This chapter reviews the existing literature related to forensic ink examination and ink ageing detection. The discussion focuses on the chemical composition of writing inks, mechanisms of ink ageing on paper and analytical techniques commonly employed in forensic document analysis. Particular attention is given to the limitations of existing ink dating approaches and the underexplored nature of fountain pen inks in ageing-related studies. By synthesising findings from previous research, this chapter establishes the scientific context and identifies key research gaps that justify the scope and objectives of the present study.

2.1 Forensic Document Examination and Ink Ageing Detection

Forensic document examination (FDE) is a specialised discipline within forensic science that focuses on the scientific analysis of documents to establish authenticity, detect alterations and resolve disputes related to questioned writings. Documents examined in forensic contexts include contracts, wills, cheques, academic certificates, medical records and legal agreements, where the integrity of written information is often central to judicial decision-making. In many cases, disputes arise not only from questions of authorship but also from uncertainty regarding the timing of entries, such as whether a signature, annotation, or clause was added after the document was originally executed (Devlin et al., 2024).

Ink ageing detection forms a crucial component of FDE because inks undergo time-dependent changes once deposited on paper. These changes may be physical, such as solvent evaporation and diffusion into paper fibres, or chemical, including oxidation and degradation of dyes and additives. Consequently, the chemical and physical properties of ink lines evolve with time, providing potential indicators that can assist forensic examiners in evaluating the relative age of written entries (Giles, 2016). Importantly, ink ageing detection in forensic practice is rarely concerned with determining an exact calendar date. Instead, it supports relative comparisons, such as whether two ink entries were written contemporaneously or at different times.

Despite decades of research, forensic ink dating remains a challenging task due to the complex interplay of factors influencing ink behaviour. Ink formulation varies widely between manufacturers and ink types, while external factors such as paper composition, storage conditions, light exposure, temperature, and humidity significantly affect ageing rates. As emphasised by Trejos et al. (2017), these variables limit the reliability of single-marker or single-technique approaches and necessitate cautious interpretation of results. Consequently, modern forensic literature increasingly advocates for multi-technique analytical strategies that combine complementary forms of evidence rather than relying on a single ageing parameter.

Recent comprehensive reviews further highlight that ink ageing detection should be framed as an interpretive tool rather than a definitive dating method. Kapoor et al. (2021) note that forensic ink analysis has progressed from isolated analytical measurements toward integrated frameworks that consider chemical composition, physical distribution and environmental context. This paradigm shift aligns with

contemporary forensic standards, which emphasise transparency, reproducibility and evidential robustness. Within this context, ink ageing detection is best understood as part of a holistic approach to questioned document examination, contributing to the overall weight of forensic evidence rather than serving as a standalone determinant.

2.2 Writing and Printing Materials in Forensic Documents

Documents submitted for forensic examination may contain a variety of writing and printing materials, each characterised by distinct formulation technologies and forensic properties. Broadly, these materials can be categorised into handwritten inks and printed materials. Differentiating between these categories is essential because the analytical techniques and ageing indicators applicable to one class may be ineffective or inappropriate for another. In forensic document examination, a variety of writing and printing traces may be encountered, each exhibiting distinct compositional characteristics and ageing behaviour. Table 2.1 summarises the taxonomy of common ink and printing materials reported in the forensic literature, highlighting their typical composition, applications, and relevance to ink ageing studies. This classification provides context for the present study and illustrates that fountain pen inks, despite their widespread use, remain comparatively underrepresented in ageing-focused forensic research.

Table 2.1

Taxonomy of Ink and Printing Traces.

Category	Writing / Printing Trace Type	Typical Composition	Common Forensic Applications	Relevance of Ink Studies	Author
Handwritten inks	Ballpoint pen ink	Oil-based vehicle containing dyes, resins, and volatile organic solvents	Signatures, handwritten notes, contracts, cheques	Extensively studied for ink dating due to solvent-loss behaviour; widely used in dynamic dating models	(Koenig et al., 2015)
	Gel pen ink	Pigments suspended in polymer gel matrix with humectants and additives	Signatures, annotations, official forms	Limited applicability of solvent-based dating; ageing studies rely on pigment stability and physical distribution	(Germinario et al., 2018)
	Rollerball pen ink	Water-based inks containing dyes and small amounts of solvents	Notes, correspondence, administrative documents	Moderately explored; dye degradation and diffusion behaviour relevant to ageing	(Simsek & Seker, 2024)
	Fountain pen ink	Water-based, dye-rich formulations with surfactants, preservatives, and stabilisers	Signatures, formal documents, archival writing	Underexplored due to rapid paper diffusion and limited solvent-loss markers.	(Sharif, Jalees, et al., 2022)

Category	Writing / Printing Trace Type	Typical Composition	Common Forensic Applications	Relevance of Ink Studies	Author
Printed materials	Inkjet printer ink	Liquid inks containing dyes or pigments dissolved/dispersed in aqueous or solvent systems	Printed documents, letters, invoices	Not suitable for solvent-based dating; examined using spectroscopic and microscopic techniques	(Vaseem et al., 2012)
	Toner (laser printing)	Polymeric particles with pigments and inorganic additives	Official records, certificates, administrative form	Not suitable for solvent-based dating; examined using spectroscopic and microscopic techniques	(Aydemir & Özsoy, 2020)

2.2.1 Handwritten inks

Handwritten inks include ballpoint pen inks, gel pen inks, rollerball inks and fountain pen inks. Ballpoint pen inks are typically oil-based and contain a mixture of dyes, resins, and volatile solvents that facilitate smooth writing and rapid drying. Due to the presence of identifiable volatile components, ballpoint inks have historically been the primary focus of ink dating research, particularly in studies employing gas chromatography-based techniques (Koenig et al., 2015). The fountain pen inks selected in this study were commercial black inks from Pilot, Pelikan and Lamy, as shown in Figure 2.1. These brands were chosen to represent commonly available fountain pen inks with water-based formulations used in handwriting and formal documentation.

Figure 2.1 Commercial Black Fountain Pen Ink Samples Used in This Study: Pilot, Pelikan and Lamy.

Gel pen inks differ substantially from ballpoint inks in that they often consist of pigments suspended in a polymeric gel matrix. This formulation confers intense colour and opacity but reduces the relevance of solvent-loss dating approaches. Rollerball inks and fountain pen inks are generally water-based and rely heavily on dye systems rather than pigments. Fountain pen inks, in particular, are formulated to ensure controlled flow through pen nibs and reservoirs, often incorporating humectants, surfactants, preservatives and stabilising additives.

Although fountain pen inks are widely used for signatures and formal writing, they have received comparatively limited attention in forensic ageing studies. This disparity reflects the historical focus on solvent-based dating methods, which are less applicable to water-based dye inks. Nonetheless, recent work suggests that fountain pen inks possess complex chemical signatures that can be exploited using combined analytical techniques (Sharif, Jalees, et al., 2022; Simsek & Seker, 2024).

2.2.2 Printed inks and toner

Printed materials encountered in forensic documents include inkjet printer inks and toner-based laser printing. Inkjet inks are liquid formulations containing dyes or pigments dissolved or dispersed in aqueous or solvent-based vehicles. Toners, by contrast, are dry powders composed primarily of polymeric materials, pigments, and inorganic additives. Due to these differences, printed materials exhibit ageing behaviour distinct from handwritten inks and are often examined using spectroscopic and microscopic techniques rather than traditional ink dating methods (Mielonen et al., 2015; Vaseem et al., 2012).

2.3 Chemical Composition of Writing Inks

The chemical composition of writing inks is a fundamental factor governing their visual appearance, performance on paper, and ageing behaviour over time. From a forensic perspective, understanding ink composition is essential because analytical techniques used in ink examination target different chemical components, and changes in these components underpin many ageing-related indicators. Although ink formulations vary between manufacturers and ink types, most writing inks consist of three principal components, which are colourants (dyes or pigments), solvents or vehicles, and additives or stabilisers. The relative proportions and chemical nature of these components determine how inks interact with paper and how they respond to environmental exposure during ageing (Coman & Copaciu, 2015; Germinario et al., 2018).

2.3.1 Dyes and Pigments

Colourants are the most visually apparent components of writing inks and are primarily responsible for ink colour and intensity. In forensic ink analysis, colourants are also among the most informative components because their chemical diversity enables discrimination between ink formulations. Colourants used in writing inks can be broadly categorised into dyes and pigments, each exhibiting distinct chemical properties and ageing behaviour.

Dyes are organic molecules that are molecularly dissolved in the ink vehicle. They are commonly used in fountain pen inks, rollerball inks, and many inkjet inks. Due to their solubility, dyes readily penetrate paper fibres and produce smooth, uniform writing. However, dyes are generally more susceptible to chemical degradation processes such as oxidation, photodegradation, and hydrolysis. Over time, these processes may lead to colour fading, changes in absorbance characteristics, or the formation of degradation products detectable by chromatographic or spectroscopic techniques (X. Liu et al., 2013; Ortiz-Herrero et al., 2020). Consequently, dye-based inks often exhibit ageing behaviour that can be monitored using techniques such as Thin Layer Chromatography (TLC), UV–Visible spectroscopy, and ATR-FTIR spectroscopy.

In contrast, pigments are insoluble particulate colourants dispersed within the ink matrix, typically with the aid of polymeric binders. Pigments are widely used in gel pen inks, toner-based printing, and some inkjet inks. Their particulate nature makes them more resistant to chemical degradation and fading, particularly under light exposure. As a result, pigment-based inks generally display greater colour stability over time compared to dye-based inks. However, their reduced solubility limits the applicability of chromatographic separation techniques, and forensic examination of pigment-based inks often relies more heavily on microscopy, FTIR, and elemental analysis (Christie & Abel, 2021; Hosu et al., 2015).

From an ageing perspective, the predominance of dyes in fountain pen inks is particularly relevant. Because dyes are chemically active and sensitive to environmental conditions, fountain pen inks may exhibit measurable ageing-related changes in spectral profiles and chromatographic patterns. Although this sensitivity complicates absolute dating, it also provides opportunities for comparative ageing assessment when combined analytical techniques are applied (Sharif, Chand, et al., 2022). This characteristic distinguishes fountain pen inks from pigment-dominated ink types and supports their suitability for multi-technique forensic studies.

2.3.2 Solvents and Vehicles

Solvents and vehicles serve as the medium in which colourants and additives are dispersed, enabling ink flow, transfer to paper and drying after writing. The nature of the solvent system strongly influences ink baseline differences that may be related to

ageing behaviour, particularly in the early stages after deposition. In forensic literature, solvent composition has been one of the most extensively studied aspects of ink dating, especially for ballpoint pen inks.

Ballpoint pen inks typically contain oil-based vehicles and volatile organic solvents, such as glycol ethers, which facilitate smooth writing and rapid drying. These volatile components gradually evaporate after ink deposition, forming the basis of dynamic solvent-loss dating approaches. Numerous studies have attempted to model the decrease in solvent concentration as a function of time using gas chromatographic techniques, demonstrating that solvent loss can provide useful relative ageing information under controlled conditions (de Carvalho et al., 2019; Koenig et al., 2015). However, such approaches are highly sensitive to environmental variables, paper type, and storage conditions, limiting their general applicability in forensic casework.

In contrast, fountain pen inks, rollerball inks, and many gel pen inks are predominantly water-based systems. Water-based vehicles promote capillary penetration into paper fibres and result in different drying dynamics compared to oil-based inks. Because water evaporates rapidly and is not typically targeted in solvent-loss dating, ageing indicators in water-based inks are more closely linked to dye chemistry, additive stability and ink–paper interactions rather than vehicle evaporation (Zhang et al., 2024). This fundamental difference explains why fountain pen inks have been less frequently studied in traditional ink dating literature, which has historically prioritised volatile solvent analysis.

For printed materials, solvent systems vary depending on technology. Inkjet inks may contain aqueous or mixed solvent vehicles, while toner-based inks are essentially solvent-free after printing. These distinctions further highlight that solvent-based ageing approaches are ink-type dependent and cannot be universally applied across all writing and printing materials (Mielonen et al., 2015).

Overall, solvent and vehicle composition play a crucial role in determining the feasibility and limitations of different ink methodologies. In the context of fountain pen inks, the absence of characteristic volatile solvents necessitates alternative strategies that focus on non-volatile components and their chemical evolution over time.

2.3.3 Additives and Stabilisers

Additives and stabilisers are incorporated into writing ink formulations to enhance performance, durability and shelf life. Although present in smaller concentrations compared to colourants and solvents, additives play a disproportionately important role in ink stability and ageing behaviour. Common additives include surfactants, humectants, preservatives, plasticisers, lubricants, and antioxidants.

Surfactants and humectants are used to control ink wetting, flow, and drying behaviour, particularly in fountain pen inks, where consistent ink delivery is essential. Preservatives are used to prevent the increase of numbers of microorganisms in water-based inks, and plasticisers and lubricants are used to make the ink writing smooth. Antioxidants and stabilisers are added in to prevent oxidative degradation of dyes and other organic components, particularly of forensic relevant (Hoang & Park, 2024).

Phenolic antioxidants and related stabilisers have been reported in various ink formulations and are frequently detected using GC–MS or FTIR techniques. These compounds function by scavenging free radicals and slowing oxidation processes, thereby influencing the long-term stability of ink colour and composition. From an ageing perspective, the presence and relative abundance of stabilisers can affect the rate at which measurable changes occur, potentially explaining differences in ageing behaviour between ink brands and formulations (Hoang et al. 2024; Liu et al. 2020).

Importantly, additives may themselves undergo chemical transformation or depletion over time, providing indirect indicators of ageing. For example, changes in antioxidant concentration or redox behaviour may be detectable using electrochemical techniques, offering complementary information to chromatographic and spectroscopic analyses. However, because additive composition varies widely between manufacturers and is often proprietary, interpretation must be comparative and supported by multiple lines of evidence.

In fountain pen inks, additive systems are particularly significant due to the water-based nature of the formulation and the need for long-term stability within pen reservoirs. Consequently, additives and stabilisers represent a key target for forensic examination and a promising avenue for ageing-related investigation when integrated with other analytical techniques.

2.4 Mechanisms of Ink Ageing on Paper

Ink ageing refers to the set of time-dependent physical and chemical changes that occur after ink has been deposited onto a paper substrate. These changes begin immediately after writing and continue throughout the lifetime of the document. From a forensic perspective, understanding the mechanisms of ink ageing is essential because analytical measurements do not reflect a static ink composition but rather a dynamic system influenced by formulation, substrate, and environmental exposure. The literature generally recognises that ink ageing mechanisms can be grouped into physical ageing processes, chemical ageing processes, and ink–paper interactions, all of which collectively influence the observable properties of ink lines over time (Y. Liu et al., 2017; Ortiz-Herrero et al., 2020).

2.4.1 Physical Ageing Process

Physical ageing processes primarily involve the redistribution and loss of ink components without changes to their chemical structure. One of the earliest and most significant physical processes is solvent evaporation. Inks often contain volatile or semi-volatile components that evaporate after deposition, leading to changes in ink composition during the initial ageing phase. This process has been extensively studied in ballpoint pen inks, where the gradual loss of solvents forms the basis of many dynamic ink dating approaches (Y. Liu et al., 2017). However, the rate of solvent evaporation is strongly influenced by environmental factors such as temperature, humidity, airflow, and document storage conditions. Figure 2.2 schematically illustrates the physical ageing processes of writing ink on paper, highlighting solvent evaporation and the diffusion and migration of ink components within the paper fibre matrix.

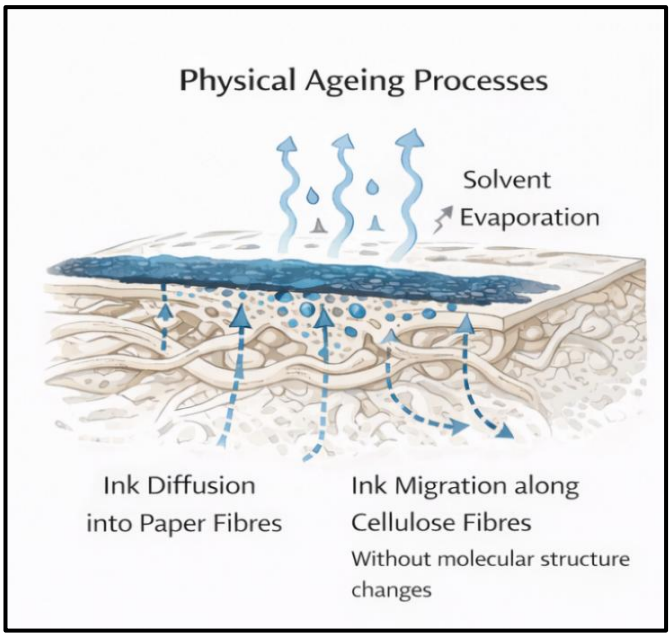


Figure 2.2 Schematic Illustration of The Physical Ageing Processes of Writing Ink on Paper.

In water-based inks, including fountain pen and rollerball inks, solvent evaporation occurs rapidly and is dominated by water loss. As a result, physical ageing in these inks is less associated with long-term solvent decay and more closely related to diffusion and migration of dissolved components into the paper substrate. After writing, ink penetrates paper fibres through capillary action, resulting in a non-uniform spatial distribution of colourants and additives. This phenomenon can produce concentration gradients across the ink line, often with higher accumulation at stroke edges or fibre junctions.

Another important physical ageing mechanism is ink spreading and feathering, which depends on paper porosity, fibre orientation, and surface sizing. These effects influence the apparent width and texture of ink strokes and may evolve subtly over time as ink components continue to migrate within the paper matrix. From a forensic standpoint, physical redistribution has significant implications for sampling strategy, as measurements taken from different regions of the same ink line may yield different analytical results.

Physical ageing processes are generally reversible only to a limited extent and do not involve molecular transformation. Nevertheless, they play a crucial role in shaping the early-stage behaviour of inks and must be considered when interpreting chemical ageing indicators. Failure to account for physical ageing may lead to

misinterpretation of analytical data, particularly in comparative studies involving different sampling locations on the ink line (de Carvalho et al., 2019; Koenig et al., 2015).

2.4.2 Chemical Ageing Process

Chemical ageing processes involve structural changes to ink components resulting from chemical reactions occurring over time. These processes primarily affect organic constituents such as dyes, solvents, and additives and are responsible for many long-term changes observed in ink appearance and composition. Among the most significant chemical ageing mechanisms are oxidation, photodegradation, and hydrolysis. Chemical ageing involves molecular-level changes in ink components driven by oxidation and environmental exposure. Figure 2.3 schematically illustrates the chemical ageing processes of writing ink on paper, highlighting dye degradation, oxidative reactions, and the transformation of ink additives over time.

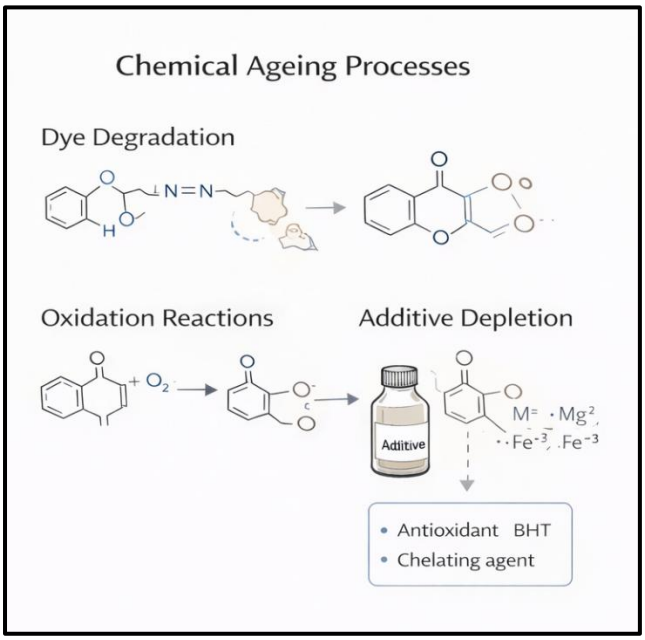


Figure 2.3 Schematic Illustration of The Chemical Ageing Processes of Writing Ink on paper.

Oxidation is a dominant ageing pathway for many dye-based inks, including fountain pen inks. Exposure to oxygen and environmental oxidants can lead to gradual degradation of dye molecules, resulting in colour fading or changes in spectral characteristics detectable by UV–Visible or FTIR spectroscopy. Photodegradation, driven by exposure to ultraviolet and visible light, can accelerate these processes, particularly for dyes with extended conjugated systems (Senior et al., 2012).

Hydrolysis may also contribute to chemical ageing, especially in water-based inks, where prolonged exposure to moisture facilitates bond cleavage in susceptible dye or additive molecules. Over time, these reactions can generate degradation products that alter chromatographic profiles and may appear as additional components in TLC or GC–MS analyses. Such changes are often subtle and formulation-dependent, underscoring the importance of comparative interpretation rather than absolute ageing claims.

Additives, particularly antioxidants and stabilisers, play a critical role in modulating chemical ageing processes. Antioxidants are designed to delay oxidative degradation by scavenging free radicals; however, they may themselves be consumed or transformed over time. The depletion of stabilisers can indirectly accelerate dye degradation, leading to observable ageing effects at later stages. As a result, chemical ageing is not linear and may exhibit different phases depending on additive concentration and environmental exposure (Germinario et al., 2018).

In forensic ink ageing studies, chemical ageing processes provide some of the most informative indicators, as they reflect intrinsic changes in ink composition. However, because reaction rates depend on numerous external factors, chemical ageing markers must be interpreted cautiously and preferably in conjunction with physical and spatial evidence.

2.4.3 Ink-Paper Interactions

Physical ageing processes primarily involve the redistribution and loss of ink components. Ink–paper interaction represents a critical interface where both physical and chemical ageing mechanisms converge. Paper is a complex substrate composed primarily of cellulose fibres, along with fillers, sizing agents, and additives that influence ink absorption and stability. Once ink is deposited, interactions between ink components and paper constituents significantly affect ageing behaviour and analytical outcomes.

Cellulose fibres provide a porous network that facilitates ink penetration and retention. Chemical interactions, such as hydrogen bonding between dye molecules and hydroxyl groups on cellulose, can stabilise certain ink components within the paper matrix. While this may enhance colour permanence, it can also complicate extraction and analysis by binding dyes more strongly over time. Additionally, paper fillers such as calcium carbonate may influence ink chemistry by altering local pH conditions, potentially affecting dye stability and degradation pathways.

Ink–paper interactions also contribute to spatial heterogeneity within ink lines. Differences in fibre density and orientation can cause uneven ink distribution, leading to microscale variations in colour intensity and chemical composition. These effects are particularly relevant in microscopic examination, where centre–edge differences or fibre-associated accumulation patterns may be observed. Such spatial features are not merely cosmetic but can influence the results of spectroscopic, chromatographic, and electrochemical analyses.

From a forensic perspective, ink–paper interactions emphasise the importance of considering the document as an integrated system rather than treating ink and paper as independent entities. Analytical results must be interpreted in light of substrate effects, especially when comparing inks across different documents or paper types. Modern forensic literature consistently highlights that robust ink ageing interpretation requires awareness of ink–paper interaction effects and the integration of complementary analytical techniques (Mielonen et al., 2015). Accordingly, robust forensic interpretation of ink ageing requires consideration of physical redistribution, chemical transformation, and substrate-related effects. Figure 2.4 presents a schematic overview of the physical, chemical, and ink–paper interaction mechanisms contributing to ink ageing on paper.

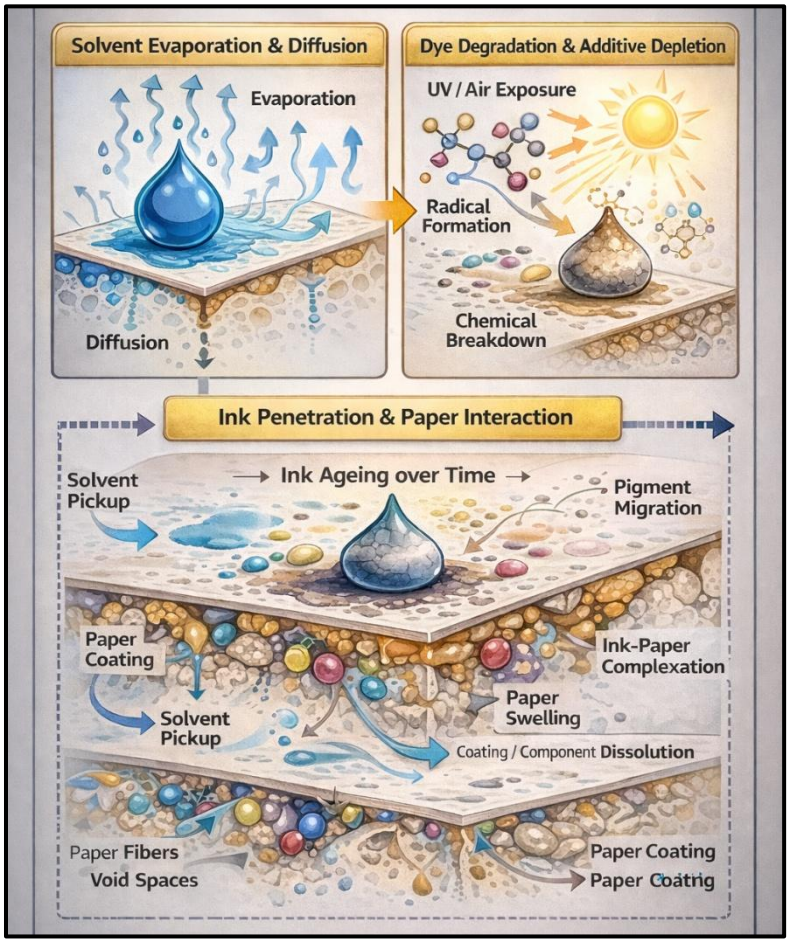


Figure 2.4 Schematic Illustration of Physical, Chemical and Ink-Paper Interaction Mechanisms Contributing to Ink Ageing on Paper.

2.5 Ink Dating Approaches in Forensic Science

Ink dating in forensic document examination refers to the assessment of the time-related characteristics of ink entries on documents. The objective of ink dating is not always to determine an exact calendar date but rather to provide scientifically supported information regarding the relative timing of ink deposition. Over the past several decades, numerous analytical approaches have been proposed for ink dating; however, the forensic literature consistently emphasises that ink dating remains one of the most complex and controversial areas within questioned document examination due to the variability of ink formulations and environmental influences (Díaz-Santana et al., 2023; Senior et al., 2012).

Broadly, forensic ink dating approaches can be divided into absolute dating approaches and relative or comparative ageing approaches. Each category is based on different conceptual assumptions and exhibits distinct strengths and limitations. Understanding these approaches is essential for contextualising the methodology adopted in the present study.

2.5.1 Absolute Ink Dating Approaches

Absolute ink dating approaches aim to estimate the time elapsed since ink deposition by measuring the concentration or decay of specific ink components over time. Historically, the most widely studied absolute dating methods are based on the loss of volatile solvents present in certain ink formulations, particularly ballpoint pen inks. These approaches rely on the premise that volatile compounds evaporate predictably after writing, allowing the ink age to be inferred under controlled conditions.

Gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) have been extensively used to quantify volatile solvents such as 2-phenoxyethanol and related glycol ethers in ballpoint inks. Pioneering studies by Sharif et al. (2022) demonstrated that the decrease in solvent concentration could be correlated with time after writing, especially during the early ageing period. Subsequent work expanded on this concept by proposing kinetic models and evaluating solvent-loss behaviour across different brands and storage conditions (Y. Liu et al., 2017).

Despite their theoretical appeal, absolute ink dating approaches face significant practical limitations. The rate of solvent evaporation is highly sensitive to environmental factors, including temperature, humidity, airflow, and light exposure. Paper type and ink deposition thickness further influence solvent retention, leading to substantial variability even among samples of the same ink. Moreover, ink formulations vary widely between manufacturers, and some modern inks contain reduced amounts of volatile solvents or alternative solvent systems, limiting the applicability of traditional solvent-loss models.

Another challenge associated with absolute dating is the difficulty of reconstructing the environmental history of a questioned document. In forensic casework, documents may have been stored under unknown or fluctuating conditions, making it impossible to apply laboratory-derived ageing curves with confidence. As a result, many forensic authorities caution against over-reliance on absolute ink dating and recommend that such results be interpreted conservatively and only within well-defined constraints (Calcerrada & García-Ruiz, 2015; Devlin et al., 2024).

Importantly, absolute ink dating approaches are largely ink-type specific. They are most applicable to ballpoint pen inks and are generally unsuitable for water-based inks such as fountain pen inks, which lack characteristic volatile solvents. This limitation further underscores the need for alternative strategies when examining non-ballpoint ink types.

2.5.2 Relative and Comparative Ink Ageing Approaches

Relative or comparative ink ageing approaches focus on determining whether two or more ink entries were written at the same time or at different times, rather than estimating an absolute age. This approach is often more realistic and defensible in forensic practice, particularly when reference samples of known age are available or when multiple entries appear on the same document.

Comparative ink ageing may involve evaluating differences in chemical composition, spectral features, chromatographic patterns, or physical appearance between ink entries. Techniques such as TLC, UV–Visible spectroscopy, ATR-FTIR spectroscopy, and GC–MS have been widely used for this purpose. For example, changes in dye composition observed by TLC or shifts in absorbance intensity detected by UV–Vis spectroscopy may indicate differential ageing between ink samples,

provided that sampling and analytical conditions are consistent (Sharif, Chand, et al., 2022).

One of the key advantages of relative ageing approaches is their reduced sensitivity to unknown environmental histories. By comparing inks under similar conditions, either within the same document or against contemporaneously stored reference samples, many confounding variables can be minimised. As highlighted by Senior et al. (2012), relative dating aligns more closely with the evidential needs of forensic investigations, where the central question is often whether an entry was added later rather than its precise age.

Several studies have demonstrated the effectiveness of comparative approaches by analysing multiple inks deposited at different times and evaluating the consistency of discrimination across methods. Notably, comparative evaluation of ink dating methods on known-age samples has shown that while individual techniques may yield ambiguous results, combined interpretation of multiple indicators significantly improves reliability (Braga et al., 2023; Senior et al., 2012).

For fountain pen inks, relative ageing approaches are particularly appropriate. Because these inks are predominantly water-based and dye-rich, ageing indicators are more likely to manifest as gradual changes in dye stability, additive composition, and ink–paper interactions rather than solvent loss. Comparative analysis using combined analytical techniques, therefore, offers a practical and scientifically defensible pathway for fountain pen ink ageing assessment. Figure 2.5 provides a conceptual comparison between absolute ink dating and relative ink ageing assessment, highlighting the interpretive nature of forensic ink dating and the limitations associated with precise chronological estimation.

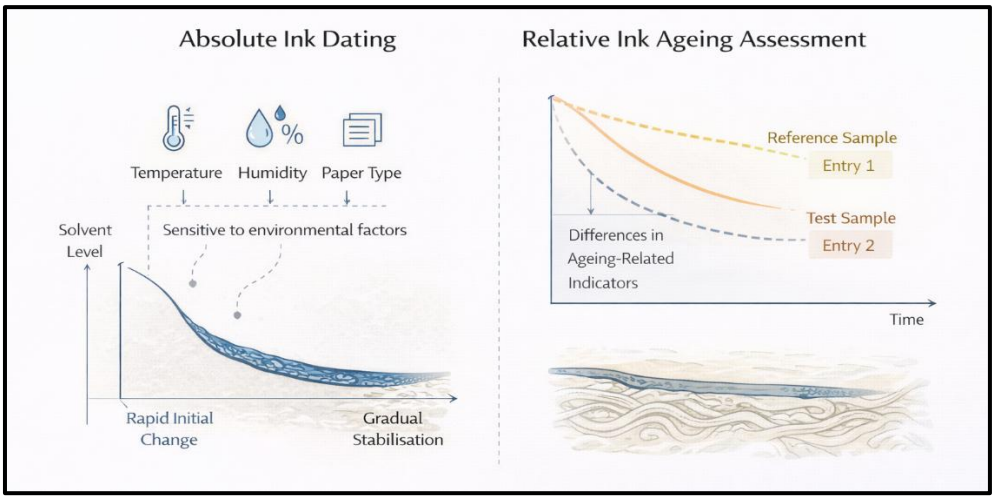


Figure 2.5 Conceptual Comparison Between Absolute Ink Dating and Relative Ink Ageing Assessment in Forensic Document Examination.

2.5.3 Limitations of Single-Technique Ink Dating and The Need for Integration

A recurring theme in forensic ink dating literature is the inadequacy of relying on a single analytical technique to draw definitive ageing conclusions. Each method probes a specific aspect of ink composition or behaviour and is subject to its own sources of uncertainty. For instance, solvent-loss measurements may be influenced by storage conditions, spectroscopic techniques may be affected by paper background interference, and chromatographic patterns may vary with extraction efficiency.

Comprehensive comparative studies have highlighted that discrepancies between techniques are common, particularly when applied to complex or modern ink formulations. These findings have led to a growing consensus that ink dating should be approached as a multi-indicator problem, where convergence of evidence from different analytical domains strengthens forensic interpretation (Devlin et al., 2024).

Therefore, the literature supports the use of integrated analytical strategies in ink ageing studies, particularly when dealing with complex ink formulations such as fountain pen inks. Combining information from different analytical domains allows baseline differences, formulation-dependent characteristics, and ageing-related trends to be interpreted more cautiously and reliably.

2.6 Analytical Techniques for Forensic Ink Examination

The forensic examination of writing inks requires analytical techniques capable of addressing the chemical complexity of ink formulations and the dynamic nature of ink baseline differences. As highlighted in earlier sections, no single technique can comprehensively capture all aspects of ink composition or ageing behaviour. Consequently, modern forensic ink analysis increasingly relies on a multi-technique analytical framework, in which complementary methods are employed to probe different chemical, physical, and spatial characteristics of inks (Mirzanli et al., 2025; Sharif, Chand, et al., 2022; Tamburini et al., 2024).

The present study adopts a combined analytical approach incorporating chromatographic, spectroscopic, microscopic, elemental, and electrochemical techniques. This section reviews the principles, forensic relevance, and limitations of each technique, with emphasis on their applicability to fountain pen inks and ink ageing detection. The analytical techniques reviewed in this section are presented in an order consistent with the sequence of experimental analyses performed in the present study.

2.6.1 Thin Layer Chromatography (TLC)

Thin Layer Chromatography (TLC) is one of the most widely used techniques in forensic ink examination due to its simplicity, low cost, and strong discriminative capability. TLC separates ink components based on their differential affinity between a stationary phase, typically silica gel, and a mobile phase solvent system. In forensic applications, TLC is most commonly employed to separate and visualise dye components present in writing inks.

TLC is particularly effective for dye-rich inks such as fountain pen inks, rollerball inks, and many gel pen inks. Because dyes differ in polarity and molecular structure, they migrate at different rates on the TLC plate, producing characteristic spot patterns and retention factor (R_f) values. These patterns can be used to differentiate inks of similar colour and to identify compositional similarities or differences between ink entries (Kravchenko et al., 2024).

From an ageing perspective, TLC can reveal changes in dye composition over time. Chemical degradation or transformation of dyes may result in the appearance of new spots, changes in spot intensity, or shifts in R_f values. Although TLC does not

directly provide temporal information, such changes can support comparative ageing assessment when inks of different deposition times are examined under identical conditions. However, TLC results are sensitive to solvent composition, plate quality, and extraction efficiency, necessitating strict procedural control for forensic interpretation (Coman & Copaciu, 2015).

2.6.2 Gas Chromatography-Mass Spectrometry (GC-MS)

GC–MS is a highly sensitive and selective analytical technique widely used in forensic ink dating studies, particularly for the analysis of volatile and semi-volatile ink components. The technique separates compounds based on volatility and polarity and identifies them through mass spectral fragmentation patterns.

In ballpoint ink analysis, GC–MS has been extensively employed to monitor the loss of volatile solvents over time, forming the basis of many absolute ink dating approaches. However, GC–MS is also valuable for identifying non-volatile additives such as antioxidants, plasticisers, and stabilisers, which are present in various ink types, including fountain pen inks (Sharif, Jalees, et al., 2022).

For fountain pen inks, GC–MS is particularly useful for detecting formulation-specific additives rather than for direct solvent-loss dating. Differences in additive profiles may influence ink stability and ageing behaviour and can serve as discriminative markers in comparative studies. Nonetheless, GC–MS analysis requires solvent extraction, which may be influenced by paper type and extraction conditions. As such, GC–MS results must be interpreted in conjunction with complementary analytical data (Carvalho et al. 2019).

2.6.3 Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR spectroscopy is a versatile technique that provides information on the functional groups present in ink components. In forensic ink examination, ATR-FTIR is valued for its minimal sample preparation requirements and its ability to analyse a broad range of organic and polymeric materials.

ATR-FTIR can detect functional groups associated with dyes, binders, solvents, and additives, making it applicable to a wide variety of ink types, including fountain pen inks, ballpoint inks, and printed materials. For fountain pen inks, ATR-FTIR may reveal bands associated with aromatic dyes, alcohols, and stabilising additives. Changes in band intensity or the appearance of new peaks may indicate chemical ageing processes such as oxidation or additive depletion (Braga et al., 2023).

One limitation of ATR-FTIR is the strong contribution of paper substrate signals, particularly cellulose-related bands. Consequently, careful interpretation and, where possible, background subtractions are required. Despite these challenges, ATR-FTIR remains a powerful screening tool that complements chromatographic and spectroscopic methods by providing functional group-level information.

2.6.4 Ultraviolet-Visible (UV-Vis) Spectroscopy

UV–Visible spectroscopy is a rapid and non-destructive or minimally destructive technique commonly used in forensic ink analysis to examine the absorbance characteristics of dye-based inks. The technique measures the absorption of ultraviolet and visible light by chromophoric groups within dye molecules, producing spectra that reflect ink colour composition.

UV–Vis spectroscopy is especially suitable for fountain pen inks, which rely heavily on soluble dyes. Differences in absorbance maxima, spectral shape, and intensity can be used to discriminate between ink formulations of similar colour. Furthermore, UV–Vis spectra may change with ageing due to dye degradation or alterations in molecular conjugation, providing potential indicators of ink baseline differences that may be related to ink ageing (Patel et al., 2024).

In comparative studies, UV–Vis spectroscopy is often used in conjunction with chemometric techniques to enhance discrimination power. However, even without

advanced data analysis, qualitative comparison of spectra can provide valuable forensic information. Limitations include potential interference from paper extracts and the dependence of spectral features on extraction concentration. As such, UV–Vis spectroscopy is most effective as part of a combined analytical strategy rather than as a standalone method (More et al., 2018).

2.6.5 Polarised Optical Microscopy (POM)

Polarised Optical Microscopy (POM) is an optical technique commonly applied in forensic document examination to assess the physical appearance and spatial distribution of ink on paper. Unlike chemical or spectroscopic methods that target ink composition, POM provides visual information on how ink is deposited, absorbed, and distributed within the paper substrate. This information is particularly relevant for understanding physical ageing phenomena associated with ink–paper interaction.

In the context of ink baseline differences studies, POM enables observation of changes arising from solvent evaporation, capillary diffusion, and redistribution of ink components over time. Features such as ink penetration depth, fibre wetting, feathering at stroke edges, and centre–edge differences within ink lines may evolve as ageing progresses. These characteristics are especially pronounced in water-based inks, including fountain pen inks, which readily penetrate paper fibres shortly after writing.

For forensic purposes, POM contributes primarily to comparative and relative ageing assessment. When examining questioned documents containing multiple ink entries, differences in ink distribution patterns observed under polarised light may indicate non-contemporaneous writing. However, these features are influenced by paper type, writing pressure, and ink formulation, and therefore cannot be interpreted in isolation. Consequently, POM is best utilised as a contextual technique that supports chemical and spectroscopic findings within a combined analytical framework (Agarwal & Chand, 2022).

2.6.6 Field Emission Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (FESEM-EDX)

While POM provides valuable optical-scale information, it is limited in spatial resolution and does not yield compositional data. To address these limitations, Field Emission Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (FESEM–EDX) is employed to examine inked paper surfaces at higher magnification and to obtain elemental information relevant to ink–paper interaction.

FESEM enables detailed visualisation of surface morphology, including ink coating on paper fibres, microstructural features of ink deposits, and changes associated with ink consolidation over time. These morphological characteristics may reflect physical ageing processes, such as changes in ink adhesion or surface texture, which are not readily observable using optical microscopy alone.

The integration of EDX allows identification of elemental components present within inked regions, providing insight into the presence of inorganic additives or paper fillers. Although elemental signals are often dominated by the paper substrate, spatial differences in elemental distribution revealed through elemental mapping can support ink discrimination and contextual interpretation of ageing-related behaviour.

From an ink baseline differences perspective, FESEM–EDX does not provide direct chronological information; however, it offers high-resolution structural and compositional context that strengthens the interpretation of results obtained from chemical, spectroscopic, and electrochemical analyses. When incorporated into a combined analytical approach, FESEM–EDX enhances the robustness of forensic ink baseline studies assessment by linking microscopic observations with chemical ageing indicators. It is noted that recent forensic ink studies predominantly employ scanning electron microscopy coupled with Energy-Dispersive X-ray (SEM–EDX), whereas the application of FESEM in ink studies remains comparatively limited (Abd Mutalib et al., 2017).

2.6.7 Electrochemical Techniques using Screen-Printed Carbon Electrodes (SPCE)

Electrochemical techniques, particularly cyclic voltammetry, represent an emerging approach in forensic ink analysis. These methods probe the redox behaviour of electroactive ink components, providing information related to oxidative stability and chemical reactivity. Screen-printed carbon electrodes (SPCEs) offer practical advantages for forensic applications due to their low cost, disposability, and suitability for small sample volumes (Giuliani et al., 2016).

In the context of ink baseline differences, electrochemical measurements may detect changes in redox-active species such as dyes or antioxidants as ageing progresses. Although electrochemical techniques have been less extensively applied to ink baseline studies compared to chromatographic and spectroscopic methods, they offer a complementary perspective by directly probing oxidation–reduction processes associated with chemical ageing.

For fountain pen inks, which rely heavily on dye chemistry and stabilising additives, electrochemical techniques may provide valuable supplementary information that supports ageing-related interpretation. When integrated with chemical and microscopic analyses, SPCE-based electrochemical methods contribute to a more holistic understanding of ink behaviour over time.

To facilitate comparison and highlight the complementary roles of the analytical techniques employed in this study, a summary of their targeted ink components and relevance to ink baseline differences assessment is presented in Table 2.2.

Table 2.2

Summary of Analytical Techniques Applied in Forensic Ink Examination.

Analytical Technique	Principle of Analysis	Ink Components / Features Targeted	Relevance to Ink Study	Author
Thin Layer Chromatography (TLC)	Separation based on differential affinity to stationary and mobile phases	Dye components and degradation products	Changes in dye composition and chromatographic profiles	(Aginsky, 2019)
Gas Chromatography–Mass Spectrometry (GC–MS)	Separation and identification based on volatility and mass spectra	Volatile and semi-volatile solvents and additives	Solvent loss and additive-related ageing indicators	(Sharif, Jalees, et al., 2022)
ATR–FTIR Spectroscopy	Infrared absorption by functional groups	Dyes, binders, stabilisers	Chemical changes associated with oxidation and degradation	(Braga et al., 2023)

Analytical Technique	Principle of Analysis	Ink Components / Features Targeted	Relevance to Ink Study	Author
UV–Visible Spectroscopy (UV–Vis)	Absorbance by chromophoric dye molecules	Dye chromophores	Spectral changes due to dye degradation	(Senior et al., 2012)
Polarised Optical Microscopy (POM)	Optical contrast enhancement using polarised light	Ink stroke morphology and spatial distribution on paper	Physical ageing effects such as ink migration and feathering	(Agarwal & Chand, 2022)
FESEM–EDX	High-resolution electron imaging and elemental analysis	Surface morphology and elemental composition	Ink–paper interaction and elemental distribution relevant to ageing	(Abd Mutalib et al., 2017)
Electrochemical Analysis (SPCE–CV)	Measurement of redox behaviour	Redox-active dyes and additives	Oxidative ageing and stabiliser depletion indicators	(Navashree & Parthasarathy, 2023)

2.7 Research Gap and Justification of The Present Study

The preceding sections have outlined key developments in forensic ink examination, including ink composition, ageing mechanisms, and the range of analytical techniques applied in questioned document analysis. Although substantial progress has been achieved in this field, the literature also reveals persistent limitations that affect the reliability and scope of forensic ink studies' interpretation.

A substantial proportion of forensic ink baseline differences research reported in the literature has focused on ballpoint pen inks, primarily due to the presence of volatile organic solvents that are amenable to solvent-loss-based dating approaches (Christie & Abel, 2021; Díaz-Santana et al., 2023). These studies have contributed significantly to the understanding of ink's behaviour under controlled conditions. However, the applicability of absolute dating models in real forensic casework remains limited, as solvent evaporation rates are strongly influenced by environmental conditions, paper type, and storage history, which are often unknown in questioned documents (Díaz-Santana et al., 2023; Kapoor et al., 2021).

In contrast, fountain pen inks remain comparatively underexplored in ink chemical fingerprint investigations, despite their widespread use in signatures, formal documents, and archival writing. Fountain pen inks are predominantly water-based and dye-rich, and therefore do not exhibit the same solvent-loss behaviour that underpins traditional ballpoint ink dating methods. As a result, ageing-related changes in fountain pen inks are more closely associated with dye degradation, additive stability, and ink–paper interaction effects. While previous studies have demonstrated that fountain pen inks can be effectively discriminated using chromatographic and spectroscopic techniques, systematic investigation of their ageing behaviour using integrated analytical approaches remains limited (Sharif, Jalees, et al., 2022).

Furthermore, the literature indicates that many forensic ink studies rely on single analytical techniques or narrowly focused methodologies. Although individual techniques such as Thin Layer Chromatography, UV–Visible spectroscopy, ATR–FTIR spectroscopy, and Gas Chromatography–Mass Spectrometry provide valuable information, each method probes only a specific aspect of ink composition and is subject to inherent limitations. Variability in ink formulation, paper substrate, and environmental exposure may lead to ambiguous interpretation when techniques are

applied in isolation, particularly in the context of ink ageing detection (Giles, 2016; Ortiz-Herrero et al., 2020).

Microscopic and elemental techniques, including optical microscopy and SEM–EDX, have been increasingly incorporated into forensic ink studies to provide spatial and morphological context. However, recent literature predominantly reports the use of conventional SEM–EDX, while higher-resolution approaches such as FESEM–EDX remain comparatively underexplored in ink investigations. Similarly, electrochemical techniques, which offer potential insight into oxidation–reduction behaviour associated with dye and additive stability, are still infrequently applied in forensic ink baseline differences research. These gaps highlight opportunities to strengthen forensic interpretation through the integration of complementary analytical domains.

Accordingly, the present study is justified by the need to address these limitations through a combined analytical approach focused on fountain pen inks. By integrating chromatographic (TLC), spectroscopic (UV–Visible and ATR–FTIR), mass spectrometric (GC–MS), microscopic (POM), elemental (SEM–EDX / FESEM–EDX), and electrochemical (SPCE-based cyclic voltammetry) techniques, this study aims to investigate fountain pen ink baseline differences behaviour from multiple, complementary perspectives. Rather than attempting absolute ink dating, the study emphasises comparative and relative ageing assessment, consistent with contemporary forensic best practice.

By focusing on an underexplored ink type and adopting a multi-technique analytical framework, the present study seeks to enhance the evidential robustness of forensic ink baseline interpretation and to contribute meaningful insights to forensic document examination. The experimental methodology employed to address these research gaps is described in detail in the following chapter.

In summary, forensic ink analysis is influenced by physical redistribution, chemical transformation and ink-paper interactions. The literature shows that chromatographic, spectroscopic, microscopic and electrochemical measurements can provide indicators relevant to ageing assessment, but robust interpretation typically requires monitoring changes over time. In the present study, these techniques are applied at a single baseline time point (fresh ink after drying) to characterise formulation-dependent differences among fountain pen inks and identify measurable features that could be monitored in future controlled ageing experiments.

CHAPTER 3
RESEARCH METHODOLOGY

3.1 Introduction

This chapter outlines the research methodology employed to achieve the objectives of ink baseline differences detection in forensic documents using combined analytical techniques. The study began with the preparation of fountain pen ink samples deposited on paper substrates, followed by systematic chemical, morphological, elemental and electrochemical analyses. Chemical characterisation was carried out using Thin-Layer Chromatography (TLC), Gas Chromatography-Mass Spectrometry (GC-MS), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Ultraviolet-Visible (UV-Vis) spectroscopy to identify ink components and spectral features. Morphological and elemental properties of the inks on paper were examined using Polarised Optical Microscopy (POM) and Field Emission Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (FESEM-EDX). In addition, Cyclic Voltammetry (CV) analysis using a potentiostat/galvanostat and Screen-printed Carbon Electrodes (SPCE) was employed to investigate the electrochemical behaviour of the inks. The overall methodology was designed to ensure reliable, reproducible and minimally destructive analysis suitable for forensic document examination. The flow of research work is presented in Figure 3.1.

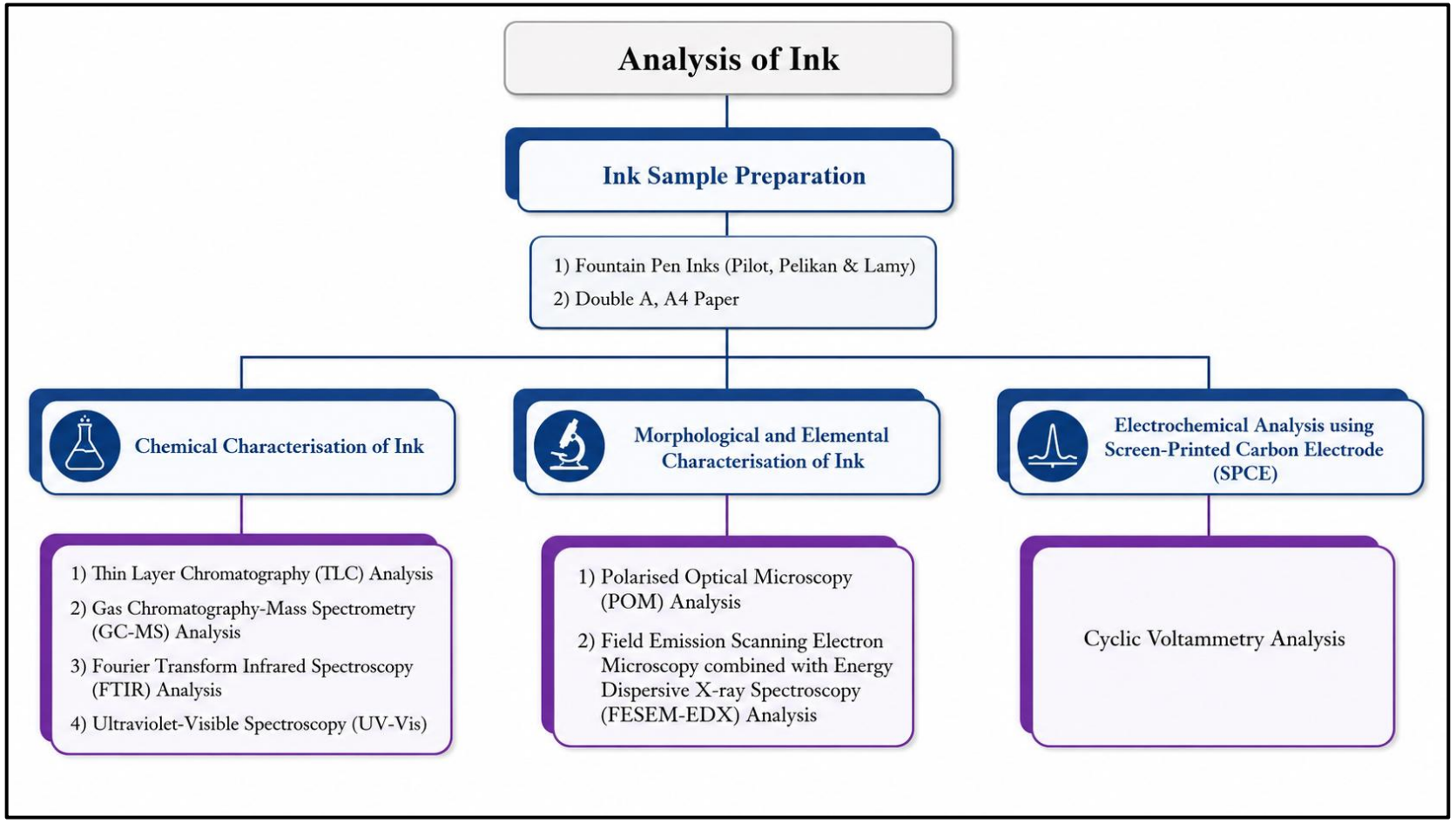


Figure 3.1 Flow of Research Work.

3.2 Chemicals and Apparatus

The chemicals and solvents used are listed in Table 3.1 and were purchased from commercial suppliers without further purification. All glassware used in the synthesis of all compounds were washed, cleaned and finally rinsed with acetone. Then, the glasswares were dried in a 50°C drying cabinet before use.

Table 3.1

List of Materials, Solvents and Chemicals Used in This Study.

Category	Material / Chemical	Grade / Source
Ink Samples	Fountain pen ink (Pilot)	Commercial supplier
	Fountain pen ink (Pelikan)	Commercial supplier
	Fountain pen ink (Lamy)	Commercial supplier
Paper Substrate	Double A A4 Paper	Commercial supplier
Material (TLC)	Silica gel 60 F254 TLC Plate (aluminium sheet)	Merck
Solvent (TLC)	Butanol ($C_4H_{10}O$)	Analytical grade
	Acetic acid (CH_3COOH)	Analytical grade
Solvent (Extraction / Dilution)	Methanol (CH_3OH)	Analytical grade (UiTM Shah Alam)
Electrolyte	Potassium chloride (KCl)	Analytical grade
Electrode	Screen-printed carbon electrode (SPCE)	Metrohm
Redox Standard	Potassium ferrocyanide ($K_4[Fe(CN)_6]$)	Analytical grade
General solvent	Deionized water (H_2O)	UiTM Shah Alam

3.3 Instrumentations

The list of instruments used to carry out this research study is tabulated in Table 3.2 and the functions of these instruments were fully discussed in this subtopic.

Table 3.2

Type and Model of These Instruments Used in This Research Study.

Instrument	Model
GC-MS	Agilent 7890 Series Gas Chromatography coupled with Agilent 5975 Mass Selective Detector
ATR-FTIR Spectrometer	PerkinElmer FT-IR 1600 spectrometer
UV-Vis Spectroscopy	PerkinElmer Lambda 35 UV-Vis Spectrophotometer
Polarised Optical Microscope	Leica DM750 P
FESEM-EDX	Jeol JSM-IT300 FESEM equipped with EDX
Potentiostat/Galvanostat	Autolab PGSTAT-302N (30V/2A)

3.3.1 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) is a vibrational spectroscopic technique used to identify functional groups and chemical bonds present in a sample based on infrared absorption. In ATR-FTIR, infrared radiation is directed through an ATR crystal, generating an evanescent wave that interacts with the sample placed in direct contact with the crystal surface. The absorbed radiation produces characteristic spectra corresponding to specific molecular vibrations.

In this study, ATR-FTIR was employed to analyse fountain pen inks deposited on paper substrates. The technique is particularly suitable for forensic document analysis as it allows direct examination of ink on paper with minimal sample preparation and minimal damage. ATR-FTIR provided information on functional groups present in the inks, contributing to the identification of chemical features relevant to ink baseline studies.

3.3.2 Ultraviolet-Visible Spectroscopy (UV-Vis)

Ultraviolet-Visible (UV-Vis) spectroscopy is an analytical technique used to measure the absorption of ultraviolet and visible light by chromophoric compounds in a sample. Absorption occurs due to electronic transitions within molecules, producing characteristic absorption bands and maximum absorption wavelengths (λ_{max}).

In this study, UV-Vis spectroscopy was used to analyse extracted fountain pen ink samples to examine their absorption characteristics. The technique is effective for detecting dye-related components commonly present in inks. The obtained UV-Vis spectra, particularly λ_{max} values, served as indicators for comparative ink analysis.

3.3.3 Polarised Optical Microscopy (POM)

Polarised Optical Microscopy (POM) is a light microscopy technique that utilises polarised light to enhance contrast and reveal structural and optical properties of materials. By using crossed polarisers, POM allows the observation of anisotropic features that may not be visible under conventional optical microscopy.

In this study, POM was used to observe the distribution and surface morphology of fountain pen inks on paper substrates. The technique enabled visualisation of ink penetration, spreading patterns, and surface features, providing complementary information to chemical analyses and supporting the assessment of physical characteristics associated with ink.

3.3.4 Field Emission Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (FESEM-EDX)

Field Emission Scanning Electron Microscopy (FESEM) is a high-resolution imaging technique that uses a focused electron beam to examine surface morphology at the micro- and nanoscale. When combined with Energy-Dispersive X-ray Spectroscopy (EDX), the elemental composition of the sample surface can also be determined based on characteristic X-ray emissions.

In this study, FESEM-EDX was employed to examine the surface morphology and elemental composition of fountain pen inks deposited on paper. FESEM provided detailed images of ink distribution and interaction with the paper fibres, while EDX enabled identification of elemental components associated with ink formulation. These findings contribute to understanding physical and elemental features relevant to ink baseline differences in forensic documents.

3.3.5 Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry (GC-MS) is an analytical technique used for the separation and identification of volatile and semi-volatile compounds in complex samples. In this technique, the sample is vaporised and introduced into a gas chromatographic column, where individual components are separated based on their volatility and interaction with the stationary phase. The separated compounds are subsequently transferred to the mass spectrometer, where they are ionised and fragmented. The resulting ions are detected according to their mass-to-charge (m/z) ratios, enabling compound identification through comparison with reference mass spectral libraries.

In this study, GC-MS was employed to analyse the chemical composition of fountain pen inks extracted from paper substrates. The technique is particularly suitable for forensic ink analysis due to its high sensitivity and capability to detect characteristic ink components, such as solvents and additives, which are relevant to ink baseline differences studies. By identifying common and distinctive compounds among different ink brands, GC-MS provides valuable chemical information that supports comparative analysis and differentiation of inks in forensic documents.

3.3.6 Potentiostat/Galvanostat

A potentiostat/galvanostat is an electrochemical instrument used to control and measure the electrical potential and current in an electrochemical cell. In cyclic voltammetry (CV), the potential is swept linearly within a defined range while the resulting current is recorded, producing voltammograms that reflect redox processes occurring at the electrode surface.

In this study, an Autolab potentiostat/galvanostat was used to perform CV measurements on fountain pen ink samples using screen-printed carbon electrodes (SPCE). CV was applied to investigate the electrochemical behaviour of inks by identifying oxidation and reduction peaks associated with redox-active components. The electrochemical signatures obtained serve as indicators for ink baseline detection and provide a minimally destructive approach suitable for forensic document analysis.

3.4 Method

3.4.1 Ink Sample Preparation

In this study, three commercial brands of black fountain pen ink, namely Pilot, Pelikan and Lamy, were selected as representative samples for forensic ink analysis. Standard A4 paper (also known as Double A) was used as the writing substrate due to its uniform surface characteristics and widespread use in document preparation. Ink application was carried out using a fountain pen filled with the respective ink, whereby approximately 1 µL of ink was carefully deposited onto the paper surface. The ink was applied consistently to achieve sufficient penetration into the paper fibres without causing oversaturation. Each ink sample was clearly labelled to prevent cross-contamination and ensure accurate identification throughout the experimental process.

After application, the inked paper samples were allowed to dry at ambient room temperature for a minimum duration of 30 minutes to facilitate solvent evaporation and stabilisation of the ink on the paper substrate. Once fully dried, the inked regions were cut into square sections, approximately 1 cm x 1 cm, using clean cutting tools. Each section was approximately labelled according to the ink brand. The prepared samples were then placed in clean petri dishes to minimise contamination and external interference as shown in Figure 3.2.

Figure 3.2 Prepared Ink-Stained Paper Section Measuring Approximately 1 cm × 1 cm, Placed in a Clean Petri Dish and Labelled According to The Ink Brand.

All samples were stored in a cool, dark environment before analysis in order to reduce the effects of light exposure and environmental degradation. This standardised sample preparation procedure was consistently applied across all analyses, including GC-MS, ATR-FTIR, UV-Vis, POM, FESEM-EDX, ensuring comparability and reproducibility of results. Table 3.3 summarises the ageing time points and analytical techniques used in this study.

Table 3.3

Ageing Time Point, Condition and Analytical Techniques Used.

Ageing time point (related to ink deposition on paper)	**Condition / handling**	**Techniques performed at this time point**
0 h (Fresh) (after 30 minutes drying)	Ink deposited on Double A A4 paper, air dried at room temperature for 30 minutes, kept in a cool, dark environment until analysis	TLC; GC-MS; ATR-FTIR; UV-Vis; POM; FESEM-EDX; SPCE-CV

3.4.2 Chemical Characterisation of Ink

a) Thin-Layer Chromatography (TLC) for Ink Analysis

Thin-Layer Chromatography (TLC) was employed to identify the chemical components present in fountain pen inks from three brands: Pilot, Pelikan and Lamy. Silica gel 60 F_{254} TLC plates on aluminium sheets (5 cm x 4.8 cm), capillary tubes, a TLC chamber, a pencil, a ruler and a UV lamp were used. The mobile phase consisted of butanol, acetic acid and water mixed in a 4:1:5 ratio.

A pencil line was drawn approximately 1 cm from the bottom and top of each plate to indicate the origin and solvent front, respectively. 1 µL of the ink samples was applied to the origin line using a clean capillary tube, ensuring spots were at least 1 cm apart and properly labelled.

The TLC plate was placed in the chamber with the mobile phase, making sure that the solvent did not touch the ink spots. During development, the plate was monitored, and once the first spot became visible, the plate was temporarily removed

and allowed to dry at room temperature. After drying, the plate was returned to the chamber to continue development until the solvent reached the top mark (solvent front).

After development, the solvent front was immediately marked, and the plates were allowed to dry completely. The TLC plates were subsequently examined under normal and UV light to visualise fluorescent bands. This procedure provided information on the chemical composition of the fountain pen inks and allowed differentiation between brands.

b) Chemical Composition using Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry (GC-MS) was used to analyse the chemical composition of fountain pen inks from three different brands, to identify common compounds present across the inks.

Ink samples were prepared by cutting small sections of paper containing the ink and placing them into sealed glass vials to minimise exposure to environmental contaminants. 2 mL of methanol was added to each vial to extract volatile ink components. The vials were sealed using caps fitted with PTFE/silicone septa to ensure airtight conditions. The samples were gently shaken or vortexed for 1-2 minutes to facilitate extraction and then allowed to stand at room temperature for 30 minutes.

The extracted samples were subsequently analysed using an Agilent 7890 gas chromatograph coupled to a mass spectrometer, equipped with an Agilent 5975 Mass Selective Detector. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. Sample injection was performed in pulsed splitless mode with an injection volume of 1.0 µL.

c) ATR-FTIR Analysis

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to analyse the chemical characteristics of fountain pen inks.

Approximately 1 µL of ink was deposited onto Double A A4 paper and allowed to dry completely at room temperature prior to analysis to ensure proper adherence to the paper substrate and effective contact with the ATR crystal.

The dried ink samples were placed directly onto the ATR crystal, and infrared spectra were recorded in the mid-infrared region 4000 to 650 cm^{-1}. The obtained spectra were used to identify functional groups and chemical bonds present in the fountain pen inks relevant to ink baseline detection.

d) UV-Vis Analysis

Ultraviolet-Visible (UV-Vis) spectroscopy was employed to analyse the absorption characteristics of fountain pen inks. Ink samples were prepared by depositing approximately 1 µL of ink onto Double A A4 paper and allowing the samples to dry at room temperature. The stained areas were cut into 1 cm x 1cm sections and extracted in 100 µL of distilled water.

A working solution was prepared by diluting 10 µL of the ink extract with 3.5 mL of distilled water, resulting in a final dilution factor of 1:350. Approximately 3 mL of the diluted solution was transferred into a quartz cuvette for analysis.

The UV-Vis spectrophotometer was set to scan the absorbance spectrum over a wavelength range of 230-800 nm. The obtained spectra were analysed with particular attention to the maximum absorption wavelength (λ_{max}) associated with chromophore components relevant to ink baseline detection.

3.4.3 Morphological and Elemental Characterisation of Ink

a) Polarised Optical Microscopy (POM) Analysis

Polarised Optical Microscopy (POM) was used to examine the surface morphology and optical characteristics of fountain pen inks deposited on paper. This technique enables the observation of ink distribution and interaction with paper fibres, which are relevant to forensic document analysis.

Approximately 1 µL of fountain pen ink was applied onto Double A A4 paper and allowed to dry at room temperature. The inked paper samples were cut into a 1 cm x 1 cm size and mounted directly onto glass microscope slides without additional treatment to preserve the original ink-paper interface.

Observations were carried out using a polarised optical microscope under plane-polarised and crossed-polarised light at 10x magnification. Images were captured using a digital imaging system for qualitative comparison between different ink brands.

The POM analysis provided visual information on ink spread, fibre staining and surface uniformity, supporting the interpretation of chemical and electrochemical analyses in this study.

b) Field Emission Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (FESEM-EDX) Analysis

Field Emission Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (FESEM-EDX) was employed to examine the surface morphology and elemental composition of fountain pen inks deposited on paper substrates. This technique provides high-resolution imaging of the ink-paper interface and enables qualitative elemental analysis relevant to forensic ink examination.

Approximately 1 µL of fountain pen ink was deposited onto Double A A4 paper and allowed to dry at room temperature. The inked paper samples were cut into small sections (1 cm x 1cm) and mounted onto aluminium stubs using conductive carbon tape. The samples were sputter-coated with a thin layer of gold to minimise charging effects during imaging.

FESEM imaging was performed at selected accelerating voltages and magnifications to observe ink distribution, surface texture and interaction between ink

components and paper fibres. Elemental analysis was conducted using the EDX detector to identify the presence and relative distribution of inorganic elements within the inked regions.

The combined FESEM-EDX analysis provided complementary morphological and elemental information, supporting the chemical and electrochemical findings and contributing to the evaluation of fountain pen inks for forensic ink baseline detection.

3.4.4 Electrochemical Analysis using Screen-printed Carbon Electrode (SPCE)

a) Cyclic Voltammetry (CV) Analysis

Cyclic Voltammetry (CV) analysis was performed using an Autolab potentiostat/galvanostat to investigate the electrochemical behaviour of fountain pen inks for ink baseline detection. Screen-printed Carbon Electrodes (SPCE) were employed as the working electrode system due to their suitability for rapid, low-volume and minimally destructive forensic analysis.

A blank measurement was performed using 0.1 M potassium chloride (KCl) solution as the supporting electrolyte. A volume of 10 µL of 0.1 M KCl was drop-cast onto a clean SPCE to cover the working, reference and counter electrodes. The blank cyclic voltammetry was recorded to establish a baseline response and to confirm the absence of electroactive interference from the electrolyte.

For sample analysis, 0.1 µL of fountain pen ink sample was drop-cast directly onto the surface of a fresh SPCE and allowed to dry completely at room temperature to ensure proper adhesion of the ink to the electrode surface. After the sample had fully dried, 10 µL of 0.1 M KCl solution was added onto the electrode to serve as the supporting electrolyte. Cyclic voltammetry measurements were then conducted under the same experimental conditions as the blank analysis.

The resulting voltammograms were evaluated for oxidation and reduction peaks associated with electroactive components in the ink samples. Variations in peak current and potential were used to differentiate the electrochemical characteristics of the fountain pen inks, providing supporting evidence for ink baseline detection in forensic document analysis.

3.5 Justification of Analytical Parameters

The selection of 0.1 M potassium chloride (KCl) as the supporting electrolyte in the electrochemical analysis was based not only on its high ionic conductivity but also on its chemical stability within the selected potential window. During preliminary consideration of suitable electrolytes, it was important to ensure that the medium would not introduce additional redox-active species that could interfere with the voltammetric signals attributed to ink components. KCl is widely recognised for its electrochemical inertness under moderate potential ranges, thereby minimising background interference and ensuring that observed current responses primarily originate from electroactive constituents within the ink samples.

In addition, the concentration of 0.1 M was selected to provide sufficient ionic strength to reduce solution resistance while maintaining stable baseline behaviour during cyclic voltammetry measurements. Adequate ionic conductivity is essential to minimise ohmic drop effects, particularly when working with small-volume drop-cast systems on screen-printed electrodes. The use of a consistent electrolyte concentration across all measurements also ensured reproducibility and comparability between ink brands analysed in this study.

Screen-Printed Carbon Electrodes (SPCE) were selected due to their practicality and suitability for forensic-type applications. In questioned document analysis, evidential material is often limited, and destructive sampling must be minimised. The disposable nature of SPCE reduces the risk of cross-contamination between samples, eliminating the need for extensive electrode polishing procedures that are typically required for conventional glassy carbon electrodes. Furthermore, SPCE platforms allow small-volume drop-casting, enabling efficient electrochemical characterisation with minimal sample consumption. Their cost-effectiveness and portability also suggest potential applicability for future on-site or screening-based forensic assessments.

The solvent system employed for Thin Layer Chromatography (TLC), consisting of butanol:acetic acid:water (4:1:5), was selected based on its balanced polarity profile and its established suitability for separating water-soluble dye systems. Fountain pen inks are predominantly dye-based and contain polar colourants that require an appropriately tuned mobile phase to achieve meaningful separation. The chosen solvent mixture provides sufficient polarity to mobilise dye components while

maintaining controlled migration rates, allowing distinguishable retention factor (R_f) values to be obtained.

Preliminary consideration of solvent strength was necessary to avoid excessive co-migration or poor resolution of dye spots. A highly polar system could result in minimal separation, whereas an insufficiently polar system may prevent adequate migration from the baseline. The selected ratio was therefore considered optimal for achieving consistent spot development and reproducible chromatographic behaviour across the three ink brands examined. Maintaining a consistent solvent composition throughout the experimental series also ensured reliability and comparability of R_f measurements.

Overall, the analytical parameters selected in this study were determined based on chemical compatibility, instrumental stability and forensic practicality. Emphasis was placed on achieving reproducible results while minimising sample destruction, in alignment with the evidential constraints typically encountered in forensic document examination.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Introduction

Chapter 4 presents the results and discussion of fountain pen ink analyses conducted using a combination of chromatographic, spectroscopic, microscopic, and electrochemical techniques. The findings are interpreted in relation to ink composition, ink–paper interactions and indicators relevant to ink baseline differences behaviour. Chemical characterisation was performed using Thin Layer Chromatography (TLC), Ultraviolet–Visible (UV–Vis) spectroscopy, Gas Chromatography–Mass Spectrometry (GC-MS) and Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) spectroscopy. Ink distribution, surface morphology and elemental composition were examined using Polarised Optical Microscopy (POM) and Field Emission Scanning Electron Microscopy coupled with Energy-Dispersive X-ray spectroscopy (FESEM-EDX). In addition, cyclic voltammetry using screen-printed carbon electrodes (SPCE) was employed to investigate electrochemical properties associated with ink stability and potential ageing processes. The combined results are discussed to highlight formulation-dependent differences between ink brands and to demonstrate the relevance of the integrated analytical approach for forensic ink baseline detection.

4.2 Thin Layer Chromatography (TLC) Analysis

4.2.1 Thin Layer Chromatography (TLC) Separation of Fountain Pen Inks

Thin Layer Chromatography (TLC) was employed to separate and visualise the dye components present in fountain pen inks from three different brands, namely Pilot, Pelikan and Lamy. The developed TLC chromatogram is presented in Figure 4.1, while the measured distances travelled by the individual spots and the calculated retention factor (R_f) values are summarised in Table 4.1. TLC allows the separation of ink components based on their relative affinity towards the stationary phase (silica gel) and the mobile phase, making it a widely used technique in forensic ink analysis (Kravchenko et al., 2024).

The retention factor (R_f) for each separated component was calculated using the following equation:

$$Retention\ Factor\ (R_f) = \frac{Distance\ Travelled\ by\ Spot\ (cm)}{Distance\ Travelled\ by\ Solvent\ Front\ (cm)} \quad (4.1)$$

The solvent front distance was measured as 2.8 cm for all samples, ensuring consistency in the calculation and comparison of R_f values across different ink brands.

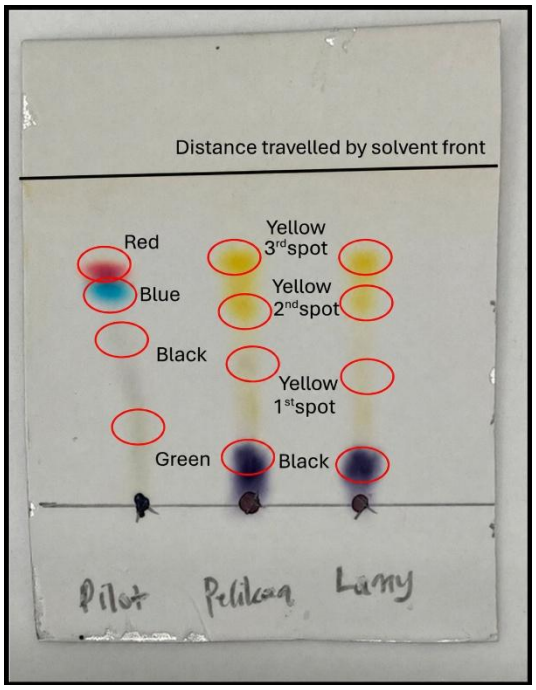


Figure 4.1 TLC Plate Developed for Fountain Pen Ink Samples.

Table 4.1

TLC Data Analysis.

Ink Brand	**Colour of Spot**	**Distance of Spot from Baseline (cm)**	**Solvent Front (cm)**	**R_f Value**
Pilot	Green	0.8	2.8	0.29
	Black	1.7	2.8	0.61
	Blue	2.0	2.8	0.71
	Red	2.2	2.8	0.79
Pelikan	Black	0.5	2.8	0.19
	Yellow 1st Spot	1.5	2.8	0.54
	Yellow 2nd Spot	1.8	2.8	0.64
	Yellow 3rd Spot	2.2	2.8	0.79
Lamy	Black	0.5	2.8	0.19
	Yellow 1st Spot	1.4	2.8	0.50
	Yellow 2nd Spot	2.0	2.8	0.71
	Yellow 3rd Spot	2.2	2.8	0.79

4.2.2 TLC Profiles of Pilot Fountain Pen Ink

The TLC analysis of Pilot ink revealed the presence of four distinct coloured components, namely green, black, blue, and red, with R_f values of 0.29, 0.61, 0.71 and 0.79, respectively, as shown in Table 4.1. The green component exhibited the lowest R_f value, indicating stronger interaction with the polar silica gel stationary phase and suggesting higher polarity. In contrast, the blue and red components showed higher R_f values, implying lower polarity and greater affinity for the mobile phase.

The presence of several well-separated coloured spots suggests that Pilot ink is composed of a mixture of different dyes rather than a single pigment, reflecting a more complex formulation. The clear separation and relatively high R_f values of the upper components suggest that these dyes remain chemically stable. Similar findings have been reported in previous studies, where Pilot inks demonstrated distinct chromatographic profiles due to the use of multiple dye classes, including azo and triarylmethane dyes (Simsek & Seker, 2024).

4.2.3 TLC Profiles of Pelikan Fountain Pen Ink

For Pelikan ink, four major components were observed, consisting of one black spot and three yellow spots at different heights on the TLC plate, as shown in Figure 4.2. The black component showed a low R_f value of 0.19, indicating high polarity and strong interaction with the stationary phase. Meanwhile, the yellow components exhibited increasing R_f values of 0.54, 0.64 and 0.79 for the first, second and third spots, respectively.

The presence of multiple yellow spots suggests that Pelikan ink contains several yellow dye components within its formulation. The variation in R_f values among these yellow components reflects differences in molecular structure and polarity. Such baseline compositional differences may influence the migration behaviour of dye components on the TLC plate (Luňáková et al., 2025).

4.2.4 TLC Profiles of Lamy Fountain Pen Ink

Similar to Pelikan ink, Lamy ink exhibited one black spot and three yellow spots with R_f values ranging from 0.19 to 0.79. The black component of Lamy ink also showed a low R_f value of 0.19, indicating strong adsorption onto the silica gel surface. The yellow components displayed R_f values of 0.50, 0.71 and 0.79, suggesting the presence of multiple dye fractions with varying polarity.

Although the overall chromatographic pattern of Lamy ink resembles that of Pelikan ink, slight differences in the R_f values of the yellow components were observed. These differences indicate variation in ink formulation between brands, even when similar colours are used. Such variations are important in forensic examinations, as they allow discrimination between inks of different manufacturers (Christie & Abel, 2021).

4.2.5 Comparative Evaluation and Relevance to Ink Studies

A comparison of three ink brands shows that Pilot ink exhibits a wider range of distinct coloured components. In contrast, Pelikan and Lamy inks are characterised by multiple yellow fractions and a strongly retained black component. The lower R_f values of black dyes in Pelikan and Lamy inks suggest higher polarity or the presence of carbon-based pigments that are less mobile during TLC development.

The observed TLC separation patterns reflect formulation-dependent differences in dye composition and polarity among the Pilot, Pelikan and Lamy inks. The multiple coloured spots, including yellow fractions observed in Pelikan and Lamy, may represent different dye components or additives present in the original formulations. Because this study analysed only a single baseline time point (fresh ink after drying), the TLC patterns cannot be interpreted as degradation products formed during ageing. However, the baseline R_f profiles reported here provide a useful reference for future controlled ageing studies, where the appearance of new spots, loss of existing spots, or changes in spot intensity may indicate dye transformation over time.

Overall, TLC remains a practical preliminary screening tool for fountain pen ink discrimination, and it can contribute to ageing assessment when applied as part of a time-series design.

4.3 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis of Fountain Pen Ink Samples

4.3.1 Comparative Evaluation and Ink Studies Implications

Gas Chromatography-Mass Spectrometry (GC-MS) was employed to characterise and identify the major organic constituents present in selected commercial fountain pen ink samples, namely Pilot, Pelikan and Lamy inks. GC-MS is a powerful analytical technique widely used for the separation and identification of volatile and semi-volatile compounds due to its high sensitivity, reproducibility and extensive spectral libraries. In ink analysis, GC-MS is particularly valuable for detecting additives such as antioxidants, stabilisers, plasticisers and silicone-based compounds, which are often present in low concentrations but play crucial roles in ink performance and stability.

The Total Ion Chromatograms (TICs) obtained from the analysis revealed both shared and distinct chemical features among the ink samples, reflecting similarities in functional formulation requirements as well as brand-specific compositional differences. The identification of compounds was achieved by matching mass spectra with reference libraries, and only compounds with acceptable match quality values were considered for discussion.

4.3.2 Total Ion Chromatogram Profiles of Fountain Pen Inks

The GC-MS analysis was carried out to compare the chromatographic profiles of Pilot, Pelikan, and Lamy black fountain pen inks. The total ion chromatograms (TICs) provide information on the volatile and semi-volatile components detected in each ink sample. In this study, the comparison was focused on the retention time region of approximately 12.5 to 13.9 minutes, where the major peaks were observed for all three ink brands.

The overlaid TICs allow direct comparison of peak retention time, peak shape, and relative abundance between the ink samples. Although the major peaks appeared within a similar retention time region, differences in peak intensity and multiplicity were observed. These differences suggest variation in the concentration and formulation complexity of the chemical components present in each ink brand.

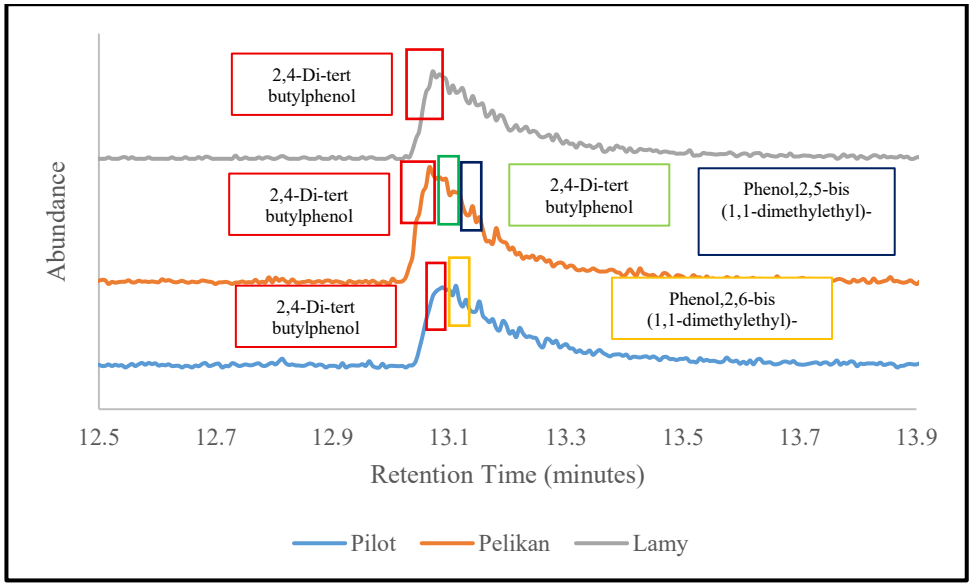


Figure 4.2 Overlaid Total Ion Chromatograms (TICs) of Fountain Pen Ink Samples.

As shown in Figure 4.2, a prominent cluster of peaks was observed in all three samples within the selected retention time range. The presence of peaks in similar retention regions suggests that the inks may contain structurally related compounds. However, the differences in peak abundance indicate that each brand has a different chemical profile.

Pilot ink showed a clear peak in the phenolic region, while Pelikan displayed multiple closely eluting peaks, suggesting the presence of related phenolic compounds or isomers. Lamy ink also showed a strong peak in the same region, indicating the possible presence of similar phenolic components. These findings show that although the inks share some common chemical features, the overall TIC profiles remain distinguishable between brands.

4.3.3 Identification of Major Compounds

The major compounds identified in the fountain pen ink samples, along with their retention times, CAS numbers, relative peak areas and match quality values are summarized in Table 4.2.

Table 4.2

Major Compounds Identified in Ink Samples via GC-MS.

Sample	RT (min)	Compound Name	CAS No	Area (%)	Match Quality	Journal supporting Data
Pilot	13.09	2,4-Di-tert-butylphenol	96-76-4	8.44	80	(R. Liu & Mabury, 2020)
	13.15	Phenol,2,6-bis(1,1-dimethylethyl)-	128-39-2	4.47	80	
Pelikan	13.07	2,4-Di-tert-butylphenol	96-76-4	3.38	87	(Hoang & Park, 2024; Liu & Mabury, 2020)
	13.11	2,4-Di-tert-butylphenol	96-76-4	2.27	80	
	13.18	Phenol, 2,5-bis(1,1-dimethylethyl)-	5875-45-6	0.67	78	
Lamy	13.08	2,4-Di-tert-butylphenol	96-76-4	40.76	50	(Hoang & Park, 2024; Sharif, Jalees, et al., 2022)
	24.01	Octasiloxane	19095-24-0	4.31	50	
	24.15	Bis(trimethylsilyl) benzene	17151-09-6	6.85	53	

Although the NIST library match qualities for the Lamy-specific peaks were relatively low, ranging from 50 to 53, the assignments were not interpreted based on GC-MS data alone. These compounds were reported as tentative identifications and were further supported by complementary FTIR and EDX findings. The FTIR spectrum of Lamy ink showed absorption associated with Si–O–Si stretching, while EDX analysis indicated the presence of silicon in the inked region. Therefore, the GC-MS assignments of siloxane-related compounds were considered chemically reasonable, although further confirmation using authentic standards would still be required for definitive compound identification.

4.3.4 Phenolic Compounds in the 13-Minute Retention Time Region

The compound 2,4-di-tert-butylphenol was detected in all three ink samples, with retention time ranging from 13.07 to 13.09 minutes. This compound exhibited the highest relative abundance in the Lamy ink sample, accounting for 40.76% of the total detected peak area, compared to 8.44% in Pilot ink and 3.38% and 2.27% in Pelikan ink. The consistently high presence of this compound across all samples suggests its importance as a core additive in fountain pen ink formulations.

2,4-Di-tert-butylphenol is a sterically hindered phenolic compound commonly used as an antioxidant and preservative. Its primary function is to inhibit oxidative degradation of organic components, thereby enhancing the shelf life and chemical stability of ink formulations (Hoang & Park, 2024; Liu & Mabury, 2020)

The significantly higher abundance observed in the Lamy ink suggests a formulation strategy that places greater emphasis on oxidative stability, possibly to improve long-term storage performance or resistance to environmental degradation.

In addition to 2,4-di-tert-butylphenol, other substituted phenolic compounds were detected in the Pilot and Pelikan ink samples. The Pilot ink contained phenol, 2-6-bis(1,1-dimetylethyl)-, while the Pelikan ink exhibited phenol, 2,5-bis(1,1-dimehtylethyl)-. These compounds are structurally similar hindered phenols and are also widely employed as antioxidants in industrial formulations, including inks, coatings and polymers (R. Liu & Mabury, 2020).

The presence of multiple phenolic antioxidants within the same retention time region explains the overlapping and shoulder peaks observed in the Pelikan TIC, as

shown in Figure 4.2. Such compositional complexity may contribute to subtle differences in ink baseline behaviour and performance characteristics.

4.3.5 Lamy Ink-Specific Compounds at Higher Retention Times

Unlike the Pilot and Pelikan inks, the Lamy ink sample exhibited additional significant peaks at longer retention times, specifically in the range of 24.0 to 24.15 minutes. These peaks are shown in Figure 4.3, which presents the TIC segment corresponding to the higher molecular weight region of the chromatogram. The chromatographic comparison of Pilot, Pelikan and Lamy inks has been presented earlier in Figure 4.2. Therefore, Figure 4.3 focuses only on the expanded high-retention-time region of the Lamy ink chromatogram because additional peaks were observed in this region for Lamy, whereas no comparable diagnostic peaks were detected for Pilot and Pelikan under the same GC-MS conditions.

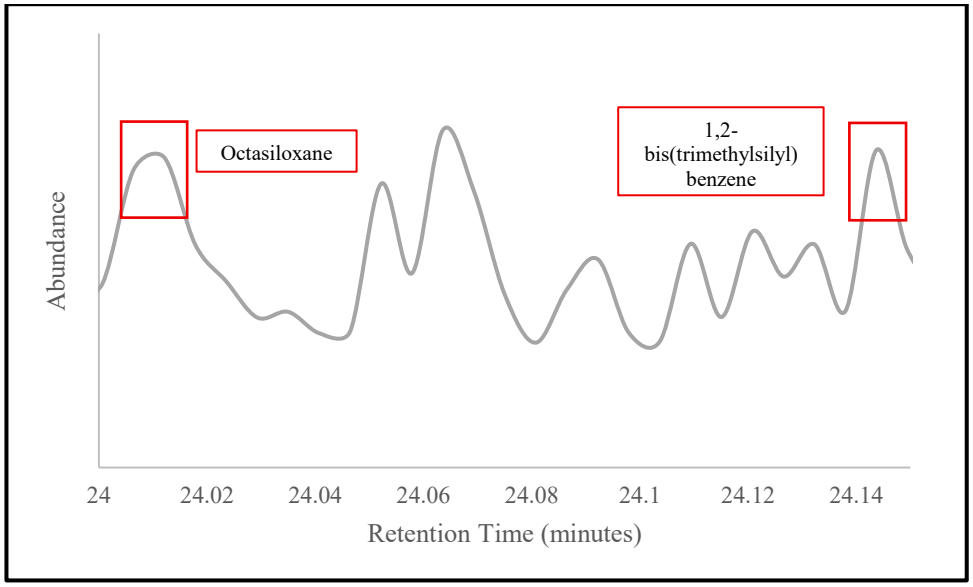


Figure 4.3 Expanded GC-MS TIC Segment of Lamy Fountain Pen Ink Showing Lamy-Specific Peaks at Higher Retention Times.

Two compounds were tentatively identified in the Lamy ink sample and supported by FTIR and EDX evidence: octasiloxane (RT = 24.01 min) and bis(trimethylsilyl)benzene (RT = 24.15 min). Octasiloxane is a cyclic siloxane compound commonly associated with silicone-based additives, which are often incorporated into ink formulations to enhance lubrication, improve flow properties, and

reduce friction during writing. Silicone compounds can also contribute to smoother ink delivery and reduced clogging in fountain pen mechanisms (Sharif, Chand, et al., 2022).

Bis(trimethylsilyl)benzene, another high-molecular-weight compound, may be associated with surface modification or compatibility enhancement within the ink matrix. The presence of these compounds exclusively in the Lamy ink indicates a more complex formulation strategy, potentially aimed at optimising writing performance or durability.

4.3.6 Comparative Discussion of Ink Formulations

A comparative analysis of the GC-MS results reveals that while all three fountain pen inks share a common reliance on phenolic antioxidants, the relative abundance and diversity of additives vary considerably between brands. The dominance of 2,4-di-tert-butylphenol across all samples underscores its critical role in ink stabilisation. However, the markedly higher concentration observed in Lamy ink suggests a formulation optimised for enhanced oxidative resistance.

The presence of silicone-based compounds solely in the Lamy ink further differentiates it from the Pilot and Pelikan inks, highlighting brand-specific approaches to ink formulation. Such compositional differences may influence key performance attributes, including ink flow consistency, drying behaviour and resistance to degradation over time.

From a forensic perspective, the combination of shared and unique chemical markers identified through GC-MS provides valuable discriminatory information. While phenolic antioxidants represent common components, the presence of octasiloxane and bis(trimethylsilyl)benzene in the Lamy ink offers potential markers for ink differentiation in questioned document analysis.

In addition, differences in the relative abundance of phenolic antioxidants may influence the long-term ageing behaviour of the inks. Inks containing lower concentrations of antioxidant compounds may be more susceptible to oxidative degradation, potentially leading to colour fading or chemical changes over time (Calcerrada & García-Ruiz, 2015). Conversely, the higher antioxidant content observed in the Lamy ink may provide greater resistance to such degradation processes (Koenig et al., 2015). This suggests that GC-MS data not only provide compositional information, but may also offer insights into the ageing stability and durability of

fountain pen inks under environmental exposure. Overall, the GC-MS findings are consistent with previous studies reporting the widespread use of phenolic antioxidants and silicone-based additives in fountain pen ink formulations (Hoang & Park, 2024; Sharif, Jalees, et al., 2022).

4.4 Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Analysis

4.4.1 Principle and Relevance of ATR-FTIR in Ink Characterisation

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy was employed in this study to examine the functional groups present in fountain pen ink samples from Pilot, Pelikan and Lamy. The selection of ATR-FTIR was based on its ability to provide rapid, non-destructive analysis with minimal sample preparation. This is particularly important for ink analysis, as fountain pen inks are complex mixtures that may contain dyes, solvents, resins, antioxidants and various performance-enhancing additives.

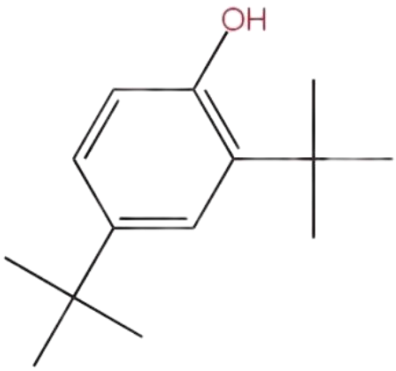
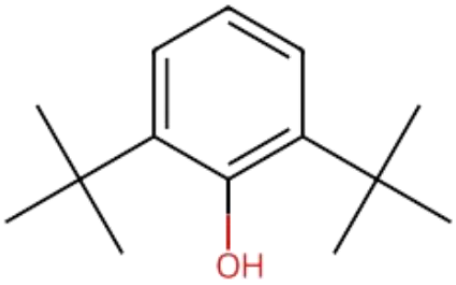
In addition, ATR-FTIR is widely used in ink and document analysis because it allows direct examination of liquid or semi-liquid samples without extensive chemical treatment. This technique provides information on molecular vibrations associated with specific functional groups, making it suitable for identifying broad classes of compounds rather than individual molecular species. For this reason, ATR-FTIR was used in this world as a complementary technique to GC-MS, which provided compound-level identification (Sharif, Chand, et al., 2022).

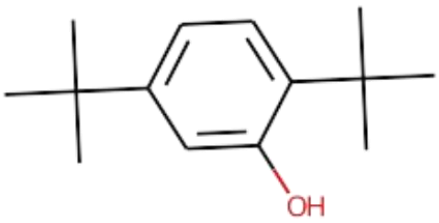
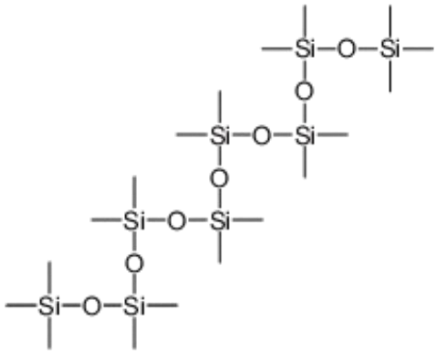
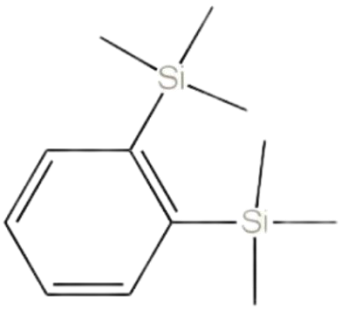
4.4.2 Use of GC-MS Identified Compounds to Support FTIR Interpretation

The interpretation of ATR-FTIR spectra was supported by compounds previously identified using GC-MS analysis. These compounds, listed in Table 4.3, were selected because their molecular structures contain functional groups that are expected to contribute significantly to the FTIR spectra.

Table 4.3

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.	Phenol,2,6-bis (1,1-dimethylethyl)-	$C_{14}H_{22}O$	

No.	Compound Name	Formula	Chemical Structure
3.	Phenol,2,5-bis (1,1-dimethylethyl)-	$C_{14}H_{22}O$	
4.	Octasiloxane	O_7Si_8	
5.	Bis(trimethylsilyl) benzene	$C_{12}H_{22}Si_2$	

The phenolic compounds identified, including 2,4-di-tert-butylphenol, phenol,2,6-bis(1,1-dimethylethyl)-, and phenol, 2,5-bis(1,1-dimethylethyl)-, share common structural features such as aromatic rings, hydroxyl groups and alkyl substituents. These features are known to produce characteristic infrared absorption bands in the O-H stretching, aromatic C=C stretching and C-O stretching regions. As a result, these compounds provide a reasonable chemical basis for assigning FTIR bands observed in the ink spectra.

In the case of the Lamy ink sample, GC-MS analysis additionally identified octasiloxane and bis (trimethylsilyl)benzene. These silicon-containing compounds introduce Si-O-Si and Si-C bonds, which exhibit strong and distinctive absorptions in the fingerprint region of the FTIR spectrum. Their presence was therefore considered important for explaining spectral features that were not observed in the Pilot and Pelikan ink samples.

4.4.3 Overview of ATR-FTIR Spectra of Fountain Pen Inks

The ATR-FTIR spectra of the Pilot, Pelikan and Lamy ink samples are shown in Figure 4.4, covering the wavenumber range from approximately 630 to 3630 cm^{-1}. Overall, the spectra display several common absorption bands, suggesting that the inks share several similar chemical components. This is expected, as fountain pen inks are generally formulated to meet similar functional requirements such as stability, flow behaviour and colour retention.

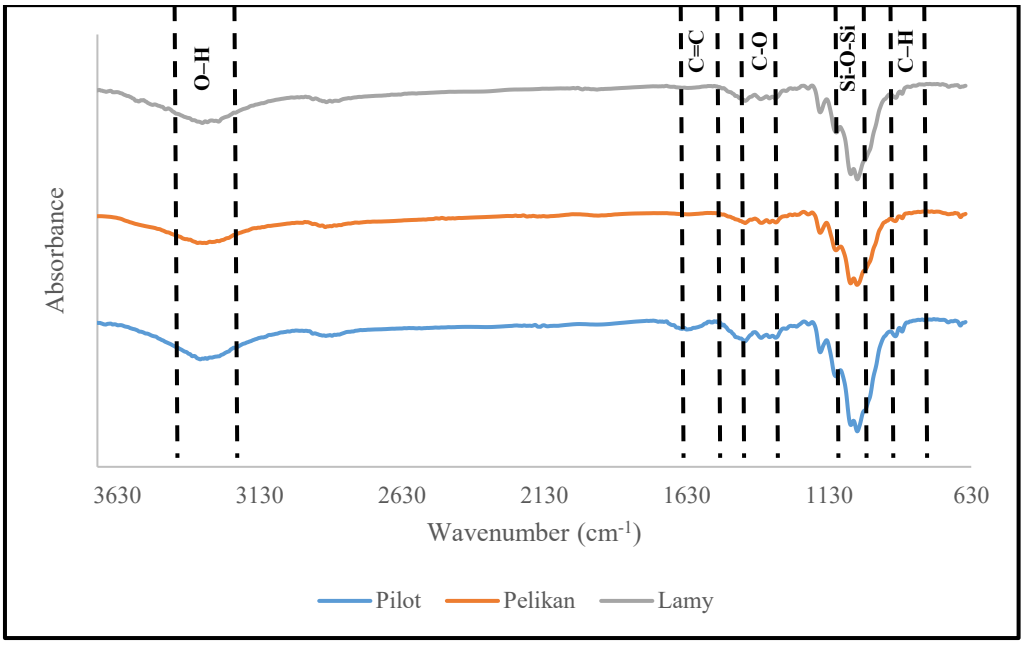


Figure 4.4 Comparative FTIR Spectra of Fountain Pen Ink Samples.

Despite these similarities, clear differences were observed in the intensity and presence of certain absorption bands, particularly in the fingerprint region. These differences indicate variations in ink formulation between brands and provide useful information for comparative analysis.

The absorption region around 1000–1100 cm^{-1} was observed in all three ink samples. This region may include overlapping contributions from C–O/C–O–C stretching of the paper substrate or dye components, as well as Si–O–Si stretching. Therefore, the presence of this band was not interpreted as exclusive to Lamy ink. However, the Lamy spectrum showed a more pronounced absorption in this region, which was consistent with the GC-MS detection of siloxane-related compounds and the EDX indication of silicon in the inked region. Thus, the Si–O–Si assignment for Lamy was interpreted using complementary evidence from FTIR, GC-MS and EDX rather than FTIR alone.

4.4.4 Detailed Discussion of Major FTIR Absorption Regions

The major FTIR absorption bands observed for the fountain pen ink samples, together with their functional group assignments and possible chemical origins, are summarised in Table 4.4. This table provides an integrated interpretation that links ATR-FTIR spectral features with GC-MS identified compounds.

Table 4.4

FTIR Peak Assignments and Functional Group Interpretation for Fountain Pen Ink Samples.

Brand	Wavenumber (cm^{-1})	Peak Intensity	Functional Group	Possible Compound Origin (chemical structure)
Pilot	3300–3400	Broad	O–H stretching (phenol)	Phenolic antioxidants or degradation products
	1600	Medium	Aromatic C=C stretching	Benzene ring structures
	1200–1250	Medium	C–O stretching	Phenolic ether or alcohol group
	1000–1100	Weak/medium	C–O/C–O–C stretching; possible Si–O–Si contribution	Paper substrate, dye components, or minor silicon-related contribution
Pelikan	3300	Broad	O–H stretching (phenol)	Hindered phenols from ink additives
	1580–1600	Weak	Aromatic C=C stretching	Aromatic ring system
	1260–1210	Medium	C–O stretching	Substituted phenols
	1000–1100	Weak/medium	C–O/C–O–C stretching; possible Si–O–Si contribution	Paper substrate, dye components, or minor silicon-related contribution
Lamy	3300	Weak/broad	O–H stretching (phenol)	Trace phenolic group or moisture
	1000–1100	Strong	Si–O–Si stretching	Siloxanes (e.g., octasiloxane)
	750–850	Sharp	Aromatic C–H bending	Aromatic benzene ring

a) O-H Stretching Region (3300 – 3400 cm^{-1})

A broad absorption band in the region of 3300 – 3400 cm^{-1} was observed in all ink samples. This band is commonly associated with O-H stretching vibrations, particularly in phenolic compounds and alcohols where hydrogen bonding is present (Espina et al., 2022). The broad nature of the band suggests a distribution of hydrogen-bonding environments rather than a single, well-defined hydroxyl group.

The Pilot and Pelikan inks exhibited relatively broader and more intense O-H bands compared to the Lamy ink. This observation is consistent with the presence of phenolic antioxidants identified by GC-MS analysis in these samples. The stronger O-H absorption suggests that hydroxyl-containing compounds contribute noticeably to the overall chemical composition of these inks.

In contrast, the Lamy ink displayed a weaker O-H stretching band. Although GC-MS results showed a high relative abundance of 2,4-di-tert-butylphenol in the Lamy ink, the reduced intensity of the O-H band may be attributed to steric hindrance caused by bulky tert-butyl groups, which can limit hydrogen bonding. Furthermore, the presence of silicone-based additives may reduce the relative contribution of polar functional groups to the FTIR spectrum.

b) Aromatic C=C Stretching Region (1580 – 1600 cm^{-1})

Medium intensity absorption bands were observed in the region of 1580 – 1600 cm^{-1} in the Pilot and Pelikan ink spectra. These bands are assigned to aromatic C=C stretching vibrations, which are characteristic of benzene ring structures (Germinario et al., 2017). The presence of these bands supports the GC-MS identification of aromatic phenolic compounds in the ink formulations.

Differences in band intensity between the Pilot and Pelikan inks may reflect variations in the concentration or substitution patterns of aromatic compounds. In the Lamy ink spectrum, the aromatic C=C stretching band was less pronounced, which may be due to overlap with other absorptions or differences in formulation composition.

c) C-C Stretching Vibrations (1200 – 1250 cm^{-1})

Absorption bands in the region of 1200 – 1250 cm^{-1} were observed in the Pilot and Pelikan ink samples and are attributed to C-O stretching vibrations. These bands are typically associated with phenolic or alcohol functional groups and further support the presence of substituted phenols identified by GC-MS.

The interpretation of this region in the Lamy ink spectrum is more complex due to overlap with siloxane-related vibrations. This overlap highlights the importance of combining FTIR and GC-MS data when analysing complex ink matrices.

d) Si–O–Si Stretching Region with Possible C–O/C–O–C Overlap (1000–1100 cm^{-1})

A The absorption region at approximately 1000–1100 cm^{-1} was observed in all three ink spectra. This region may be attributed to overlapping C–O/C–O–C stretching vibrations from the paper substrate or dye components, as well as possible Si–O–Si stretching. Therefore, this band was not interpreted as exclusive to Lamy ink based on FTIR evidence alone.

However, the Lamy spectrum showed a stronger absorption in this region compared with Pilot and Pelikan. This observation was further supported by the GC-MS detection of siloxane-related compounds and the EDX indication of silicon in the inked region (Sharif, Jalees, et al., 2022).

Thus, the Si–O–Si assignment in Lamy was interpreted using complementary evidence from FTIR, GC-MS and EDX rather than from FTIR alone. The stronger siloxane-related contribution in Lamy may be associated with silicone-based additives used to improve ink flow, lubrication or writing smoothness.

e) Aromatic C-H Out-of-Plane Bending (750 – 850 cm^{-1})

All ink samples exhibited sharp absorption bands in the region of 750 to 850 cm^{-1}, which are attributed to aromatic C-H out-of-plane bending vibrations. These bands are commonly observed in substituted benzene rings and further confirm the widespread presence of aromatic structures in fountain pen inks.

4.4.5 Overall Interpretation and Implications

The ATR-FTIR results indicate that phenolic compounds were present in all three fountain pen ink samples, consistent with their role as antioxidants or stabilising additives. While the overall spectral features are similar, the Lamy ink sample exhibits distinct characteristics, particularly the presence of strong Si-O-Si stretching vibrations.

The combined ATR-FTIR and GC-MS results suggest that Lamy ink employs a more complex formulation strategy that includes silicone-based additives, whereas Pilot and Pelikan inks rely primarily on phenolic compounds. These differences may influence ink properties such as flow behaviour, stability and interaction with paper surfaces.

From a forensic perspective, the presence or absence of siloxane-related FTIR bands provides a useful discriminating feature for differentiating ink brands using non-destructive techniques.

4.5 Ultraviolet-Visible (UV-Vis) Spectroscopy Analysis

4.5.1 Application of UV-Vis Spectroscopy in Ink Analysis

Ultraviolet-Visible (UV-Vis) spectroscopy was employed to investigate the optical absorption characteristics of fountain pen ink samples from Pilot, Pelikan and Lamy brands. UV-Vis Spectroscopy is a widely used analytical technique for the analysis of coloured compounds, particularly dyes and pigments, due to its ability to detect electronic transitions associated with chromophoric systems. In ink analysis, UV-Vis spectroscopy provides valuable information regarding the colour-producing components and their relative concentrations, making it useful for comparative studies and forensic examinations (More et al., 2018; Liu et al., 2013).

Fountain pen inks typically contain complex mixtures of organic dyes, many of which possess conjugated π-electron systems. These systems absorb light in the ultraviolet and visible regions of the electromagnetic spectrum, resulting in characteristic absorption bands. By analysing the absorption spectra and maximum absorption wavelengths (λ_{max}), insights into dye composition and formulation differences between ink brands can be obtained.

4.5.2 UV-Vis Absorption Spectra of Fountain Pen Ink Samples

The UV-Vis absorption spectra of the Pilot, Pelikan and Lamy fountain pen ink samples were recorded over the wavelength range of 400 – 750 nm and are presented in Figure 4.5. This range was selected as it covers the visible region relevant to colour perception and dye absorption behaviour.

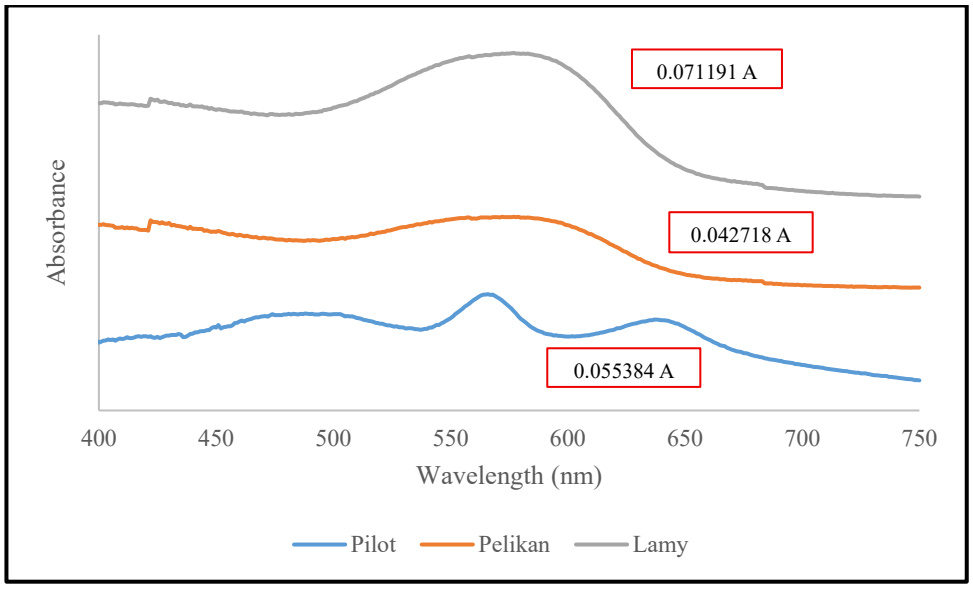


Figure 4.5 UV-Visible Absorption Spectra for Fountain Pen Ink Samples.

Overall, all three ink samples exhibited broad adsorption bands within the visible region, indicating the presence of coloured dye components. However, differences in spectral shape, absorption intensity and peak position were observed among the samples, suggesting variations in dye composition and concentration.

4.5.3 Maximum Absorption Wavelengths and Absorbance Values

The maximum absorption wavelengths (λ_{max}) and corresponding absorbance values for each ink sample are summarised in Table 4.5. The λ_{max} values were determined from the highest absorption peaks observed in the UV-Vis spectra.

Table 4.5

Summary of The Maximum Absorption Wavelengths (λ_{max}) and Corresponding Absorbance Values for Pilot, Pelikan, and Lamy Fountain Pen Inks Obtained from UV-Vis Spectroscopy.

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

Pilot ink exhibited λ_{max} at 566.96 nm with an absorbance value of 0.055384 A, while Pelikan and Lamy inks showed λ_{max} values at 576.16 nm and 576.31 nm, respectively. The absorbance values recorded were 0.042718 A for Pelikan ink and 0.071191 A for Lamy ink.

The proximity of the λ_{max} values among the three samples suggests that the inks may contain dyes with similar chromophoric structures. Such behaviour is commonly observed in fountain pen inks, where manufacturers often employ similar dye classes to achieve comparable colour tones (Simsek & Seker, 2024).

4.5.4 Interpretation of UV-Vis Absorption Behaviour

a) Absorption Intensity and Dye Concentration

Although the λ_{max} values of Pelikan and Lamy inks are nearly identical, notable differences were observed in their absorbance values. Lamy ink exhibited the highest absorbance among the three samples, indicating a higher concentration of light-absorbing dye molecules. In contrast, Pelikan ink showed the lowest absorbance value, suggesting a lower dye concentration or differences in dye molar absorptivity.

According to the Beer-Lambert law, absorbance is directly proportional to the concentration of absorbing species, provided that the optical path length and molar absorptivity remain constant (Senior et al., 2012). Therefore, the higher absorbance observed for the Lamy ink may reflect a more concentrated dye formulation or the presence of dyes with stronger absorption characteristics.

b) Bathochromic Shift and Dye Structure

A slight shift in λ_{max} was observed between Pilot ink, Pelikan and Lamy inks. Pilot ink exhibited a λ_{max} at a shorter wavelength (566.96 nm), whereas Pelikan and Lamy inks absorbed maximally at approximately 576 nm. This shift towards longer wavelengths, known as a bathochromic shift, may be attributed to differences in the chemical structure of the dyes, such as extended conjugation or the presence of electron-donating substituents (Patel et al., 2024).

Such structural variations can alter the energy gap between electronic states, resulting in changes in absorption wavelength. The observed bathochromic shift in Pelikan and Lamy inks suggests that these inks may contain dyes with slightly more extended conjugated systems compared to those present in the Pilot ink.

c) Spectral Broadening and Dye Mixtures

The broad nature of the absorption bands observed in all three spectra indicates that each ink sample likely contains a mixture of dyes rather than a single colourant. This observation is consistent with the TLC results discussed previously, which revealed multiple coloured components within each ink brand.

The overlap of absorption bands from different dyes can result in broad and smooth spectral profiles, as observed in Figure 4.5. Such behaviour is typical of commercial ink formulations, where multiple dyes are blended to achieve desired colour intensity, hue stability and performance characteristics (Luňáková et al., 2025).

4.5.5 Comparative Discussion of Ink Brands Based on UV-Vis Analysis

A comparative evaluation of the UV-Vis results indicates that while all three fountain pen inks exhibit similar absorption behaviour in terms of λ_{max}, clear differences exist in absorbance intensity. Lamy ink demonstrated the highest absorbance value, followed by Pilot ink, while Pelikan ink showed the lowest absorbance.

These differences suggest variations in dye concentration and formulation strategies among the brands. The higher absorbance observed for Lamy ink may contribute to a more intense colour appearance on paper, while lower absorbance values may result in lighter or less saturated writing. Such differences are relevant not only from a consumer performance perspective but also in forensic ink discrimination.

From a forensic standpoint, UV-Vis spectroscopy provides a useful preliminary screening tool for differentiating inks based on absorbance characteristics and λ_{max} values. Although the technique may not uniquely identify specific dyes, it offers complementary information that supports findings from TLC, GC-MS and ATR-FTIR analyses.

4.5.6 Implications for Ink Studies and Stability

Although the present study measured only a baseline time point (fresh ink after drying), UV–Vis absorption behaviour provides an important reference for future ageing studies because dye degradation often appears as peak intensity reduction, band broadening or wavelength shifts over time.

Differences in absorption maxima and absorbance values observed among Pilot, Pelikan and Lamy inks reflect differences in chromophore composition and electronic structure. These baseline spectral features may influence how each formulation responds to environmental factors such as light exposure, humidity and oxygen. Therefore, the UV–Vis results in this study should be interpreted as baseline spectral fingerprints and as candidate features to monitor in future controlled ageing experiments.

4.6 Polarised Optical Microscopy (POM) Analysis of Fountain Pen Ink Samples

4.6.1 Purpose and Application of POM in Ink Examination

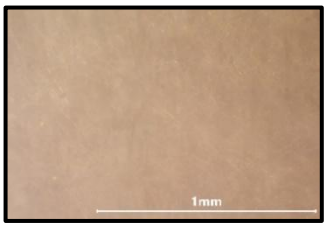
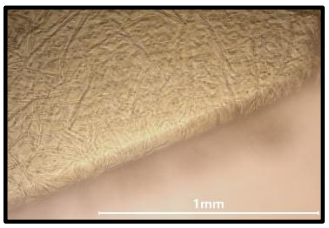
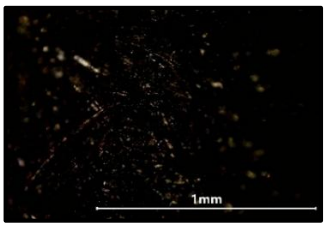
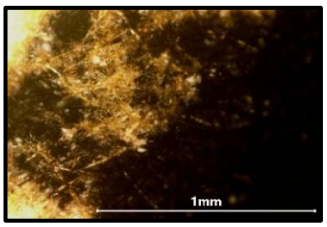
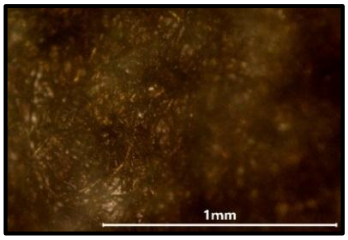
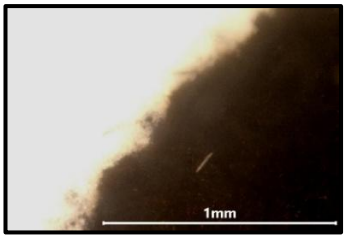
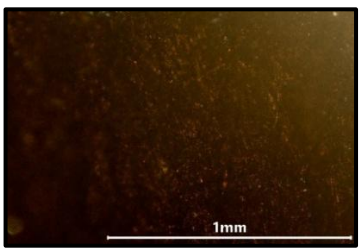
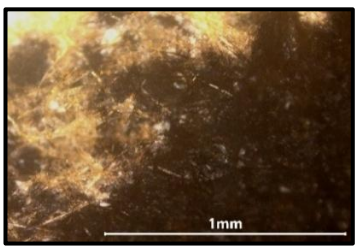
Polarised Optical Microscopy (POM) was employed to examine the microstructural features and distribution behaviour of fountain pen inks deposited on paper. POM is a useful qualitative technique for visualising the interaction between ink components and paper fibres, as well as observing pigment or dye aggregation, dispersion uniformity and optical anisotropy. In forensic ink studies, POM is commonly used as a complementary method to chemical analyses, as it provides spatial and morphological information without altering the sample (Trejos & Almirall, 2017).

In this study, POM analysis was conducted at a magnification of 10x to allow comparative observation of ink distribution across different regions of the ink line. Both the centre and edge regions of the ink lines were examined, as these areas are known to exhibit differences arising from solvent evaporation and pigment migration during the drying process. A blank paper sample was also analysed as a control to provide a baseline reference for distinguishing ink-related features from the inherent microstructure of the paper substrate.

4.6.2 POM images of Fountain Pen Ink Samples

Table 4.6

Summary of POM Observations for Fountain Pen Ink Samples at 10x Magnification, Illustrating The Morphological Characteristics of Ink Deposition at The Centre and Edge of Ink Lines. Images Include (a-b) Paper Substrate (Control), (c-d) Pilot Ink, (e-f) Pelikan Ink, and (g-h) Lamy Ink.

	Centre of Ink Line	**Edge of Ink Line**
Paper (control)		
	Figure 4.6 (a)	Figure 4.6 (b)
Pilot		
	Figure 4.6 (c)	Figure 4.6 (d)
Pelikan		
	Figure 4.6 (e)	Figure 4.6 (f)
Lamy		
	Figure 4.6 (g)	Figure 4.6 (h)

The POM images obtained for the fountain pen ink samples and the blank paper control are presented in Figure 4.6 (a-h). The figure shows the microstructural features observed at the centre and edge regions of ink lines deposited on paper for Pilot, Pelikan and Lamy inks, all recorded at 10x magnification.

The blank paper image in Figure 4.6 (a) and Figure 4.6 (b) reveals the characteristic fibrous structure of cellulose with inherent birefringence under polarised light. This image serves as a reference for identifying features that originate from the ink rather than from the paper itself.

4.6.3 Microstructural Features of Ink at the Centre Region

At the centre of the ink line, differences in ink distribution and microstructural appearance were observed among the three ink brands. The Pilot ink in Figure 4.6 (c) exhibited a relatively uniform distribution of fine dispersed particles, suggesting good dispersion of ink components within the paper matrix. The optical response appeared weak to moderate, indicating limited aggregation or crystallinity in the central region.

In contrast, the Pelikan ink centre region in Figure 4.6 (e) displayed a more uneven texture, with visible fine aggregates distributed within the ink layer. This non-uniform appearance suggests variability in the dispersion of ink components, which may be related to differences in dye composition and interaction with the paper fibres. This observation is consistent with the UV-Vis result, where Pelikan ink recorded the lowest absorbance value among the three ink samples. The lower absorbance may indicate a lower concentration of light-absorbing dye components or differences in dye molar absorptivity. Therefore, the uneven microstructural appearance observed under POM may reflect non-uniform dye distribution and weaker optical absorption behaviour in the Pelikan ink formulation.

The Lamy ink centre region in Figure 4.6 (g) showed a comparatively smoother and more uniform appearance, with minimal visible aggregates. The weak optical response observed under crossed polars indicates a relatively homogeneous ink deposition. This observation suggests that the ink components are well distributed within the central region of the ink line.

4.6.4 Microstructural Features at the Edge of the Ink Line

More pronounced differences were observed at the edge regions of the ink lines, where ink accumulation and redistribution effects are typically more evident. The Pilot ink edge in Figure 4.6 (d) exhibited denser clustered structures near the ink boundary, indicating pigment or dye migration towards the edge during drying. This behaviour is consistent with solvent flow towards the perimeter of the ink line, often referred to as edge accumulation effects.

For the Pelikan ink, the edge region in Figure 4.6 (f) showed a thick and highly concentrated accumulation along the ink boundary. The strong optical response observed suggests significant aggregation of ink components at the edge. Such pronounced accumulation may be associated with solvent evaporation dynamics and stronger interactions between ink components and paper fibres.

The Lamy ink edge in Figure 4.6 (h) displayed moderate aggregation with visible interaction between ink components and the fibrous paper structure. Although some degree of pigment redistribution was observed, the accumulation was less pronounced compared to the Pelikan ink. This suggests a more controlled ink spreading behaviour at the edge region.

4.6.5 Summary of POM Observations

A qualitative summary of the microstructural features observed in the POM images is presented in Table 4.7. The table highlights differences in ink distribution, aggregation behaviour and optical response between the centre and edge regions for each ink brand.

The optical behaviour was determined qualitatively from the brightness, contrast and birefringence response observed under crossed-polarised light. Areas showing faint colour or low contrast were classified as weak, while brighter or more distinct responses were classified as moderate to strong, indicating greater interaction of ink components with the paper fibres or higher local aggregation within the ink layer.

The table provides a systematic comparison of observations derived from Figure 4.6 and assists in correlating visual features with ink formulation behaviour.

Table 4.7

Qualitative Observations from Polarised Optical Microscopy (POM) Images of Fountain Pen Ink Samples at 10x Magnification.

Sample	Region of Ink Line	Microstructural Appearance	Ink Distribution	Optical Behaviour
Paper (control)	Centre	Cellulose fibre network visible	Uniform	Natural birefringence from fibres
Pilot	Centre	Fine dispersed particles within ink layer	Relatively uniform	Weak to moderate
	Edge	Dense clustered structures near boundary	Highly concentrated	Moderate to strong
Pelikan	Centre	Uneven texture with visible aggregates	Non-uniform	Moderate
	Edge	Thick accumulation along ink boundary	Strongly concentrated	Strong
Lamy	Centre	Smooth appearance with minimal aggregates	Uniform	Weak
	Edge	Moderate aggregation with fibrous interaction	Moderately concentrated	Moderate

A qualitative summary of the microstructural features observed in the POM images is presented in Table 4.7. The table highlights differences in ink distribution,

aggregation behaviour and optical response between the centre and edge regions for each ink brand.

The table provides a systematic comparison of observations derived from Figure 4.6 and assists in correlating visual features with ink formulation behaviour.

4.6.6 Comparative Discussion of Ink Distribution Behaviour

Comparative analysis of the POM results indicates that all three fountain pen inks exhibit differences in microstructural behaviour between the centre and edge regions of the ink line. This behaviour is consistent with drying-induced redistribution processes commonly observed in ink deposition on porous substrates (e Brito et al., 2017).

Among the samples, Pelikan ink showed the most pronounced edge accumulation and aggregation, suggesting stronger pigment migration or less uniform dispersion during drying. Pilot ink exhibited moderate edge concentration with relatively uniform dispersion at the centre, while Lamy ink demonstrated the most uniform overall appearance, particularly at the centre region, with less pronounced edge effects.

These differences may be related to variations in ink formulation, including dye concentration, solvent composition and the presence of additives identified through GC-MS and FTIR analyses. For instance, inks with higher dye concentrations or different solvent evaporation rates may exhibit stronger edge accumulation and aggregation behaviour.

4.6.7 Implications for Ink Studies and Forensic Examination

Because POM observations were obtained at a single baseline time point (fresh ink after drying), the features described here represent initial distribution behaviour rather than time-dependent physical ageing. From an ink analysis perspective, areas of higher pigment concentration, particularly at the edges of ink lines, may be more susceptible to chemical degradation or colour changes over time. The pronounced aggregation observed in certain inks may therefore influence their long-term stability and visual appearance.

In forensic document examination, the microstructural differences observed using POM provide valuable supplementary information for ink discrimination. The distinct distribution patterns and aggregation behaviours observed among the ink brands support the use of POM as a non-destructive screening tool that complements TLC, UV-Vis, GC-MS and ATR-FTIR analyses (Trejos & Almirall, 2017).

4.7 Field Emission Scanning Electron Microscopy (FESEM) and Energy-Dispersive X-ray (EDX) Analysis of Fountain Pen Ink Samples

4.7.1 Application of FESEM-EDX and Elemental Mapping in Ink Examination

Field Emission Scanning Electron Microscopy (FESEM) coupled with Energy-Dispersive X-ray (EDX) analysis was employed to investigate the surface morphology, elemental composition and spatial elemental distribution of fountain pen inks deposited on paper. FESEM provides high-resolution imaging of ink-paper interactions, while EDX enables identification of elemental constituents associated with both ink formulations and the paper substrate. In addition, EDX elemental mapping allows visualisation of the spatial distribution of elements across the inked regions, offering further insight into ink dispersion and penetration behaviour (Abd Mutalib et al., 2017; Christie & Abel, 2021).

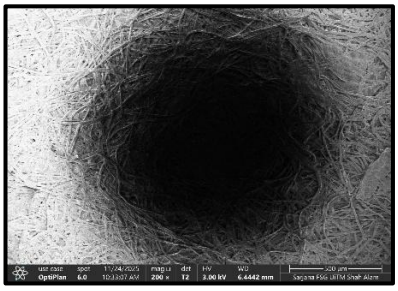
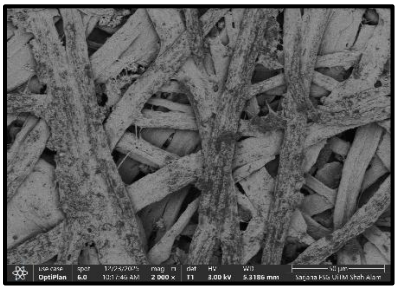
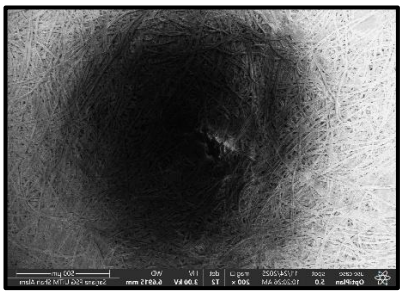
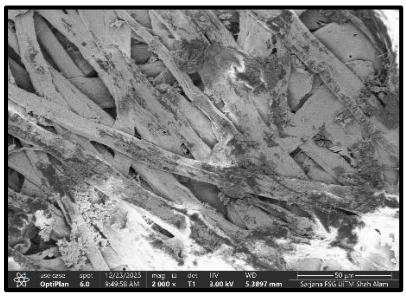
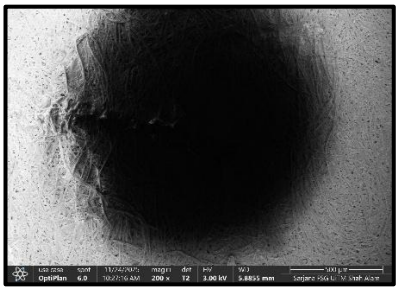
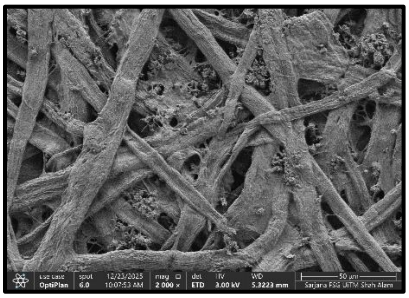
In forensic ink analysis, the combination of FESEM imaging, EDX spectra and elemental mapping is particularly valuable, as it enables correlation between morphological features and elemental composition. This approach complements the molecular and chemical information obtained from GC-MS and ATR-FTIR analyses.

4.7.2 FESEM Morphological of Fountain Pen Inks at Different Magnifications

FESEM images of fountain pen inks deposited on paper at 200x and 2000x magnifications are presented in Table 4.8. These magnifications were selected to observe both the overall ink deposition pattern and the detailed interaction between ink components and cellulose fibres.

Table 4.8

FESEM Images of Fountain Pen Inks Deposited on Paper at 200x and 2000x Magnifications, Illustrating Ink Distribution and Fibre Interaction for (a–b) Pilot, (c–d) Pelikan, and (e–f) Lamy Inks.

Brand	**Magnifications**	
	200x	**2000x**
Pilot		
	Figure 4.7 (a)	Figure 4.7 (b)
Pelikan		
	Figure 4.7 (c)	Figure 4.7 (d)
Lamy		
	Figure 4.7 (e)	Figure 4.7 (f)

At 200x magnification, all ink samples appear as darkened circular regions corresponding to ink deposition. However, differences in the extent, density and boundary definition of these regions were observed among the ink brands. At 2000x magnification, the cellulose fibre network becomes clearly visible, allowing assessment of fibre coating, aggregation and ink penetration behaviour, which are important parameters in forensic ink studies (Trejos & Almirall, 2017).

4.7.3 FESEM Morphological of Pilot Fountain Pen Ink

The FESEM micrographs of the Pilot ink sample in Figure 4.7 (a) and Figure 4.7 (b) show relatively uniform ink deposition across the paper surface. At higher magnification, the ink appears to coat the cellulose fibres evenly, with minimal evidence of large aggregates. Individual fibres remain distinguishable, indicating moderate penetration of ink into the paper matrix rather than excessive surface accumulation.

This relatively uniform morphology suggests a good dispersion of ink components and balanced interaction with the paper substrate. Such behaviour is consistent with previous studies reporting that well-dispersed inks tend to exhibit smoother surface morphology and more stable writing characteristics (Vaseem et al., 2012).

4.7.4 FESEM Morphological of Pelikan Fountain Pen Ink

The FESEM images of the Pelikan ink sample in Figure 4.7 (c) and 4.7 (d) reveal a more concentrated and uneven deposition pattern. At higher magnification, thicker ink deposits and clustered structures are visible, particularly at fibre intersections. In several regions, ink components appear to bridge between fibres, forming dense aggregates.

This aggregation behaviour suggests non-uniform dispersion of ink components during deposition and drying. Similar aggregation phenomena have been associated with higher pigment content or differences in solvent evaporation dynamics, which can lead to localised concentration of ink components on paper surfaces (Mielonen et al., 2015). These observations are consistent with the TLC and POM results, which indicated multiple dye components and pronounced edge accumulation for Pelikan ink.

4.7.5 FESEM Morphological of Lamy Fountain Pen Ink

The FESEM micrographs of the Lamy ink sample in Figure 4.7 (e) and 4.7 (f) show comparatively smooth and homogeneous ink coverage. At higher magnification, the ink layer appears thinner and more evenly distributed than that observed for Pelikan ink, with limited aggregation. The cellulose fibres remain clearly visible, indicating controlled ink spreading and penetration.

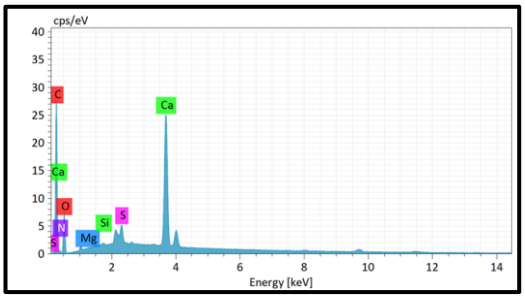
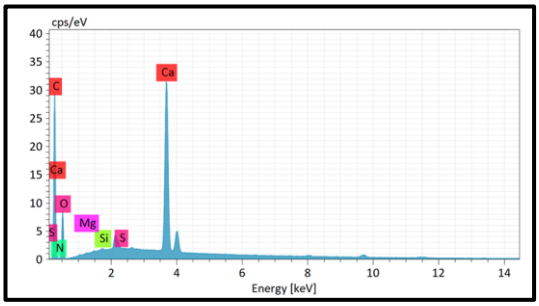
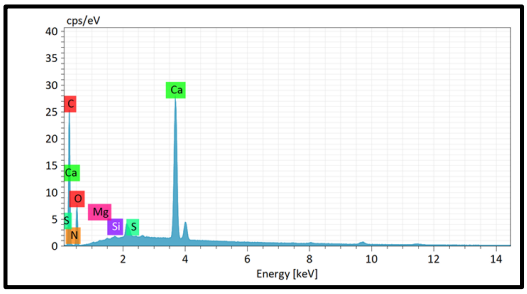
The relatively uniform morphology observed for Lamy ink may be attributed to formulation additives that influence surface tension and wetting behaviour. Silicone-base additives, which were identified in the Lamy ink by GC-MS and ATR-FTIR analyses, are known to improve ink flow and surface interaction (Sharif, Chand, et al., 2022).

4.7.6 Elemental Composition of Fountain Pen Inks by EDX Spectral Analysis

EDX spectra obtained at 1000x magnification for Pilot, Pelikan and Lamy inks are presented in Figure 4.8 (a) until Figure 4.8 (c) as summarised in Table 4.9.

Table 4.9

EDX Spectra of Fountain Pen Inks Deposited on Paper at 1000x Magnification. Spectra Correspond to (a) Pilot, (b) Pelikan, and (c) Lamy Ink Samples.

Sample	Spectrum
Pilot	 Figure 4.8 (a)
Pelikan	 Figure 4.8 (b)
Lamy	 Figure 4.8 (c)

The corresponding elemental composition data are summarised in Figure 4.9. Carbon (C) and Oxygen (O) were dominant elements detected in all ink samples, reflecting contributions from both the organic ink components and the cellulose-based paper substrate. Minor amounts of Calcium (Ca) were detected and are attributed to paper fillers such as Calcium carbonate ($CaCO_3$), which are commonly used in paper manufacturing (Dölle, 2021).

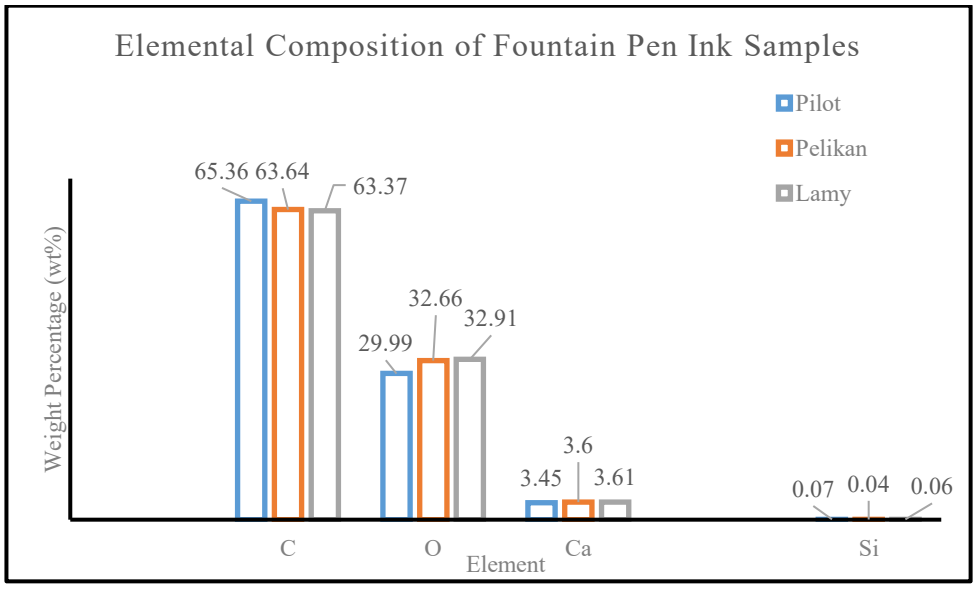


Figure 4.9 Elemental Composition of Fountain Pen Ink Samples.

Trace levels of silicon (Si) were detected in all ink samples, with comparable low weight percentages observed for Pilot, Pelikan and Lamy inks. Therefore, the Si signal was not interpreted as exclusive to Lamy ink based on EDX analysis alone. The presence of Si may originate from minor ink additives, paper-related contributions, or trace inorganic components within the ink–paper matrix. However, in the case of Lamy ink, the Si signal was interpreted together with the GC-MS tentative identification of siloxane-related compounds and the stronger FTIR absorption in the 1000–1100 cm^{-1} region. Thus, the evidence for siloxane-related additives in Lamy was based on complementary GC-MS, ATR-FTIR and EDX findings rather than EDX alone (Sharif, Chand, et al., 2022).

4.7.7 Elemental Mapping of Fountain Pen Inks

EDX elemental mapping images for Pilot, Pelikan and Lamy inks are presented in Figure 4.10 until Figure 4.12.

For Pilot ink in Figure 4.10, the elemental maps show a relatively uniform distribution of carbon and oxygen, indicating even dispersion of organic ink components. Calcium signals are sparsely distributed and primarily associated with the paper fibres. Silicon signals are weak and scattered, suggesting a low concentration of silicon-containing additives.

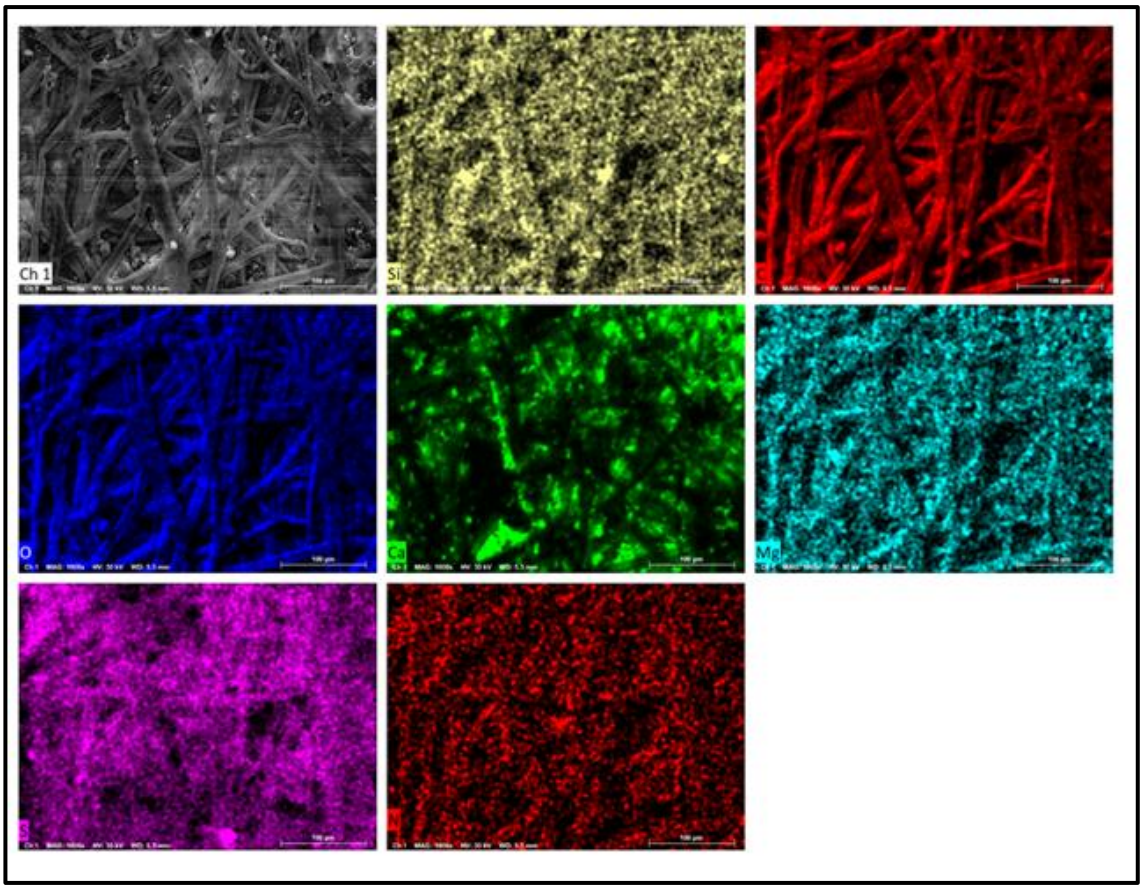


Figure 4.10 Pilot Ink Mapping.

In the Pelikan ink in Figure 4.11, carbon and oxygen maps exhibit areas of higher intensity, corresponding to regions of thicker ink accumulation observed in FESEM images. This non-uniform elemental distribution supports the aggregation behaviour observed morphologically. Silicon distribution remains minimal, indicating limited contribution from silicon-based additives.

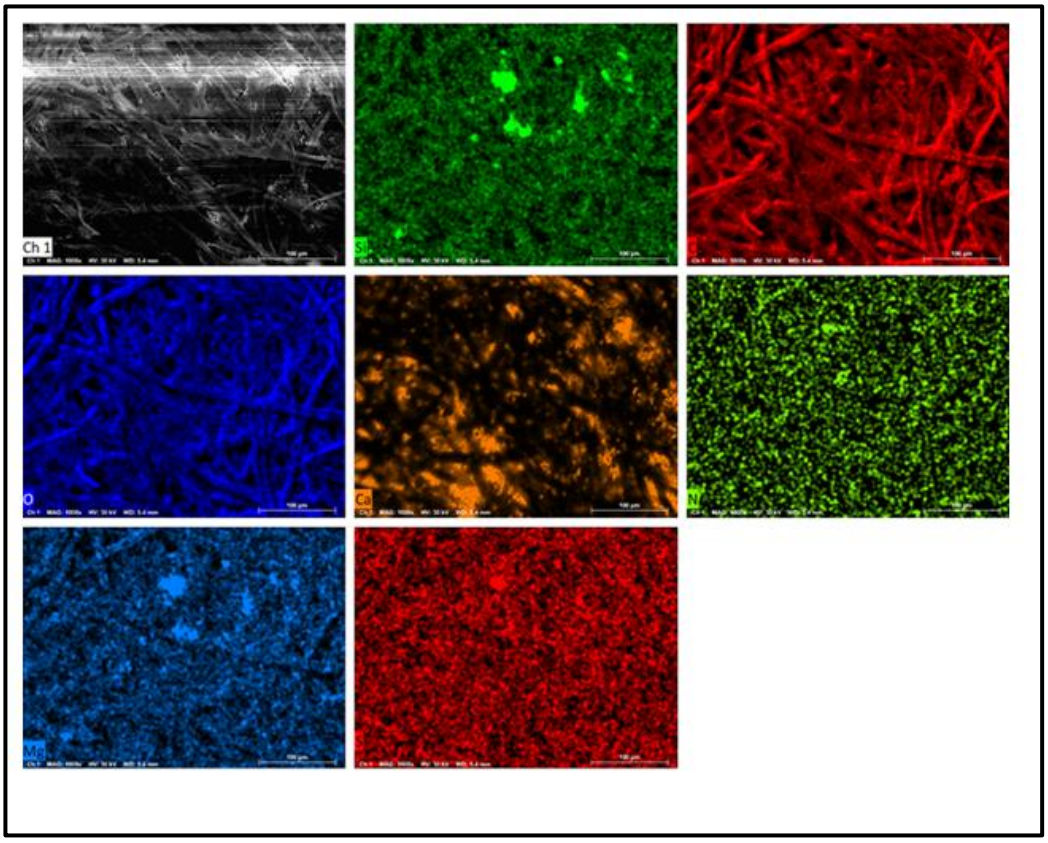


Figure 4.11 Pelikan Ink Mapping.

For the Lamy ink in Figure 4.12, elemental mapping reveals a more uniform distribution of carbon and oxygen, consistent with its smoother morphology. Silicon signals are more evenly distributed across the inked region, supporting the presence of siloxane-based additives identified through GC-MS and ATR-FTIR analyses (Sharif, Jalees, et al., 2022).

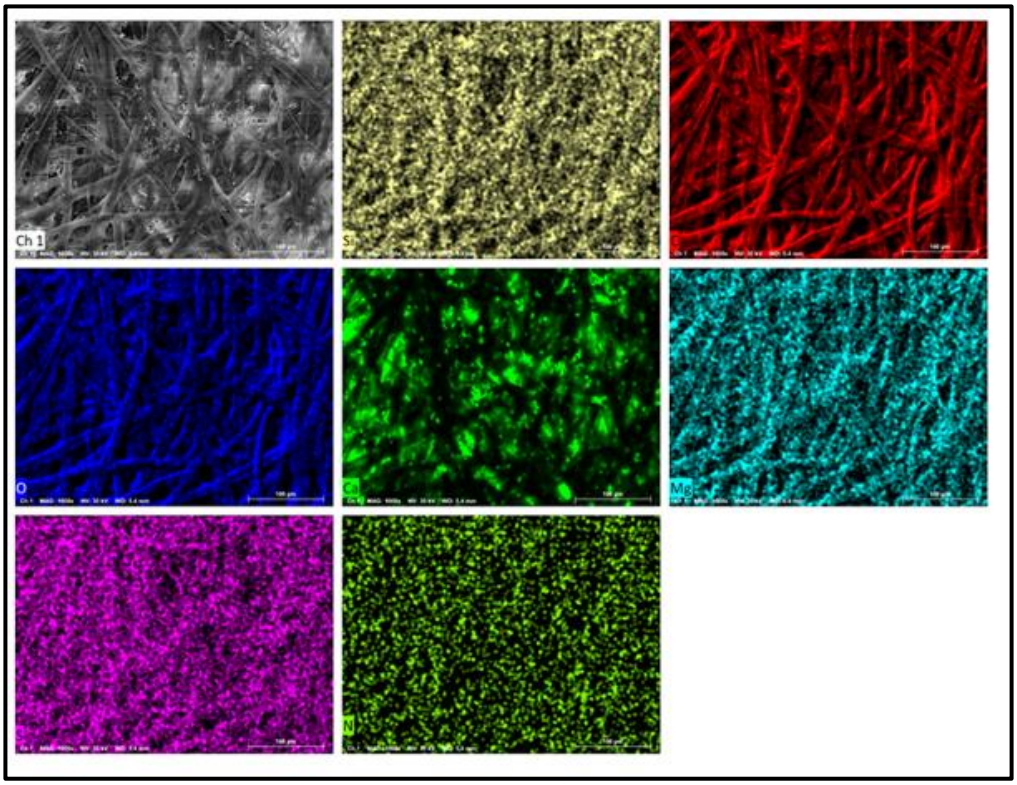


Figure 4.12 Lamy Ink Mapping.

4.7.8 Comparative Discussion and Forensic Implications

Comparative analysis of FESEM morphology (figure), EDX spectra and elemental mapping (figure) highlights clear differences in ink deposition behaviour and elemental distribution among the fountain pen inks. Pelikan ink exhibits the most pronounced aggregation and non-uniform elemental distribution, while Pilot and Lamy inks show more homogeneous dispersion.

These observations correlate well with findings from TLC, UV-Vis, POM, GC-MS and ATR-FTIR analyses. The combined use of FESEM-EDX and elemental mapping, therefore, enhances the discriminatory power of the analytical approach and

provides valuable supplementary information for forensic ink examination (Christie & Abel, 2021).

4.8 Electrochemical Analysis of Fountain Pen Ink Samples using Screen-Printed Carbon Electrode (SPCE)

4.8.1 Application of Cyclic Voltammetry in Ink Analysis

Cyclic Voltammetry (CV) using a screen-printed carbon electrode (SPCE) was employed to investigate the electrochemical behaviour of fountain pen ink samples from Pilot, Pelikan and Lamy brands. Electrochemical techniques such as CV are widely used to study redox-active species in complex matrices, as they provide information on oxidation-reduction processes, electron transfer behaviour and electrochemical stability of organic compounds (Kahlert, 2026; Ortiz Ortega et al., 2022).

In the context of ink analysis, CV is particularly useful for detecting electroactive components such as dyes, phenolic antioxidants and degradation products. These compounds may undergo oxidation or reduction at characteristic potentials, allowing comparison between ink formulations and assessment of potential ageing behaviour (Ortiz-Herrero et al., 2020). In this study, SPCE was selected due to its low cost, ease of use and suitability for small volumes, making it attractive for forensic and screening applications.

4.8.2 Cyclic Voltammetry Profiles of Fountain Pen Ink Samples

The cyclic voltammograms obtained for Pilot, Pelikan and Lamy ink samples are presented in Figure 4.13, together with a blank electrolyte (0.1 M KCl) as control.

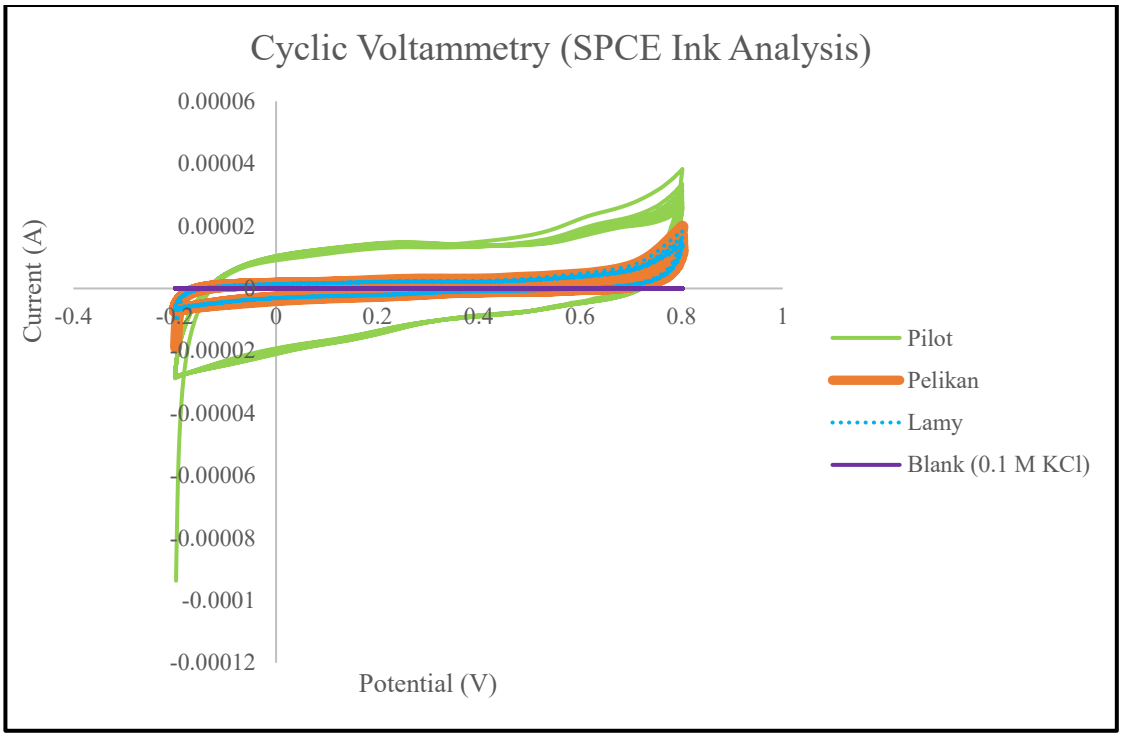


Figure 4.13 Cyclic Voltammograms of Fountain Pen Ink Samples.

The blank electrolyte exhibited a relatively flat voltammogram with no prominent redox peaks, confirming that the observed electrochemical responses in the ink samples arise from electroactive ink components rather than the supporting electrolyte.

All ink samples displayed measurable anodic and cathodic currents within the applied potential window, indicating the presence of electrochemically active species. However, differences in current magnitude, peak shape and overall voltametric profiles were observed among the ink brands, reflecting variation in ink composition and electrochemical behaviour.

In this study, the cyclic voltammetry analysis was conducted within a potential window of −0.2 to +0.6 V. This potential range was selected to observe the redox behaviour of electroactive ink components while maintaining a stable electrolyte background. Within this window, the blank KCl electrolyte showed no prominent

faradaic peaks, indicating that the observed current responses were mainly contributed by the ink components rather than the supporting electrolyte.

The CV analysis provides electrochemical values in the form of current response and oxidation behaviour within the selected potential window. Although no sharp single redox peak was observed, the inks displayed different voltammetric profiles, indicating differences in electroactive dye or additive components. Pilot ink showed the strongest current response and earlier oxidation behaviour, suggesting a higher level of electroactive components or more favourable electron transfer at the electrode surface. Lamy ink showed an intermediate response, while Pelikan ink produced the lowest overall current response. Therefore, the CV analysis provides a complementary electrochemical fingerprint for differentiating the fountain pen inks rather than serving as a direct ink ageing value.

4.8.3 Electrochemical Behaviour of Pilot Fountain Pen Ink

The Pilot ink exhibited the highest overall current response among the three samples. A pronounced cathodic current was observed at negative potentials, followed by a gradual increase in anodic current towards positive potentials. This behaviour suggests the presence of electroactive species capable of undergoing both reduction and oxidation processes within the scanned potential range.

The relatively high current magnitude indicates a greater concentration of redox-active components or more favourable electron transfer kinetics at the electrode surface. This observation may be associated with the presence of phenolic compounds and dye molecules identified in GC-MS analysis, such as 2,4-di-tert-butylphenol, which are known to exhibit electrochemical activity due to their aromatic and phenolic functional groups (Prasain et al., 2012).

The broader and less sharply defined peaks observed for Pilot ink suggest overlapping redox processes from multiple electroactive species, consistent with the TLC results that revealed multiple dye components in this ink.

4.8.4 Electrochemical Behaviour of Pelikan Fountain Pen Ink

The Pelikan ink displayed a lower overall current response compared to Pilot ink. The voltammogram shows a smoother profile with less pronounced peaks, indicating weaker or less concentrated electroactive species.

This reduced electrochemical activity may be attributed to differences in ink formulation, such as lower concentrations of redox-active dyes or antioxidants. The GC-MS analysis indicated the presence of phenolic antioxidants in Pelikan ink at lower relative abundance compared to Lamy and Pilot inks, which may contribute to the reduced current response observed in the CV profile (Zabik et al., 2016).

In addition, the more uniform voltammogram shape suggests that the electrochemical processes in Pelikan ink may be dominated by fewer electroactive species or slower electron transfer kinetics compare to Pilot and Lamy inks. This behaviour aligns with the POM and FESEM observations, which indicated stronger aggregation and non-uniform deposition, potentially limiting effective interaction between electroactive components and the electrode surface.

4.8.5 Electrochemical Behaviour of Lamy Fountain Pen Ink

The Lamy ink exhibited an intermediate electrochemical response between Pilot and Pelikan inks. The voltammogram shows distinct current changes at higher positive potentials, indicating oxidation processes likely associated with organic ink components.

Although the overall current magnitude was lower than that of Pilot ink, the Lamy ink demonstrated a relatively stable and reproducible voltametric profile. This behaviour may be related to the presence of stabilising additives identified through GC-MS and FTIR analyses, such as siloxane-based compounds, which may influence ink dispersion and electrode interaction.

Furthermore, the presence of phenolic antioxidants at high relative abundance in Lamy ink, as observed in the GC-MS results, may contribute to its electrochemical activity, as phenolic compounds are known to undergo oxidation reactions at carbon electrodes (Giuliani et al., 2016; Sharif, Jalees, et al., 2022).

4.8.6 Comparative Discussion of Electrochemical Responses

A comparative evaluation of the cyclic voltammograms reveals clear differences in electrochemical behaviour among the fountain pen inks. The magnitude of the electrochemical response follows the general trend:

Pilot > Lamy > Pelikan

This trend suggests variation in the concentration and nature of electroactive species present in the inks. Inks containing higher levels of redox-active dyes or phenolic antioxidants are expected to exhibit stronger current responses, as observed for Pilot and Lamy inks.

The absence of sharp, well-defined redox peaks in all samples indicates that the electrochemical behaviour likely arises from multiple overlapping redox processes rather than a single dominant electroactive compound. This is consistent with the complex formulation of commercial fountain pen inks, which typically contain mixtures of dyes, additives and stabilisers (Li et al., 2025).

Therefore, the electrochemical value of the CV analysis lies in its ability to compare oxidation behaviour, current magnitude and overall voltammetric profiles within a fixed potential window. These parameters provide an additional redox-based signature that complements the chemical, spectroscopic and morphological findings. However, because this study was conducted at a single baseline time point, the CV response should be interpreted as a baseline electrochemical fingerprint and not as a direct measurement of ink age.

4.8.7 Implications for Ink Stability

Redox-active compounds, particularly phenolic antioxidants, can contribute to resistance against oxidative degradation and are therefore relevant to ink stability considerations. In this study, differences in current response and voltammetric profiles among the inks reflect differences in the presence and/or concentration of redox-active dyes and stabilising additives. These electrochemical responses should be interpreted as baseline signatures rather than direct evidence of ageing because only a single time point was measured.

Nevertheless, inks showing lower electrochemical response may have lower baseline levels of redox-active stabilisers, which could potentially be associated with reduced resistance to oxidation under environmental exposure. Controlled ageing experiments with repeated CV measurements over time are required to validate whether the baseline electrochemical behaviour predicts ageing-related chemical or colour changes (Navashree & Parthasarathy, 2023).

4.8.8 Forensic Relevance of SPCE-Based CV Analysis

From a forensic perspective, SPCE-based CV analysis offers a rapid and minimally invasive approach for differentiating fountain pen inks based on their electrochemical signatures. While CV alone may not uniquely identify individual ink formulations, it provides complementary information that enhances discrimination when combined with TLC, UV-Vis, GC-MS, ATR-FTIR, POM and FESEM-EDX analyses.

Differences in current magnitude, voltammogram shape and oxidation behaviour can serve as additional markers for ink comparison, particularly in questioned document examinations where sample quantity is limited (Ortiz Ortega et al., 2022; Vaseem et al., 2012).

4.9 Comparative Interpretation of Analytical Findings

The integration of chromatographic, spectroscopic, morphological and electrochemical analyses provides a comprehensive understanding of the compositional differences among the fountain pen inks studied. While each technique produces independent data, combining these results strengthens the reliability of ink differentiation and offers a multidimensional perspective that is particularly valuable for forensic purposes.

Thin-layer chromatography (TLC) revealed separation patterns consistent with compositional profiles from gas chromatography–mass spectrometry (GC–MS). Variations in band number and R_f values corresponded to differences in volatile and semi-volatile compounds detected at retention times around 12.9–13.3 minutes. Although certain phenolic derivatives appeared in all samples, differences in peak

intensity in GC–MS chromatograms matched variations in TLC band intensity, reflecting differences in relative dye or additive concentrations.

ATR–FTIR and UV–Vis spectroscopy provided complementary insights. Functional groups identified through infrared absorption, particularly aromatic C=C and C–O vibrations, are associated with chromophores responsible for visible light absorption. Variations in FTIR absorbance were reflected in UV–Vis spectra through differences in λ_{max} values and peak absorbance, suggesting that minor structural or substituent differences influence the electronic behaviour of the inks.

Morphological observations under polarised optical microscopy (POM) and field emission scanning electron microscopy (FESEM) supported these chemical findings. Differences in ink penetration and interaction with paper fibres aligned with variations in solvent composition and additive content identified by GC–MS. Inks with higher concentrations of certain volatile components showed altered spreading, indicating that formulation differences affect both chemical and physical properties.

Electrochemical analysis via cyclic voltammetry further confirmed these differences. Variations in oxidation peak current and potential corresponded to the presence of redox-active compounds detected in chromatographic and spectroscopic analyses. The consistency of findings across these multiple platforms demonstrates that a combined analytical approach is robust and reliable for forensic ink comparison, enabling both chemical and physical differentiation with higher confidence.

CHAPTER 5
CONCLUSION

5.1 Conclusion

This study successfully evaluated the chemical composition, morphological characteristics and electrochemical behaviour of three commercial fountain pen inks, namely Pilot, Pelikan and Lamy, using complementary analytical techniques.

Thin-Layer Chromatography (TLC) analysis demonstrated distinct separation profiles for all three ink brands. The developed chromatograms produced clearly differentiated bands with reproducible R_f values, confirming variations in dye composition. Although certain components exhibited comparable migration behaviour, differences in band intensity and number of resolved spots enabled discrimination between brands.

Gas Chromatography–Mass Spectrometry (GC-MS) analysis revealed the presence of phenolic derivatives within the retention time region of approximately 12.9–13.3 minutes. Compounds such as 2,4-di-tert-butylphenol and substituted phenol derivatives were consistently detected across samples; however, their relative peak intensities varied among Pilot, Pelikan and Lamy inks. These variations indicate compositional differences in additives and stabilising agents, providing molecular-level markers suitable for comparative ink profiling.

ATR-FTIR spectra recorded in the mid-infrared region (4000–400 cm^{-1}) confirmed the presence of characteristic functional groups, including aromatic C=C stretching, O–H stretching and C–O vibrations. While the general spectral profiles showed similarities due to shared dye structures, measurable differences in absorbance intensity and peak sharpness were observed between brands. These spectral variations reflect differences in formulation and relative functional group concentration.

UV-Visible spectroscopic analysis further supported ink differentiation. Each ink exhibited a characteristic absorption maximum (λ_{max}) associated with its chromophoric system. Variations in peak position and absorbance intensity indicate differences in dye composition and electronic transition behaviour, thereby providing optical signatures for brand comparison.

Morphological examination using Polarized Optical Microscopy (POM) revealed differences in ink penetration depth, fibre interaction and surface distribution patterns on the paper substrate. FESEM analysis confirmed microstructural variations in ink film formation and surface texture. Elemental analysis via EDX detected differences in inorganic constituents, contributing additional discriminatory parameters between samples.

Electrochemical characterisation using cyclic voltammetry demonstrated distinct oxidation–reduction responses for each ink when analysed using SPCE in 0.1 M KCl electrolyte. Differences in peak current magnitude and oxidation potential suggest variation in redox-active species present within the ink formulations. These findings confirm that electrochemical profiling provides measurable parameters relevant for comparative analysis.

Overall, the results obtained from chromatographic, spectroscopic, morphological and electrochemical analyses consistently demonstrate that Pilot, Pelikan and Lamy fountain pen inks possess distinguishable chemical and physical characteristics. The integration of these techniques provides a comprehensive analytical framework for ink differentiation and supports their applicability in forensic document examination.

5.2 Recommendations for Future Work

Although this study successfully established baseline discrimination of three selected fountain pen inks using a multi-technique approach, several limitations were identified throughout the experimental process. These limitations provide important direction for future research, particularly in strengthening the applicability of ink profiling for ageing purposes.

Firstly, the present study focused only on freshly deposited ink samples. As such, the findings represent compositional differentiation at a single time point rather than progressive ageing behaviour. Future studies should therefore incorporate structured time-series monitoring to evaluate whether the analytical parameters observed in this study exhibit measurable temporal variation. For example, selected chemical markers identified through GC–MS and electrochemical profiles obtained from SPCE analysis may be re-examined at defined ageing intervals such as 1 month, 3 months, 6 months and 12 months. Observing whether these parameters change consistently over time would provide stronger support for any ageing-related inference.

During experimentation, it was also observed that environmental exposure may influence ink behaviour, particularly in terms of colour intensity and surface interaction with paper fibres. However, these factors were not systematically controlled in the present work. Future research should consider conducting controlled environmental simulations, including regulated temperature, humidity and light exposure conditions. Such an approach would allow differentiation between natural degradation and environmentally induced variation. Comparison between natural ageing and accelerated ageing conditions may also assist in determining whether predictive degradation trends can be modelled.

Another limitation of this study lies in sample diversity. Only three black fountain pen inks were examined. While sufficient for baseline discrimination, broader inclusion of additional brands, pigment-based fountain pen inks and coloured formulations would improve generalisability. It is possible that different dye classes or additive systems may exhibit distinct stability characteristics, which could influence both chemical and electrochemical behaviour. Expanding the sample pool would therefore strengthen the robustness of comparative interpretation.

From an analytical perspective, the integration of multi-technique data in this study was primarily qualitative. Although clear differentiation was achieved, future

work may benefit from incorporating chemometric analysis to enhance statistical confidence. Application of multivariate tools such as Principal Component Analysis (PCA) could assist in identifying clustering behaviour and subtle inter-brand variation that may not be visually apparent. Statistical modelling may also improve defensibility in forensic reporting contexts.

Additionally, validation parameters such as repeatability and inter-day precision were not extensively evaluated in the present study. For practical forensic implementation, systematic validation studies should be conducted to assess measurement reliability and reproducibility. Establishing uncertainty ranges and identifying potential analytical variability would ensure that reported conclusions remain scientifically responsible.

Finally, consideration should be given to the development of a structured interpretative framework for fountain pen ink ageing. While this study demonstrates the feasibility of multi-technique discrimination, translation into courtroom-applicable evidence requires careful evaluation of limitations, uncertainty and reporting standards. Future research integrating ageing kinetics, environmental modelling and statistical validation may contribute toward the eventual establishment of a more standardised comparative ink ageing methodology.

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APPENDICES

APPENDIX 1

Table of Instrumental Parameters and Experimental Conditions

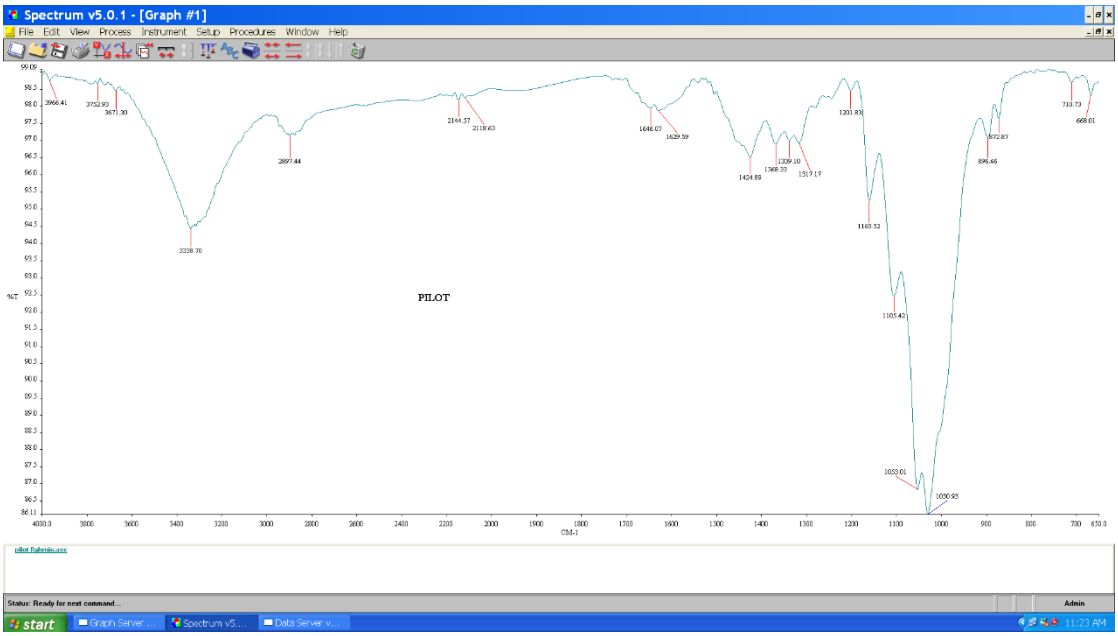
Technique	Parameter	Condition / Setting
TLC	Stationary phase	Silica gel 60 F_{254}
	Mobile phase	Butanol : Acetic acid : Water
	Development distance	2.8 cm
GC-MS	Injection mode	Splitless
	Carrier gas	Helium
	Flow rate	1.0 mL/min
	Injection volume	1.0 µL
	Ionisation mode	El (70 eV)
ATR-FTIR	Spectral range	4000 – 650 cm^{-1}
	Resolution	8 cm^{-1}
	Number of scans	4
UV-Vis	Wavelength range	200 – 800 nm
	Scan mode	Absorbance
POM	Magnification	10x
FESEM-EDX	Accelerating voltage	5 – 15 kV
	Working distance	8 – 10 mm
	Magnification	200x, 2000x
SPCE-CV	Electrode type	1.0 M KCl
	Potential window	-0.2 to + 0.6 V
	Scan rate	0.02 V/s

APPENDIX 2

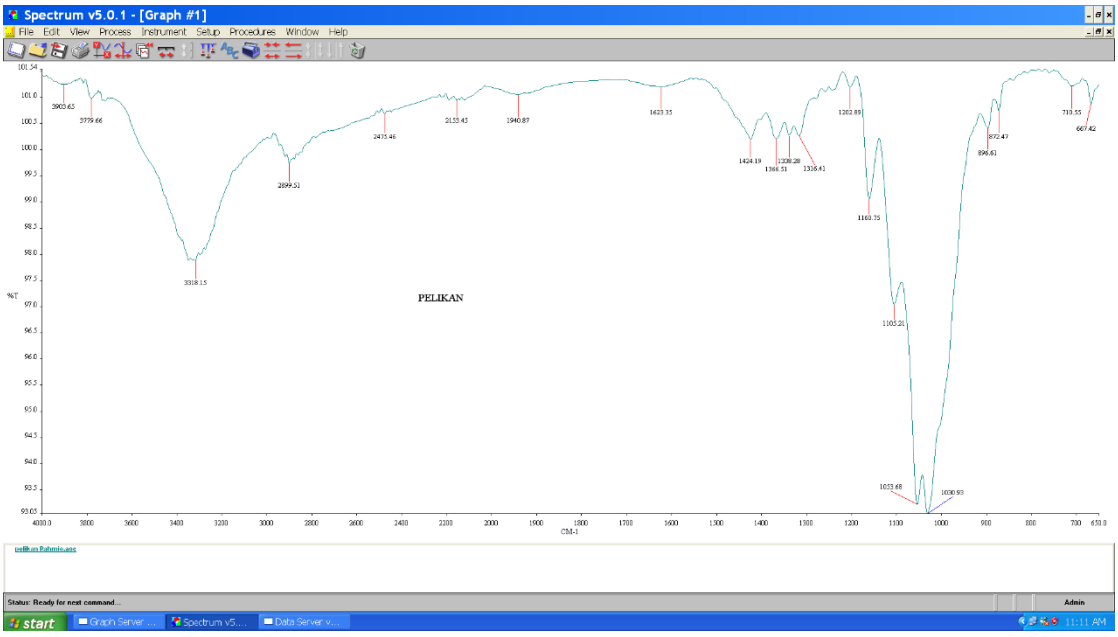
Supplementary Spectral and Electrochemical Data

i) Full ATR-FTIR Spectra of Fountain Pen Ink Samples

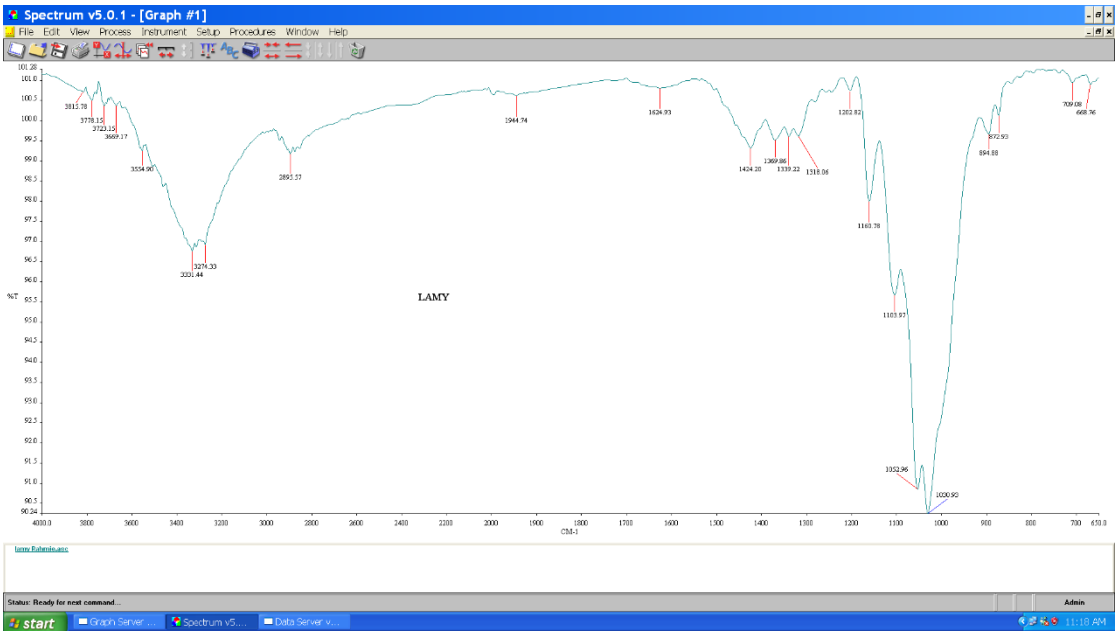
PILOT



PELIKAN

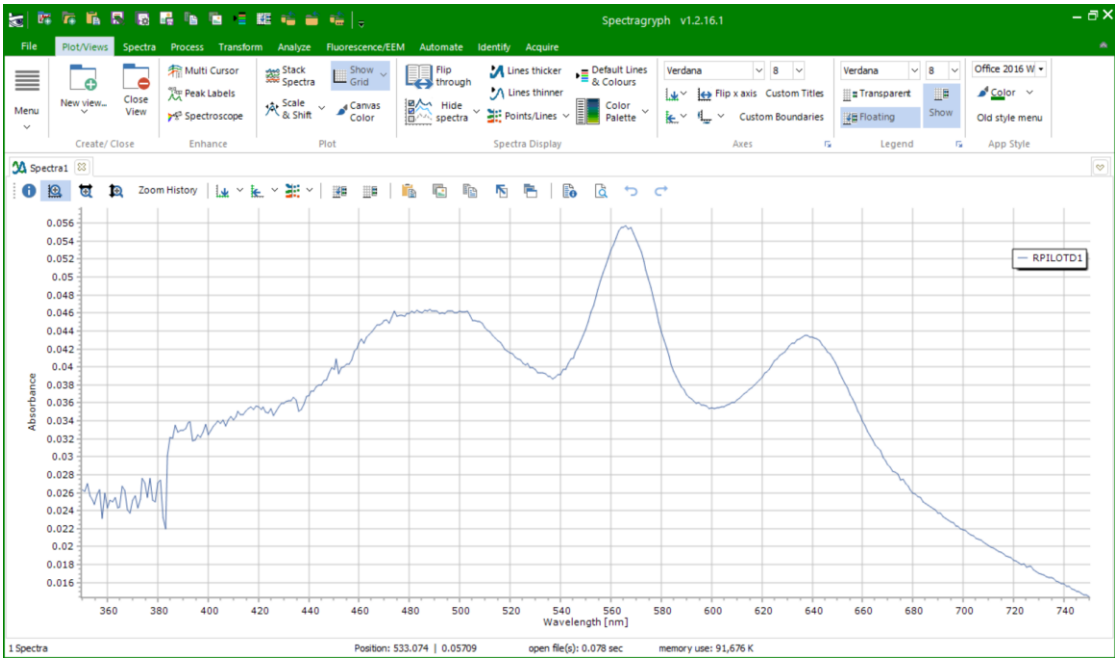


LAMY


Spectrum v5.0.1 - [Graph #1]
File Edit View Process Instrument Setup Procedures Window Help
LAMY
%T
CM-1
Status: Ready for next command...
Admin
start
Graph Server ...
Spectrum v5...
Data Server v...
11:18 AM

ii) UV-Vis Absorption Spectra of Fountain Pen Ink Samples

PILOT



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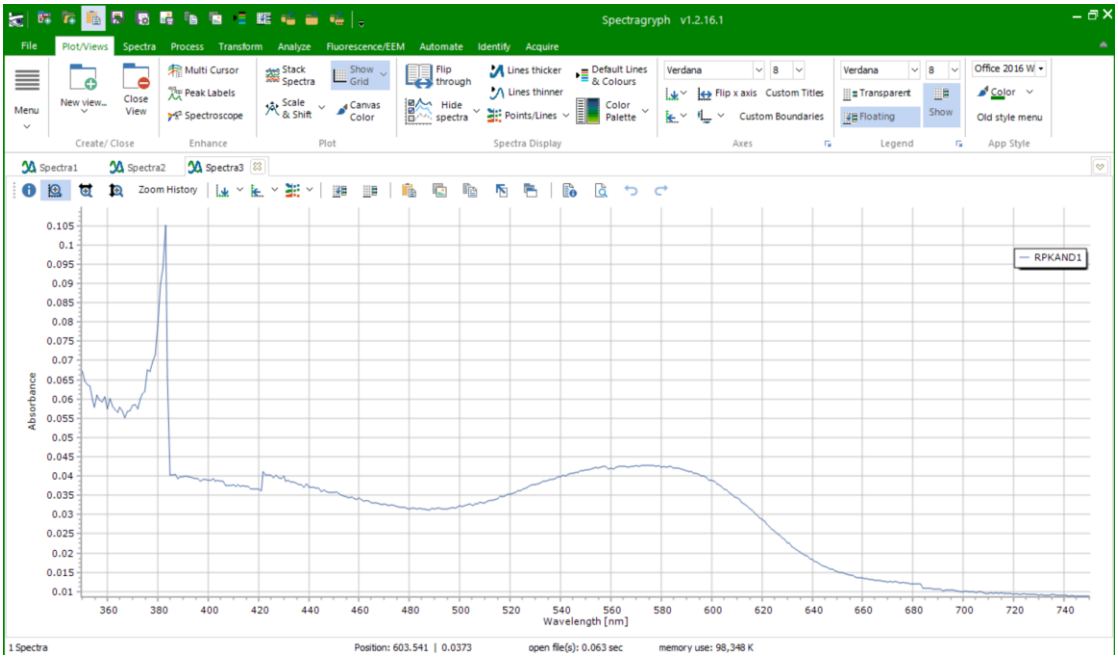

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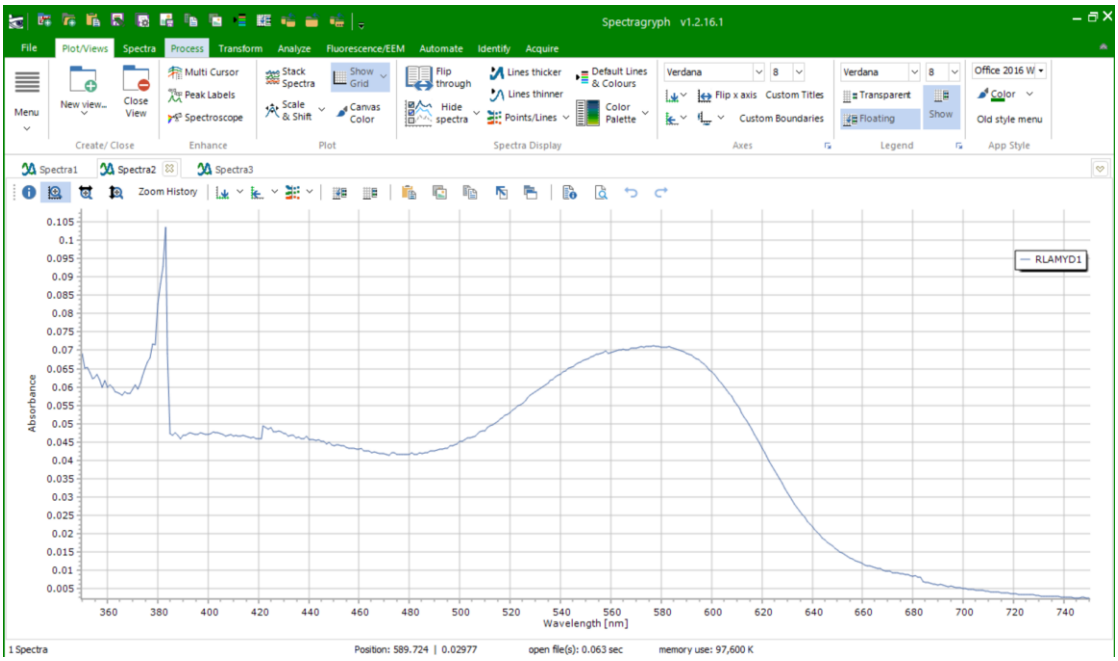
Spectragryph v1.2.16.1
File
Plot/Views
Spectra
Process
Transform
Analyze
Fluorescence/EEM
Automate
Identify
Acquire
Menu
New view...
Close View
Multi Cursor
Peak Labels
Spectroscope
Stack Spectra
Show Grid
Scale & Shift
Canvas Color
Flip through
Hide spectra
Lines thicker
Lines thinner
Points/Lines
Default Lines & Colours
Color Palette
Verdana
Flip x axis
Custom Titles
Custom Boundaries
Transparent
Floating
Show
Office 2016 W
Color
Old style menu
Create/ Close
Enhance
Plot
Spectra Display
Axes
Legend
App Style
Spectra1
Spectra2
Spectra3
Zoom History
RLAMYD1
Absorbance
Wavelength [nm]
1 Spectra
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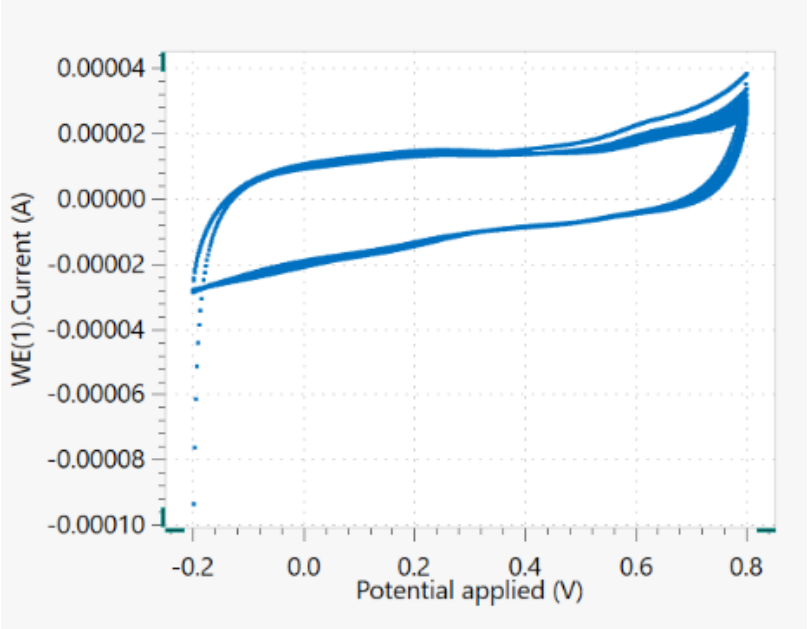
iii) Cyclic Voltammograms Obtained for Fountain Pen Ink Samples

PILOT



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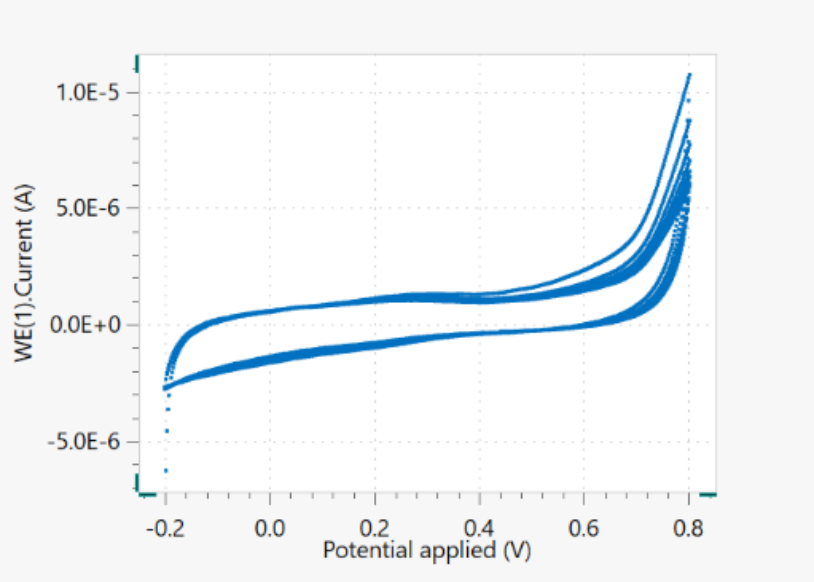

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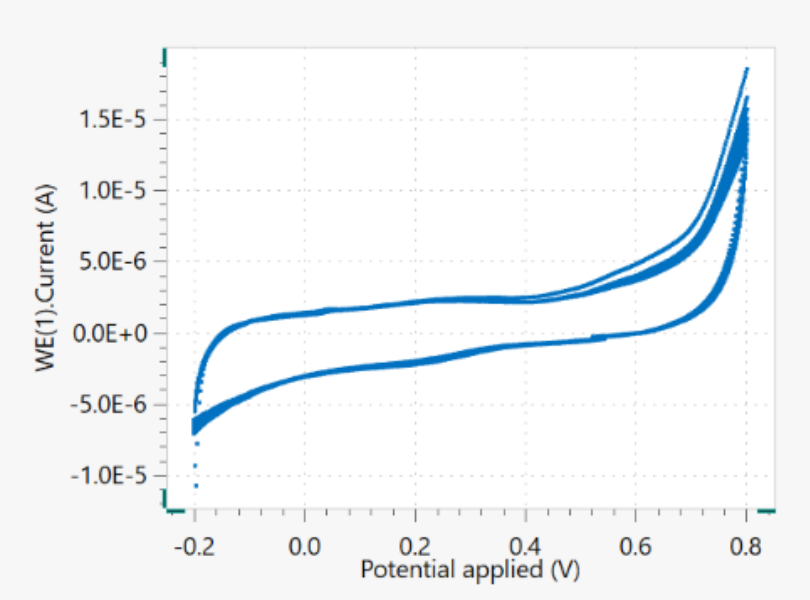
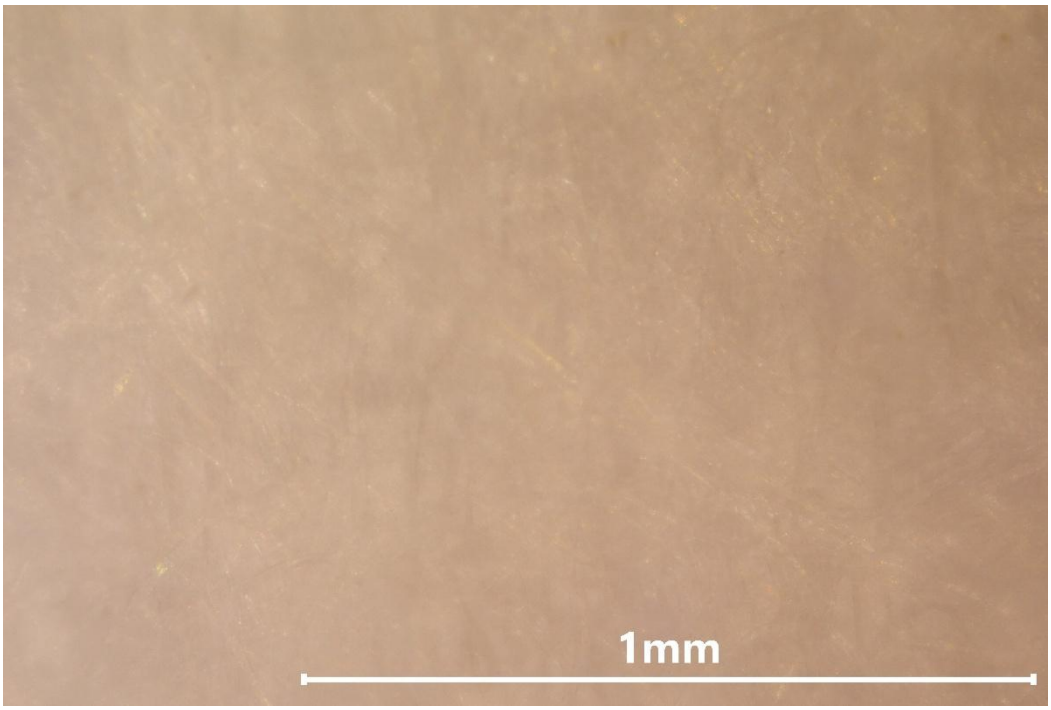

1.5E-5
1.0E-5
5.0E-6
0.0E+0
-5.0E-6
-1.0E-5
WE(1).Current (A)
-0.2
0.0
0.2
0.4
0.6
0.8
Potential applied (V)

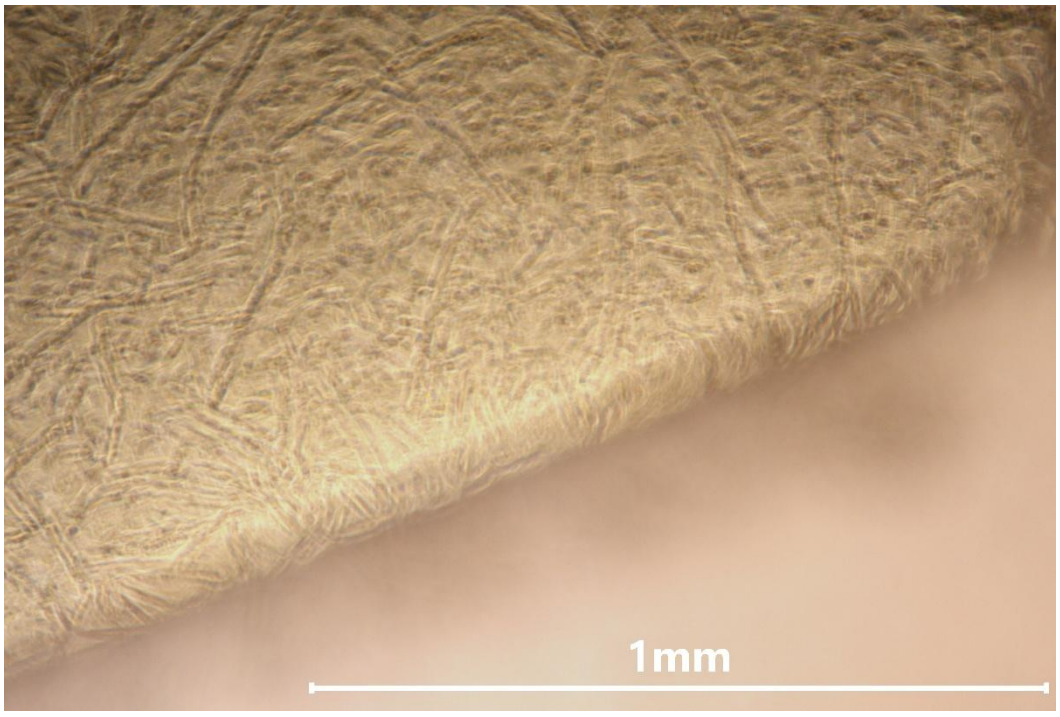
APPENDIX 3

POM Image for Paper Substrate

CENTRE



EDGE



APPENDIX 4

Elemental Composition of Fountain Pen Ink Samples Obtained from EDX Analysis at 1000x

Element	Pilot	Pelikan	Lamy	Possible Origin
C	65.36	63.64	63.37	Organic dyes / binders
O	29.99	32.66	32.91	Paper fibres / organics
Ca	3.45	3.6	3.61	Paper filler ($CaCO_3$)
Si	0.07	0.04	0.06	Ink additive / siloxane

AUTHOR'S PROFILE

Nur Syazwani Rahmie Binti Rahman obtained her Diploma in Science from Universiti Teknologi MARA (UiTM), Kampus Kota Kinabalu, Sabah, in 2022, followed by a Bachelor of Science (Hons.) in Chemistry (Forensic Analysis) from Universiti Teknologi MARA (UiTM), Shah Alam, completed in 2025. She is currently pursuing a Master of Applied Chemistry, focusing on forensic ink analysis and ink ageing detection. Her master's research, entitled *"Multi-Technique Profiling of Fountain Pen Inks on Paper"*, focuses on the baseline characterisation and comparative profiling of fountain pen inks through the integration of chromatographic, spectroscopic, microscopic, elemental, and electrochemical techniques. She is a Graduate Research Assistant (GRA) under the grant 600-UiTMSEL (PI. 5/4/11) (031/2025) and has also served as a UiTM Postgraduate Teaching Assistant (UPTA) from 2024 to 2025. Her research interests include forensic chemistry, forensic document examination, and the application of combined analytical techniques for reliable forensic interpretation.

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Rahman, N. S. R. B., Hashim, N. Z. N., Hamid, F. H. B., Hanibah, H., & Samsi, N. S. (2025). Corrosion Inhibition of Mild Steel in 1.0 M HCl Solution by Amine Derivatives. *Asian Journal of Chemistry*, *37*(4), 909–917. https://doi.org/10.14233/AJCHEM.2025.33376

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LIST OF CONFERENCES

Title : International Conference of Applied Sciences and Education (i-CASE 2025) in Conjuction with 13th International Postgraduate Conference on Science and Mathematics (IPCSM 2025)

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

Date : 12 – 14 December 2025

Organizer : Universiti Pendidikan Sultan Idris (UPSI)

Venue : Universiti Pendidikan Sultan Idris (UPSI), Tanjong Malim, Perak, Malaysia

Title : Mini Conference for Post Graduate, Mobility Programme Between Universiti Teknologi MARA (UiTM) and Universitas Negeri Malang (UM)

Paper : Forensic Multi-Technique Profiling of Fountain Pen Inks on Paper

Date : 19 – 26 Mei 2026

Organizer : Engineering Faculty of Universitas Negeri Malang (UM)

Venue : Universitas Negeri Malang (UM), Indonesia

LIST OF INNOVATION COMPETITIONS

Invention, Innovation & Design Exposition (iidex)

Project: Tracing Signatures: Innovative Forensic Characterization of Black Fountain Pen Inks

Date : 28 – 30 October 2025

Organizer : Department of Research and Innovation, Universiti Teknologi MARA

Venue : Dewan Agung Tuanku Canselor (DATC), Universiti Teknologi MARA (UiTM), Shah Alam, Selangor, Malaysia

The 15th International Invention, Innovation & Design Competition (INDES)

Project: Gearbox Freshness

Date : 14 Mei 2026

Organizer : Universiti Teknologi MARA, Perak Branch

Venue : Dewan Ibn Al-Khatib, UiTM Cawangan Perak (Seri Iskandar)

LIST OF AWARDS

Bronze Award in Invention, Innovation & Design Exposition (iidex) with project title of Tracing Signatures: Innovative Forensic Characterization of Black Fountain Pen Inks

Best Oral Presenter in International Conference of Applied Sciences and Education (i-CASE 2025) in Conjuction with 13th International Postgraduate Conference on Science and Mathematics (IPCSM 2025) with paper title of Ink Matters: Comparative Analysis of Black Fountain Pen Inks from Three Popular Brands

Gold Medal in The 15th International Invention, Innovation & Design Competition (INDES) 2026