

**CHEMICAL PROFILING OF ERASABLE AND NON-ERASABLE BLACK
GEL PEN INKS USING ATR-FTIR SPECTROSCOPY AND CHEMOMETRICS
TECHNIQUES**

CHEE JIA INN

**SCHOOL OF HEALTH SCIENCES
UNIVERSITI SAINS MALAYSIA**

2026

**CHEMICAL PROFILING OF ERASABLE AND NON-ERASABLE BLACK
GEL PEN INKS USING ATR-FTIR SPECTROSCOPY AND
CHEMOMETRICS TECHNIQUES**

By

CHEE JIA INN

**Dissertation submitted in partial fulfilment of the requirements for the degree
of Bachelor of Science (Honours) (Forensic Science)**

FEBRUARY 2026

CERTIFICATE

This is to certify that the dissertation entitled “Chemical Profiling Of Erasable And Non-Erasable Black Gel Pen Inks Using ATR-FTIR Spectroscopy And Chemometrics Techniques” is the bona fide record of research work done by Ms. Chee Jia Inn during the period from October 2025 to February 2026 under my supervision. I have read this dissertation and that in my opinion it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation to be submitted in partial fulfillment for the degree of Bachelor of Science (Honours) (Forensic Science).

Main supervisor,

.....

Dr Dzulkiflee bin Ismail

Lecturer

School of Health Sciences

Universiti Sains Malaysia

Health Campus

16150 Kubang Kerian

Kelantan, Malaysia

Date:

DECLARATION

I hereby declare that this dissertation is the result of my own investigation, except where otherwise stated and duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degrees in Universiti Sains Malaysia or other institutions. I grant Universiti Sains Malaysia the right to use the dissertation for teaching, research and promotional purposes.

.....

Chee Jia Inn

Date:

ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my supervisor, ChM Dr. Dzulkiflee Ismail, for his invaluable guidance, encouragement, and constructive feedback throughout this research. His expertise and patience have been instrumental in shaping both my understanding and approach to this project. I am also thankful to the staff of the Forensic Science Programme, Universiti Sains Malaysia, for providing access to the necessary facilities, equipment, and resources that enabled the successful completion of the experimental work. Their support made it possible to conduct the ATR-FTIR analyses and other practical components of this project efficiently. Special thanks to Mohamad Amirul Hakim Bin Mohd Salimi, a fellow student under the supervision of ChM Dr. Dzulkiflee Ismail, who kindly volunteered as my second participant during sample preparation, which greatly assisted in completing my project in ensuring the reproducibility and completeness of the data. I also wish to thank my lab mates and friends for their assistance, guidance, and moral support throughout the experimental work and data collection process. Their encouragement helped me stay motivated during challenging moments in the laboratory. Finally, I would like to extend my heartfelt appreciation to my family for their unwavering support, patience, and understanding throughout my undergraduate studies and research journey. Their constant encouragement has been a source of strength and motivation during the completion of this project. Completing this research has been a challenging yet rewarding experience, and I am grateful for the personal growth and knowledge I have gained through this process.

TABLE OF CONTENTS

AKNOWLEDGEMENT	v
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF SYMBOLS	x
LIST OF ABBREVIATIONS	xi
ABSTRAK	xii
ABSTRACT	xiv
CHAPTER 1 : INTRODUCTION	1
1.1 Introduction/Background of Study	1
1.2 Problem Statement	3
1.3 Objective of Study	4
1.3.1 General Objective	4
1.3.2 Specific Objective	5
1.4 Significance of Study	5
CHAPTER 2 : LITERATURE REVIEW	7
2.1 Introduction	7
2.2 Composition of Writing Pens	8
2.2.1. Gel Pen Inks	8
2.2.2 Erasable Gel Pen Inks	9
2.3 Dissolution Test	11
2.4 Analytical Method	12
2.5 Chemometrics Techniques	14
2.5.1 Data Pre-processing Techniques	15
2.5.2 Unsupervised Exploratory Analysis	16
2.5.3 Supervised Classification and Predictive Modeling	17
CHAPTER 3 : METHODOLOGY	19
3.1 Research Design	19
3.1.1 Study Scope	19
3.1.2 Sampling Method	19
3.2 Sample Collection and Preparation	20
3.2.1 Data Collection	22

3.2.2 Dissolution Test	23
3.3 Statistical Analysis	24
3.3.1 Repeatability and Reproducibility	24
3.3.2 Data Preprocessing and Analysis	24
3.2.3 Principal Component Analysis.....	25
3.2.4 Linear Discriminant Analysis	26
CHAPTER 4 : RESULTS AND DISCUSSION	27
4.1 Repeatability and Reproducibility	27
4.2 Infrared (IR) Spectral Acquisition	29
4.3 Dissolution Test	34
4.4 Principal Component Analysis	35
4.5 Linear Discriminant Analysis	39
CHAPTER 5: CONCLUSION AND FUTURE RECOMMENDATIONS	42
5.1 Conclusion	42
5.2 Limitation of the Study	43
5.3 Future Recommendations	44
REFERENCES.....	46

LIST OF TABLES

Table 1: Pen ink sample information (brands, ink types, models, and codes)	22
Table 2: IR Absorption Band and its Assignment	33
Table 3: Visual assessment of dissolution behaviour of erasable (A–J) and non-erasable (K–T) gel pen ink samples in selected organic solvents	35
Table 4: Wilks' Lambda table from Linear Discriminant Analysis.....	40
Table 5: Classification table generated from normalized dataset of black gel ink sample	41

LIST OF FIGURES

Figure 1: ATR-FTIR spectra of seven replicates from the fifth pen, coded J	29
Figure 2: ATR-FTIR spectra of ink from seven pens coded H	30
Figure 3: FTIR spectra of erasable black gel pen ink spectrum.....	31
Figure 4: FTIR spectra of non-erasable black gel pen ink spectrum	31
Figure 5: PCA score plot of the normalized dataset for black gel pen ink samples.....	38

LIST OF SYMBOLS

cm^{-1}	Square Centimeter
O-H	Hydroxyl Bond
C-H	Carbon-Hydrogen Bond
C=O	Carbon–Oxygen Double Bond
N=N	Nitrogen-Nitrogen Double Bond
C-O	Carbon–Oxygen Single Bond
Ar–O	Aromatic Ether Group
%	Percentage

LIST OF ABBREVIATIONS

ATR-FTIR	Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy
UV-Vis	Ultraviolet-Visible Spectroscopy
TLC	Thin Layer Chromatography
HPTLC	High-Performance Thin Layer Chromatography
HPLC	High-Performance Liquid Chromatography
PCA	Principal Component Analysis
LDA	Linear Discriminant Analysis
IR	Infrared
SNV	Standard Normal Variate
AHC	Agglomerative Hierarchical Clustering
T-SNE	T-Distributed Stochastic Neighbor Embedding
UMAP	Uniform Manifold Approximation and Projection
PLS-DA	Partial Least Squares Discriminant Analysis
USM	Universiti Sains Malaysia
LN-MCT	Liquid Nitrogen Cooled Mercury Cadmium Telluride
RSD	Relative Standard Deviation
PCs	Principal Components
IBM SPSS	IBM Statistical Package for The Social Science
DP	Discrimination Power
EtOH	Ethanol
MeOH	Methanol
HOAc	Acetic Acid
DCM	Dichloromethane

CHEMICAL PROFILING OF ERASABLE AND NON-ERASABLE BLACK GEL PEN INKS USING ATR-FTIR SPECTROSCOPY AND CHEMOMETRICS TECHNIQUES

ABSTRAK

Analisis dakwat merupakan komponen penting dalam pemeriksaan dokumen, yang membantu pakar dokumen forensik mengesan perubahan fizikal atau kimia, pemalsuan, atau manipulasi dokumen, khususnya dalam kes melibatkan pemalsuan, pengesahan, atau kesalahan lain berkaitan bukti bertulis dan bercetak. Pen gel lazim ditemui dalam dokumen yang dipertikai, dan pembezaan antara dakwat gel boleh padam dan tidak boleh padam adalah penting dari sudut forensik. Objektif kajian ini adalah untuk memprofil dan membezakan secara kimia 10 jenama dakwat pen gel hitam boleh padam dan 10 jenama dakwat pen gel hitam tidak boleh padam menggunakan spektroskopi ATR-FTIR yang digabungkan dengan analisis kemometrik. Sampel dakwat daripada pen gel boleh padam dan tidak boleh padam dianalisis terlebih dahulu menggunakan ATR-FTIR dalam julat nombor gelombang 4000 cm^{-1} hingga 600 cm^{-1} . Rantau cap jari spektrum, iaitu antara 1200 cm^{-1} hingga 600 cm^{-1} , kemudiannya diproses menggunakan Analisis Komponen Principal (PCA) untuk pengecaman corak. Analisis Diskriminan Linear (LDA) diaplikasikan bagi mengklasifikasikan dakwat kepada kumpulan masing-masing. Spektroskopi ATR-FTIR memberikan maklumat mengenai kumpulan berfungsi yang terdapat dalam dakwat pen hitam tetapi menunjukkan keupayaan diskriminasi yang terhad apabila digunakan secara bersendirian untuk membezakan sampel boleh padam dan tidak boleh padam. PCA menunjukkan pengelompokan yang jelas antara dakwat boleh

padam dan tidak boleh padam. Tiga komponen utama (PC) pertama PCA merangkumi 98.4% daripada jumlah varians data sampel dakwat pen (PC1 89.2%, PC2 8.2% dan PC3 1.0%). Peratusan ini menunjukkan perwakilan data yang sangat baik, menandakan bahawa PCA berjaya mengekalkan hampir keseluruhan variasi bermakna dalam sampel dakwat pen dengan kehilangan maklumat yang minimum. LDA menunjukkan prestasi diskriminasi yang kukuh, dengan kadar pengelasan tepat sebanyak 95.0% bagi data asal dan ketepatan 90.0% di bawah pengesahan silang tinggal-satu (leave-one-out cross-validation), yang menunjukkan kestabilan model dan keupayaan ramalan yang baik. Penggabungan spektroskopi ATR-FTIR dengan PCA dan LDA secara ketara meningkatkan keupayaan diskriminasi dan pengelasan dakwat pen gel dengan mengekstrak corak kimia yang bermakna daripada data spektrum yang kompleks, sekali gus menyediakan pendekatan yang kukuh, tidak merosakkan, dan boleh dipercayai secara forensik untuk pemeriksaan dokumen dipertikai.

**CHEMICAL PROFILING OF ERASABLE AND NON-ERASABLE BLACK
GEL PEN INKS USING ATR-FTIR SPECTROSCOPY AND
CHEMOMETRICS TECHNIQUES**

ABSTRACT

Ink analysis is a key component of forensic document examination, aiding forensic document experts in detecting physical or chemical alterations, fabrication, or tampering of documents, particularly in cases involving forgery, authentication, or other offenses related to written and printed evidence. Gel pens are commonly encountered in questioned documents, and differentiating erasable and non-erasable inks is forensically important. The aim of this study is to chemically profile and discriminate 10 different brands of erasable and 10 different brands of non-erasable black gel pen inks using ATR-FTIR spectroscopy combined with chemometric analysis. Pen ink samples from erasable and non-erasable gel pens were firstly analysed using ATR-FTIR at wavelength of 4000 cm^{-1} to 600 cm^{-1} . Fingerprint region of spectral data which between 1500 cm^{-1} to 600 cm^{-1} were then processed using Principal Component Analysis (PCA) for pattern recognition. Linear Discriminant Analysis (LDA) was applied to classify the inks into their respective groups. ATR-FTIR spectroscopy provided information on the functional groups present in black pen inks but demonstrated limited discriminatory capability when used alone to distinguish between erasable and non-erasable samples. PCA showed clear clustering between erasable and non-erasable inks. The first three principal components (PCs) of PCA achieved 98.4% of total variance data of pen ink samples (PC1 89.2%, PC2 8.2% and PC3 1.0%). This percentage indicates an excellent data representation, showing that

PCA successfully retained almost all meaningful variation in the pen ink samples with minimal information loss. LDA showed strong discriminative performance, with 95.0% correct classification in the original data and 90.0% accuracy under leave-one-out cross-validation, indicating good model stability and predictive ability. The coupling of ATR-FTIR spectroscopy with chemometric techniques of PCA and LDA markedly improves the discrimination and classification of gel pen inks by extracting meaningful chemical patterns from complex spectral data, thereby providing a robust, non-destructive, and forensically reliable approach for questioned document examination.

CHAPTER 1 : INTRODUCTION

1.1 Introduction/Background of Study

Ink analysis is a key component of document examination, aiding forensic experts in detecting physical or chemical alterations, fabrication, or tampering of documents, particularly in cases involving forgery, authentication, or other offenses related to written and printed evidence (Gautam, *et al.*, 2021). The purpose of ink analysis involves both the classification of inks and the comparison of their chemical compositions with those of visually similar samples (Sharma & Kumar, 2017). Additionally, it assists in determining whether two questioned writings were produced using the same pen or ink formulation (Sharma & Kumar, 2017).

Writing inks are typically composed of colorants either dyes or pigments combined with solvents, resins, surfactants, lubricants, emulsifiers, and various additives to produce the desired flow and colour intensity (Gannetion, *et al.*, 2021). In modern writing instruments, gel pens have become increasingly popular because they offer smooth ink delivery and produce vivid, consistent lines (Kaur, *et al.*, 2025). These characteristics have made black gel pens a common choice for signing and preparing formal documents, thus increasing their forensic significance.

However, the introduction of erasable gel pens has complicated forensic ink analysis. Unlike conventional non-erasable gel inks, erasable formulations contain thermosensitive microcapsules that enclose a color former (leuco dye), a color developer, and a temperature-sensitive agent (Liu & Li, 2019). When frictional heat is applied, these components undergo a reversible chemical reaction that causes the ink

to disappear, allowing text modification without obvious evidence of alteration. This property presents a potential challenge in questioned document examination, as erased writings may not be visually detectable but still leave chemical residues on paper.

Various analytical approaches have been developed to characterize writing inks and distinguish between similar formulations in forensic investigations. These methods are generally categorized into destructive and non-destructive techniques (Fatima, 2020). Destructive techniques, such as Thin Layer Chromatography (TLC) and High-Performance Liquid Chromatography (HPLC), provide detailed chemical information on dye components and colorants (Kravchenko, *et al.*, 2024). However, they require ink extraction from the document surface, which permanently alters or damages the evidence, making them unsuitable for valuable or limited forensic samples (Khofar, *et al.*, 2022).

In contrast, non-destructive analytical techniques allow the examination of ink directly on the document without causing physical alteration. Commonly used non-destructive methods include UV–Visible spectroscopy, Raman spectroscopy, and Fourier Transform Infrared (FTIR) spectroscopy. Among these, FTIR spectroscopy is particularly advantageous because it identifies the molecular vibrations associated with specific functional groups in the ink composition (Khofar, *et al.*, 2022). This allows the detection of differences in resins, dyes, binders, and additives that may not be visually apparent.

The application of chemometric techniques, such as Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA), further enhances the

analytical value of FTIR data (Gawad *et al.*, 2022; Zaharullil *et al.*, 2023). These multivariate statistical tools enable objective classification and discrimination of inks based on spectral patterns, increasing the accuracy and reproducibility of the analysis (Gannetion, *et al.*, 2021).

1.2 Problem Statement

Forgery, alteration, and manipulation of written documents are increasingly reported in legal, financial, and administrative contexts (Gupta, *et al.*, 2024). In such cases, questioned document examiners are required to determine whether different entries were written using the same ink or if certain portions have been added, replaced, or modified. However, this task is becoming more challenging due to the widespread use of modern gel pens, especially black gel pens, which often produce visually similar strokes regardless of brand or ink formulation.

Although considerable research has been devoted to the characterization of blue inks, the scientific literature demonstrates a notable lack of focus on black inks, including those from ballpoint and gel pens (Gautam, *et al.*, 2021). This gap is problematic because black pens are the preferred writing instrument for official records, contracts, and legal documents, meaning they are directly involved in many disputed cases. Additionally, erasable gel pens represent an emerging category of writing tools with unique chemical compositions designed for thermal erasure, yet they remain severely understudied. Prior work indicates that only 3% of analyzed pens were erasable types (Liu & Li, 2019), suggesting that current research coverage is insufficient to support reliable forensic comparison.

The limited availability of comparative chemical data makes it difficult for forensic examiners to distinguish between erasable and non-erasable black gel inks, particularly when they appear identical to the naked eye. Traditional visual inspection and handwriting comparison alone are incapable of resolving such similarities. Moreover, without a systematic analytical approach, the risk of misinterpretation increases—potentially leading to uncertainty in casework and weakened evidentiary conclusions.

Another challenge lies in the absence of comprehensive spectral databases or standardized analytical workflows for black gel inks. Many laboratories also lack validated, non-destructive methods capable of discriminating between closely related ink formulations. As a result, examiners may be unable to confirm whether multiple entries originate from the same pen or if an erasable ink has been used to facilitate concealed alterations.

Therefore, there is a critical need for a structured, analytical investigation that focuses specifically on erasable and non-erasable black gel pens using FTIR-based chemical profiling supported by chemometric analysis. Addressing this gap will provide foundational data necessary for objective comparison and improve the reliability of ink differentiation in questioned document examinations.

1.3 Objective of Study

1.3.1 General Objective

To perform the chemical profiling of black non-erasable and erasable gel pen inks using ATR-FTIR spectroscopy and chemometrics methods.

1.3.2 Specific Objective

1. To evaluate the solubility characteristics of the ink samples through dissolution test to distinguish between dye-based and pigment-based inks.
2. To evaluate the similarity and differences between FTIR spectra of erasable and non-erasable black gel inks.
3. To apply chemometric techniques of PCA and LDA onto FTIR data for discrimination and classification of erasable and non-erasable black gel pen inks.

1.4 Significance of Study

This study provides valuable contributions to the field of forensic document examination by establishing chemical profiles of erasable and non-erasable black gel pen inks through Fourier Transform Infrared (FTIR) spectroscopy supported by chemometric analysis. The resulting profiles can assist forensic experts in differentiating between visually similar black inks during document authentication or forgery investigations.

As black gel pens are frequently used in formal and legal documents, the ability to accurately determine whether an ink is erasable or non-erasable is highly significant for identifying documents that may be susceptible to alteration. Furthermore, the findings from this study can contribute to the development of forensic ink databases and support the advancement of non-destructive analytical approaches in questioned document analysis.

Importantly, this study addresses a current gap in forensic literature, as erasable gel inks represent a relatively new and understudied category of writing instruments. By characterizing these inks, the study provides baseline chemical data that can guide future research and establish reference standards for forensic laboratories.

The study also has practical implications for real-world casework. The ability to discriminate between inks rapidly and objectively using FTIR and chemometrics can improve the efficiency, reliability, and scientific credibility of forensic reporting in court. Such analytical evidence strengthens expert testimony and supports judicial decision-making in cases involving fraud, alteration, or unauthorized modification of documents.

In addition, the research promotes a cost-effective and minimally damaging approach to ink examination. Since FTIR analysis requires limited sample destruction, it preserves the integrity of questioned documents—an essential requirement for legal proceedings. This enhances the feasibility of routine ink screening in laboratories that may lack access to more complex or destructive analytical instruments.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

Forensic ink analysis is a specialised application of analytical chemistry within forensic science that supports questioned document examination (QDE). It is primarily concerned with the examination and comparison of writing inks to address forensic questions related to document authenticity, such as detecting alterations, identifying additions made at different times, and determining whether multiple entries originate from the same or different writing instruments (Quinteros, 2022). In forensic casework, ink analysis contributes to the evaluation of evidential consistency and assists examiners in forming objective conclusions regarding the authenticity of disputed documents.

The principal objectives of forensic ink analysis include the comparative discrimination of ink entries, assessment of ink similarity or difference, and, in certain cases, estimation of the relative sequence or age of ink deposits (Kravchenko *et al.*, 2024). Rather than relying solely on visual examination, forensic ink analysis employs analytical techniques to reveal subtle chemical differences between inks that may not be apparent to the naked eye. These chemical differences provide a scientific basis for distinguishing inks from different sources or batches, thereby strengthening the evidential value of the findings.

Writing inks are chemically complex formulations comprising colourants (dyes or pigments), solvents, resins, and functional additives. From a forensic perspective, variations in ink composition arising from differences in formulation, manufacturing

processes, and ink type form the basis for discriminating inks in questioned documents (Gawad *et al.*, 2022; Fatima, 2020). For example, conventional ballpoint pen inks generally consist of dye-based colourants dissolved in an oil-based medium, whereas gel pen inks contain pigment particles suspended within a water-based gel matrix. These chemical and physical differences can be exploited analytically to distinguish entries made using different writing instruments (Fatima, 2020; Khofar *et al.*, 2022).

Analytical approaches in forensic ink examination are generally classified as non-destructive or destructive techniques. Non-destructive methods are especially valued in forensic practice because they preserve the integrity of questioned documents while allowing direct analysis of the ink on the paper substrate (Sharif *et al.*, 2022). These approaches are typically preferred in forensic investigations, as they enable reliable comparative analysis without compromising the evidential value of the document, a critical requirement for materials intended for submission in legal proceedings.

2.2 Composition of Writing Pens

2.2.1. Gel Pen Inks

Gel pen inks generally employ a water-based medium in which finely dispersed pigments serve as the principal colorants (Khofar *et al.*, 2022). These inks may incorporate both pigments and dyes, although pigments are predominantly responsible for their enhanced durability, including improved resistance to light exposure, water, and various forms of chemical degradation (Asri, *et al.*, 2022).

The formulation of gel inks typically consists of colouring agents, a water-based solvent acting as the vehicle, and a range of functional additives such as plasticisers, surfactants, waxes, and driers that regulate viscosity, flow behaviour, and stability (Zaharullil *et al.*, 2023). Common volatile solvents used in gel ink formulations include 1,2-propanediol, ethane-1,2-diol, 2,2'-oxydi(ethan-1-ol), and glycerine (Gautam *et al.*, 2021); phenoxyethanol may also be incorporated as a co-solvent due to its favourable solvency and antimicrobial properties (Qureshi *et al.*, 2022).

Gel pen inks are generally classified as viscous writing materials. Notably, certain gel inks often described as hybrid formulations share characteristics with ballpoint inks. These hybrid inks may contain dye-based colorants and exhibit solubility in methanol, despite retaining the microscopic structural characteristics associated with gel ink systems (Gannetion et al, 2021).

Spectroscopic analyses, particularly Fourier Transform Infrared Spectroscopy (FTIR), have identified several characteristic components of gel ink formulations. These include features attributable to azo pigments, as well as distinct C–N and N–H vibrational modes associated with organic colorants (Gawad et al, 2022). Additionally, symmetric C–O–C stretching vibrations, indicative of saturated ether compounds, are commonly observed in FTIR spectra of gel pen inks (Qureshi *et al.*, 2022).

2.2.2 Erasable Gel Pen Inks

Erasable pens, particularly modern formulations utilizing thermosensitive technology, rely on a heat-responsive chemical system that enables reversible

coloration. These inks are typically viscous and are engineered to undergo a colour disappearance reaction when exposed to elevated temperatures (Liu & Li, 2019).

The core mechanism is based on microencapsulation technology, in which microscopic capsules generally measuring approximately 2–3 μm in diameter encase three key functional components (Liu & Li, 2019). First, a leuco dye (or colour former) serves as the primary chromogenic material. Second, a colour developer (or chromogenic agent) interacts with the leuco dye at ambient temperatures to produce visible colour. Third, a colour-change temperature regulator modulates the stability of the dye–developer complex. When the ink is exposed to heat, typically above approximately 65 °C, the regulator disrupts the interaction between the colour former and colour developer, resulting in a transition to a colourless state (Liu & Li, 2019; Cordeiro & Gondikas, 2024; Li *et al.*, 2018).

When erasable ink strokes are examined under low-magnification optical instruments, such as a stereo microscope, several characteristic morphological features can be observed. These features are often useful in distinguishing erasable ink from conventional gel or ballpoint inks and may provide valuable information for forensic document examiners.

According to Cordeiro and Gondikas (2024), unaltered erasable ink strokes exhibit several distinctive features under low magnification (e.g., stereomicroscopy). Firstly, unaltered erasable ink strokes frequently exhibit a pasty or rubber-like surface texture. This pasty appearance is most pronounced in regions where the ink has accumulated, suggesting localized thickening of the ink layer. Ink accumulation is

commonly observed at the terminal points of the stroke, which can assist in determining writing direction. In some instances, unaltered strokes display a reduced quantity of ink within the central zone of the stroke compared to its outer margins. Although not universally observed, one study reported that approximately 13% of examined samples demonstrated this characteristic consistently across all produced strokes. Slight relief or elevation in regions of heavy ink deposition particularly along the external borders of the stroke and at stroke termination points can be observed under stereomicroscopy or when illuminated using raking light. This morphological feature was documented in roughly 80% of tested cases and is indicative of the viscous nature of erasable ink formulations. Due to the viscous nature of erasable inks, grooves and occasional striations may appear within the stroke, and normal writing pressure may also produce noticeable indentations in the paper substrates.

2.3 Dissolution Test

Previous forensic studies have employed dissolution tests to differentiate dye-based and pigment-based inks using solvents of varying polarities. Methanol, ethanol, and acetic acid were commonly tested, where several pen inks were found to be insoluble in these solvents. Among them, ethanol proved most effective, successfully dissolving 26 out of 30 ink samples (Sombut, *et al.*, 2020). Similarly, Liu and Li (2019) observed that black (FXB1, FXB2) and blue (FXL1, FXL2, CCL1) erasable gel inks faded after methanol and acetic acid extraction, indicating dye-based compositions.

Gannetion *et al.* (2021) also reported that dye-based ballpoint inks were soluble in methanol, consistent with their microscopic morphology, while some gel inks exhibited similar solubility patterns. In another study, a range of solvents such as

acetone, ethanol, methanol, chloroform, acetic acid, benzene, water, and n-hexane were tested, and methanol was found to be the most efficient, dissolving 96 out of 110 pen inks (Gupta, *et al.*, 2024).

Zaharullil *et al.* (2023) reported black gel pen inks were found to contain mixtures of dyes or pigments blended to achieve a uniform black colour. Solubility testing revealed that 21 samples were insoluble in organic solvents, indicating pigment-based formulations, while nine inks dissolved in methanol and ethanol, confirming dye-based compositions. These findings, consistent with Reed (2013), demonstrated that dissolution testing serves as an effective preliminary method for distinguishing inks based on their colourant type. Collectively, these findings suggest that dissolution testing using polar solvents such as ethanol or methanol can provide a simple yet effective preliminary differentiation between erasable and non-erasable gel pen inks before detailed chemical profiling by FTIR.

In this study, solvents with different polarity characteristics were used to assess ink solubility. Polar solvents such as ethanol, methanol, and acetic acid were expected to preferentially dissolve dye-based inks, while dichloromethane, a moderately polar aprotic solvent, was included to evaluate its interaction with ink components.

2.4 Analytical Method

Several previous studies have investigated the application of analytical techniques for forensic ink analysis, particularly in the discrimination of pen inks. Mohamad Asri *et al.* (2022) demonstrated the capability of Raman spectroscopy in differentiating 140 black gel ink samples from 14 brands based on their spectral

characteristics. Zaharullil *et al.* (2023) and Gannetion *et al.* (2021) applied ATR-FTIR to determine the colorant type in black and blue gel inks, respectively, highlighting its effectiveness in distinguishing dye-based and pigment-based inks through infrared absorption features. Sharma and Kumar (2017) compared destructive and non-destructive approaches for blue ballpoint ink analysis and reported that ATR-FTIR provided higher discriminating power while preserving the integrity of the document. Kaur *et al.* (2025) evaluated gel pen inks using Thin Layer Chromatography and UV-Visible spectroscopy, observing that each technique showed limited discrimination when used individually due to poor dye separation and overlapping absorption features. Similarly, Liu and Li (2019) investigated erasable gel pens using non-destructive optical techniques, including infrared visual analysis, FTIR spectroscopy, and fluorescence analysis, concluding that these methods were effective for distinguishing erasable gel inks, particularly when applied in combination.

Spectroscopic techniques are widely favoured in forensic document examination due to their non-destructive nature, allowing direct analysis of ink on paper without altering the evidence. Fourier Transform Infrared (FTIR) spectroscopy provides comprehensive information on the molecular vibrations of ink components, including colorants, resins, solvents, and additives, resulting in a characteristic chemical fingerprint of the ink formulation. Raman spectroscopy complements FTIR by offering high sensitivity toward inorganic pigments such as carbon black, which are commonly present in black and blue gel inks. In contrast, UV-Visible spectroscopy is rapid and simple but offers limited specificity, as overlapping absorption bands often reduce its discriminatory power.

Chromatographic techniques, such as Thin Layer Chromatography (TLC), High-Performance Thin Layer Chromatography (HPTLC), and High-Performance Liquid Chromatography (HPLC), rely on the physical separation of ink components and are inherently destructive, requiring ink extraction from the document. TLC and HPTLC provide visual separation of dye components, allowing comparative assessment of ink formulations, while HPLC offers superior resolution and quantitative information for complex ink mixtures. However, the destructive nature of these methods limits their applicability in forensic casework where preservation of evidence is critical.

In this study, ATR-FTIR spectroscopy was selected because it is well suited to the chemical nature of pen inks, which are complex mixtures of organic dyes, polymers, resins, solvents, and additives that exhibit characteristic infrared absorption bands. The technique enables direct, non-destructive analysis of ink on paper with minimal sample preparation, which is essential in forensic document examination. By providing molecular fingerprint information based on functional groups present in gel pen inks, ATR-FTIR offers a reliable approach for the chemical characterisation and differentiation of erasable and non-erasable inks.

2.5 Chemometrics Techniques

Chemometrics in forensic ink analysis refers to the application of mathematical and statistical methods to chemical data to provide reliable, objective, and unbiased results for classification and model development (Zaharullil *et al.*, 2023). This discipline has become essential because visual inspection of complex spectral data such as that produced by ATR-FTIR, Raman, or UV-Vis spectroscopy is often

subjective and prone to human error, particularly when different ink brands share similar functional groups (Gawad, *et al.*, 2022). By using chemometric tools, forensic document examiners can extract maximum information from multi-component datasets and achieve a significantly higher discrimination power (DP) than through qualitative observation alone (Zaharullil *et al.*, 2023).

2.5.1 Data Pre-processing Techniques

Before statistical analysis, raw spectral data must be subjected to appropriate pre-processing to reduce instrumental noise and enhance chemically relevant variations (Gautam, *et al.*, 2021). Previous studies, including those by Gawad *et al.* (2022), Sharma and Kumar (2017), and Gautam *et al.* (2021), have employed normalization techniques during data pre-processing, such as Standard Normal Variate (SNV) and row scaling, to correct for intensity variations arising from differences in ink deposition or instrumental conditions.

In addition, derivative-based pre-processing methods have been reported by Qureshi *et al.* (2022) and Gautam *et al.* (2021), where first- and second-order derivatives, commonly calculated using the Savitzky–Golay algorithm, were applied to reduce baseline effects and resolve overlapping spectral bands. These pre-processing approaches enhance spectral clarity and improve the discrimination of chemical components present in pen ink samples.

SNV data preprocessing was chosen in this study to correct spectral variations from ink thickness, uneven deposition, and instrumental noise. Centering and scaling

spectra enhance comparability, ensuring multivariate models capture chemical differences rather than artefacts, thus improving forensic ink discrimination robustness.

2.5.2 Unsupervised Exploratory Analysis

Unsupervised analytical methods are commonly applied to explore inherent patterns and groupings within spectral data without prior knowledge of sample classes. Among these methods, Principal Component Analysis (PCA) is the most widely used technique for dimensionality reduction, as it converts a large set of correlated spectral variables into a smaller number of uncorrelated principal components (Zaharullil *et al.*, 2023). In many ink analysis studies, the first two or three principal components typically account for more than 80–90% of the total variance, enabling effective visualization of sample distribution and clustering in two- or three-dimensional score plots, where chemically similar inks tend to group together (Gautam *et al.*, 2021; Gawad *et al.*, 2022).

In addition to PCA, Agglomerative Hierarchical Clustering (AHC) has been employed to assess similarities between ink samples by calculating distance or correlation measures, such as Pearson's correlation coefficient. The resulting dendrogram provides a visual representation of the relationships among different ink brands and types, facilitating comparative interpretation (Qureshi *et al.*, 2022).

More recently, advanced manifold learning techniques, including t-distributed Stochastic Neighbor Embedding (t-SNE) and Uniform Manifold Approximation and Projection (UMAP), have been introduced for the analysis of high-dimensional forensic datasets. UMAP, in particular, has been highlighted for its computational

efficiency and its ability to project new samples into an existing low-dimensional representation, making it suitable for large-scale ink discrimination studies (Mohamad Asri *et al.*, 2022).

Principal Component Analysis (PCA) was selected as the unsupervised method in this study to reduce spectral dimensionality while preserving maximum variance from preprocessed ink. This approach reveals natural patterns and clusters in questioned document inks without prior class assumptions, mitigating multicollinearity among wavelengths. PCA thus enhances forensic interpretability, visualization, and model efficiency for reliable ink discrimination.

2.5.3 Supervised Classification and Predictive Modeling

Supervised classification and predictive modeling are foundational to modern forensic ink analysis, delivering objective statistical frameworks for identifying and categorizing entries on questioned documents. Unlike exploratory unsupervised methods, these techniques leverage known "training" datasets of authenticated samples to construct models that classify unknown "blind" samples into predefined groups with high precision and evidential reliability.

Partial Least Squares-Discriminant Analysis (PLS-DA) is a robust supervised classification technique particularly well suited for datasets with highly correlated or multicollinear variables. It has been widely applied in forensic ink analysis and has demonstrated exceptionally high accuracy, often achieving near-perfect classification when distinguishing between ballpoint and gel inks or determining the specific source of a signature (Mohamad Asri *et al.*, 2022; Gautam *et al.*, 2021; Qureshi *et al.*, 2022).

Linear Discriminant Analysis (LDA) seeks to maximize the ratio of between-class variance to within-class variance, identifying the axes that optimally separate sample groups. When combined with PCA to form a PCA-LDA model, this approach has been shown to classify ink samples with very high precision. LDA models not only separate groups effectively but also provide quantitative metrics of predictive performance, such as classification accuracy, with studies reporting rates of up to 98% for both original and cross-validated datasets of gel inks (Zaharullil *et al.*, 2023).

In this study, Linear Discriminant Analysis (LDA) was chosen because it provides a reliable supervised classification method that maximizes separation between predefined ink groups while minimizing variation within each group. LDA is particularly suitable for ATR-FTIR data, as it efficiently handles datasets with multiple correlated variables and allows quantitative assessment of classification performance.

CHAPTER 3 : METHODOLOGY

3.1 Research Design

This study aimed to analyse, discriminate, and characterise black gel pen erasable and non-erasable black gel pen inks from different brands. This study comprises both qualitative and quantitative analyses. All black pen ink samples were written on the same type and batch of A4 paper and subsequently analysed using ATR-FTIR spectroscopy to assess the functional groups present in the ink formulations. Subsequently, the ink samples were discriminated between erasable and non-erasable categories using Principal Component Analysis (PCA), an unsupervised pattern recognition technique applied to the spectral data obtained from ATR-FTIR analysis. Lastly, Linear Discrimination Analysis (LDA), a supervised pattern recognition method, was employed using the PCA-derived data to further characterise and classify the ink samples according to their ink types.

3.1.1 Study Scope

The scope of this study was limited to black erasable and non-erasable gel pen inks written on the same type of A4 paper. Chemical profiling was performed using ATR-FTIR spectroscopy, followed by chemometric evaluation using PCA and LDA. Factors such as ink ageing, brand comparison, alternative substrates, and additional analytical techniques were excluded from the scope of this study.

3.1.2 Sampling Method

During the sampling process, ten different brands of black erasable gel pens and ten different brands of black non-erasable gel pens were purchased via the online

platform (Shopee) to represent the diversity of ink formulations available in the market. Seven pens were purchased per brand, with the exception of one brand that comprised of six pens. All pens were systematically coded and categorized to ensure proper identification and traceability throughout the study.

3.2 Sample Collection and Preparation

During the sample preparation stage, two participants produced ink strokes on white A4 office paper under controlled conditions to account for inter-writer variability. Each participant used separate paper sheets to prevent cross-contamination and while the same individually coded pen samples were used by both participants to allow comparison of ink strokes produced by different writers. The written samples were allowed to dry at room temperature for 5 minutes to ensure complete solvent evaporation prior to analysis. Subsequently, all paper samples were stored in sealed bags to maintain uniform environmental conditions and to prevent contamination or physical damage. Each brand or model was assigned a specific identification code, as listed in Table 1.

Table 1: Pen ink sample information (brands, ink types, models, and codes)

No	Brand	Type	Model	Code
1	Bai Jin	Erasable	Friction Falix BJ5055	A
2	Deli	Erasable	G7 G7-BK	B
3	Flexoffice	Erasable	flexMazzic Stick FO-GELE001	C

4	Joyko	Erasable	Shokyo Gel GP-279	D
5	Le α	Erasable	K9855	E
6	M&G	Erasable	iEraseV AKPH32R9	F
7	Meng Pai	Erasable	MP-6031	G
8	Pilot	Erasable	Frixion Ball Knock LFBK-23EF-B	H
9	Unicorn	Erasable	rubX UEP-555	I
10	Zhi Xin	Erasable	K-11ER	J
11	Deli	Non-erasable	6600S	K
12	Faber Castell	Non-erasable	RX Gel	L
13	Faster	Non-erasable	Eco Gel GP-F-050	M
14	Flexoffice	Non-erasable	T1 Gel FO-GEL036	N
15	G-soft	Non-erasable	Ex 5 Gel	O
16	Joyko	Non-erasable	Q3 Gel GP-265NT	P
17	M&G	Non-erasable	R3	Q
18	Pilot	Non-erasable	Wingel BL-WG-5	R
19	Unicorn	Non-erasable	UX5 Gel UGP-UX5	S

20	Zui Xua	Non-erasable	Diamond	T
----	---------	--------------	---------	---

3.2.1 Data Collection

The instrument used for data collection was LUMOS (Bruker Germany) IR spectrometer. LUMOS is a fully automated FTIR microscope which designed for high-performance infrared analysis of microscopic samples. It supports transmission, reflection, and attenuated total reflectance (ATR) modes (Bruker, 2026). ATR mode was chosen in this study as it requires little to no sample preparation and ensures precise, high-resolution imaging at the microscopic level (Bruker, 2026). FTIR spectrometer provides non-destructive molecular analysis by measuring infrared absorption patterns that serve as unique vibrational fingerprints, enabling the identification of functional groups, crystal structures, and chemical compositions (Bruker, 2026). LUMOS was linked to the computer and OPUS 7.5 software was used for IR spectra acquisition of pen ink samples.

The Liquid Nitrogen cooled Mercury Cadmium Telluride (LN-MCT) detector that being used in LUMOS FTIR spectrometer (Bruker, 2026) was heated due to thermal processes during the usage of this instrument. Liquid nitrogen was used to cool the detector, minimizing thermal noise and maintaining its high sensitivity (Woodis, 2025). Thus, the LUMOS FTIR spectrometer was filled up with nitrogen liquid and waited for the instruments to ready around 15 minutes before starting the analysis.

Next, the ATR crystal that was being used in this LUMOS ATR-FTIR spectrometer was germanium (Ge) crystal. As a precaution step, the germanium crystal

was wiped using the isopropyl alcohol each time before analyzed each sample to avoid any contamination. Furthermore, the pressure of ATR scan was set to low mode due to the nature of paper sample.

Once the LUMOS instrument was ready, the written paper sample was placed on the stage and secured at all four corners using plasticine to prevent any unintended movement during analysis. The spectral measurement for all spots was acquired in range of 4000 cm^{-1} to 600 cm^{-1} with resolution of 4 cm^{-1} and 16 number of scans per seconds. In addition, background of the samples also was measured prior to scanning each spot to minimize potential errors. After the spot has been scanned, the spectra data was saved in DPT form and subsequently used to generate graphs and perform further analysis using two chemometric techniques, namely PCA and LDA. The resulting graphs were plotted as absorbance versus wavenumber.

3.2.2 Dissolution Test

Pen ink samples were prepared by scribbling onto $1\text{ cm} \times 1\text{ cm}$ squares of 80 gsm A4 paper until each square was fully covered with ink. Four identical sets of ink samples were prepared to allow testing with four different solvents. Following 10 minutes of drying at room temperature, the inked paper square was cut, transferred to a glass vial, and labelled accordingly. Thereafter, for each pen ink sample, 5 mL of methanol was added using a dropper, after which the vial was shaken vigorously for 1 minute and left to stand at room temperature for 15 minutes for observation. After 15 minutes, the solvent was then discarded, and the sample was allowed to dry on a tissue paper. This procedure was subsequently repeated sequentially with ethanol, acetic acid, and dichloromethane using the same sample. The entire process was carried out for all

four ink sample sets, and the solubility behaviour of the ink in each solvent was observed and recorded.

3.3 Statistical Analysis

3.3.1 Repeatability and Reproducibility

Repeatability and reproducibility of the FTIR measurements were evaluated to assess the precision and reliability of the analytical method. Repeatability was assessed by analysing the same pen ink sample under identical experimental conditions, including the same instrument, operator, and measurement parameters within a short time interval. Seven consecutive ATR-FTIR measurements were performed at different locations along the same pen ink stroke to evaluate within-sample variability. The obtained spectra were overlaid and compared in terms of peak positions and intensities to evaluate spectral consistency and the relative standard deviation (RSD) of selected characteristic absorption bands was calculated to quantify repeatability.

Reproducibility was assessed by analysing ink samples from different pens of the same brand using the same experimental protocol. The resulting spectra were evaluated through visual spectral overlay and comparison of characteristic absorption bands, and quantitative assessment was performed by calculating the relative standard deviation (RSD) of selected spectral peaks.

3.3.2 Data Preprocessing and Analysis

All individual spectral data saved in DPT format were converted into Microsoft Excel files. The raw dataset comprised 1,946 spectra obtained from pen ink samples over the wavenumber range of 4000 cm^{-1} to 600 cm^{-1} . For data analysis and