FORENSIC CHARACTERISATION OF BLACK STAMP PAD INK AND PRINTED INKS

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UNIVERSITI SAINS MALAYSIA

2025

FORENSIC CHARACTERISATION OF BLACK STAMP PAD INK AND PRINTED INKS

by

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Dissertation submitted in partial fulfilment of the requirements for the degree of
Bachelor of Science in Forensic Science with Honours

February 2025

CERTIFICATE

This is to certify that the dissertation entitled 'Forensic Characterisation of Black Stamp Pad and Printed Inks' is the bona fide record of research work done by Ms. Seow Zhi Lin during the period from October 2024 to February 2025 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 fulfilment for the degree of Bachelor of Science in Forensic Science with Honours.

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DECLARATION

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

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(SEOW ZHI LIN)

Date: 27 Feb 2025

ACKNOWLEDGEMENTS

I would like to extend my heartfelt gratitude to my supervisor, ChM Dr.Dzulkiflee Ismail, and my co-supervisor, ChM Dr. Wan Nur Syuhaila Mat Desa, for their invaluable guidance, insightful feedback, and unwavering support throughout my final year project. Their expertise and encouragement have been crucial in helping me overcome challenges and complete this study. I am also sincerely thankful to all the laboratory staff of the Forensic Science Laboratory and the Analytical Laboratory for their assistance and guidance during my laboratory work, particularly with TLC analysis and ATR-FTIR spectroscopy. My deepest appreciation goes to my family for their unconditional love, patience, and encouragement during this journey. Their belief in me has been my greatest source of strength and motivation to persevere. Lastly, a special thank you goes to my wonderful friends, especially Chiong Su Peng, Ethel Lim Yi, Koh Pei Yee, and Nayomi Khoo Ya Mun for being my pillars of support, whether it was through words of encouragement, lending a helping hand, or simply being there when I needed someone.

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LIST OF SYMBOLS AND ABBREVIATIONS

ATR	Attenuated Total Reflectance
FTIR	Fourier Transform Infrared
CMYK	Cyan, Magenta, Yellow, Black
CIJ	Continuous Inkjet
DOD	Drop-On-Demand
GCMS	Gas Chromatography-Mass Spectrometry
HCA	Hierarchical Cluster Analysis
HPLC	High-Performance Liquid Chromatography
IPSB	Inkjet Photocopied Black Samples
IR	Infrared
LDA	Linear Discriminant Analysis
MACC	Malaysian Anti-Corruption Commission
MSDS	Material Safety Data Sheet
PCA	Principal Component Analysis
PCs	Principal Components
PLS-DA	Partial Least Squares Discriminant Analysis
SD	Standard Deviation
TLC	Thin Layer Chromatography
USA	United States of America
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible Spectrophotometry
%	percentage
$\bar{X}$	mean
3D	three-dimensional
et al.	et alia- and others
cm^{-1}	per centimetre
cm	centimetre
C-H	carbon hydrogen bond
C-O	carbon oxygen bond

C=O	carbon oxygen double bond
C-F	fluorine compound
C-O-C	ether compound
O-H	hydroxyl group
R_f	retention factor
S=O	sulphur compound

PENCIRIAN FORENSIK DAKWAT PAD COP HITAM DAN DAKWAT CETAK

ABSTRAK

Dalam era digital masa kini, kemajuan dalam teknologi percetakan telah mempermudahkan pelbagai tugas dalam kehidupan harian. Namun, kemajuan ini turut membawa kesan negatif iaitu peningkatan dalam kes penipuan dan pemalsuan dokumen. Membezakan dokumen tulen daripada yang palsu boleh menjadi cabaran, terutamanya jika hanya bergantung kepada pemeriksaan visual. Kajian ini bertujuan untuk menyiasat ciri-ciri forensik dakwat pad cop hitam dan dakwat cetak dengan menggunakan pendekatan menyeluruh yang menggabungkan pelbagai teknik analisis. Teknik-teknik ini termasuk mikroskop digital, kromatografi lapisan nipis (TLC), dan spektroskopi Pantulan dilemahkan - Fourier Transform Inframerah (ATR-FTIR), bersama kaedah statistik multivariat lanjutan seperti Analisis Komponen Utama (PCA) dan Analisis Kluster Hierarki (HCA). Sebanyak sembilan sampel berbeza telah dikaji. Pemeriksaan fizikal yang dijalankan dalam kajian ini menunjukkan perbezaan morfologi yang ketara antara kesan cop tangan dan sampel dakwat cetak. Analisis TLC berjaya memisahkan komponen dakwat menggunakan sistem pelarut kloroform-etanol, dengan nilai R_f yang tinggi menunjukkan bahawa komposisi kimia beberapa jenis dakwat adalah serupa. Spektroskopi ATR-FTIR pula memberikan cap jari molekul unik bagi setiap jenis dakwat. Walau bagaimanapun, cabaran timbul disebabkan oleh pertindihan spektrum dalam kawasan cap jari, yang menyukarkan pembezaan sepenuhnya antara jenis dakwat. Meskipun begitu, PCA dan HCA membuktikan keberkesanannya dalam mengelompokkan sampel dakwat berdasarkan komposisi kimia mereka, dengan kelompok yang jelas membolehkan pengenalpastian dan pembezaan pelbagai jenis dakwat.

FORENSIC CHARACTERISATION OF BLACK STAMP PAD INK AND PRINTED INKS

ABSTRACT

In today's digital age, the advancements in printing technologies have significantly simplified various tasks in daily life. However, these advancements have also led to an unfortunate consequence, which is the increase in document fraud and forgery. Distinguishing authentic documents from counterfeit ones can be challenging, particularly when relying on visual inspection alone. This study aimed to investigate the forensic characteristics of black stamp pad ink and printed inks, employing a comprehensive approach that combines multiple analytical techniques. These included microscopy, thin layer chromatography (TLC), and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy, alongside advanced multivariate statistical methods of Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA). A total of nine different samples were examined. The physical examination conducted in this study revealed significant morphological differences between hand-stamped impressions and printed ink samples. TLC analysis effectively separated the ink components using a chloroform-ethanol solvent system, with high R_f values indicating that the chemical compositions of certain ink types shared similar characteristics. ATR-FTIR spectroscopy, on the other hand, provided unique molecular fingerprints of the inks. However, challenges arose due to spectral overlap in the fingerprint region, making it difficult to fully distinguish between the ink types. Despite these challenges, PCA and HCA demonstrated their effectiveness in grouping the ink samples based on their chemical compositions, revealing distinctive clusters that allowed for the identification and differentiation of various ink types.

CHAPTER 1 : INTRODUCTION

1.1 Background of the Study

Stamps play a vital role in corporate documentation, serving as an official seal describing government, private officer's designation, and department information. It is widely used to validate legal documents such as ratified contracts, receipts, identity documents, agreements, and deeds, ensuring their legitimacy and reinforcing trust in the transactions (Li, 2014). The simplicity and efficiency of the stamp as a signing method have made it particularly popular among businesspeople, who often create personalised stamps of their signatures for frequent document authentication.

In Malaysia, black stamp pad ink is extensively utilised by government departments in Malaysia for authenticating vital documents such as land titles *('geran tanah')* and court records. On the other hand, red stamp pad ink is often used to create visible fingerprints on signatures, serving as personal verification of a document, much like a stamp impression signifies a company's approval in traditional Chinese practices (Sun et al., 2022). The application of a stamp impression not only legitimizes a document but also helps prevent tampering, thereby marking it as certified and original.

A contract between a company and another party, also referred to as *consensus ad idem*, signifies mutual agreement between both parties. This agreement, represented by the contract or instrument of dealing, must be stamped at the *Lembaga Hasil Dalam Negeri (LHDN)*, also known as the Inland Revenue Board. If an unstamped agreement is presented in court, it may still be admitted as evidence; however, a penalty will be imposed for the delay in stamping, as stipulated under Section 47A of Stamp Act 1949 (Erman, 2021). In simpler terms, stamping a document ensures its admissibility in court, providing an additional layer of protection for the parties involved. This practice reinforces the legitimacy of contracts and ensures that disputes can be addressed within the legal framework if they arise.

The handwriting of doctors has often been criticised for being difficult to read or, in some cases, completely illegible. In recent years, studies have confirmed that medical case notes frequently contain entries that are unclear, illegible, or lack proper identification (Lyons et al., 1998; Rodríguez-Vera et al., 2002). This issue can lead to serious challenges in maintaining accurate and traceable medical records, potentially compromising patient care. To address these concerns, personalized self-inking rubber stamps featuring a unique General Medical Council (GMC) number were introduced, as shown in **Figure 1.1** (MacKeith et al., 2012). These stamps provide a standardised and legible method for identifying medical professionals in records, significantly improving documentation accuracy and accountability in healthcare settings.

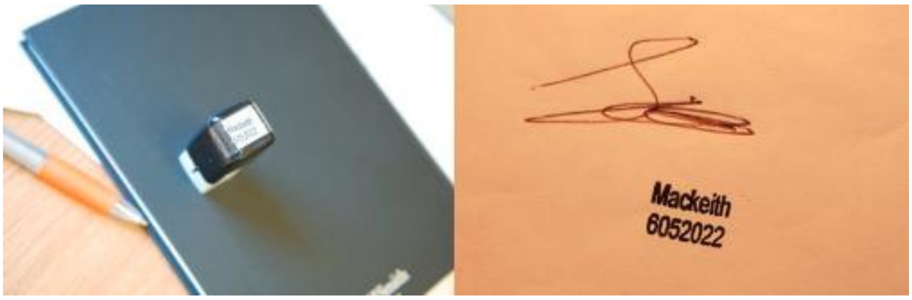

Figure 1.1*: Self-inking rubber stamp with name and individual GMC number of the doctor (MacKeith et al., 2012).*

One serious concern is that fraudulent documents could bypass scrutiny, potentially leading to significant legal and financial consequences. If undetected, these forged documents could result in legal disputes, financial loss, and erosion of trust in document security. One example is a case where the Malaysian Anti-Corruption Commission (MACC) is seeking three individuals to aid in an investigation related to a corruption syndicate involved in the misuse of entry and exit stamps at Malaysian borders (Bernama, 2020).

However, the widespread adoption of stamp pad ink has introduced certain vulnerabilities. With the advent of high-resolution printing technologies, counterfeiters can now replicate these stamp impressions with impressive accuracy. Tools like inkjet and laser printers make it easier to produce stamps that closely mimic authentic hand-stamped impressions. This has led to a rise in document fraud and forgery, a type of white-collar crime involving the manipulation of documents to mislead others, often for illegal financial gain (Zakariah et al., 2020). Individuals may unlawfully pursue their objectives by forging official documents using printed or photocopied methods, making it challenging to visually differentiate between printed and authentic documents without the assistance of specialized tools or the expertise of forensic document examiners. Printed samples and photocopied samples may differ in ink formulation.

Given these challenges, this study focused on forensic characterisation techniques that would provide a reliable basis for distinguishing between black stamp pad and printed inks. By employing advanced chemical and microscopic methods, this study aimed to develop a systematic approach that aids forensic document examiners in accurately differentiating between the two types of ink. Since many legal and forensic cases involve both printed and photocopied documents, making it essential to study both types to develop robust identification methods. This differentiation is crucial not only in verifying the authenticity of official documents but also in supporting the legal framework against forgery and fraud.

1.2 Problem Statement

The visual similarity between black stamp pad ink and printed ink makes it difficult to authenticate documents without the use of specialised tools or techniques. This issue complicates the verification process, potentially leading to disputes regarding the validity of important documents. As many institutions and legal processes require original documents, any uncertainty about their authenticity can create substantial problems. Such doubts can lead to legal complications, delays, and financial risks, affecting the credibility of both individuals and organizations. The inability to confidently differentiate between genuine and forged documents may result in serious consequences, including fraud, identity theft, and damage to reputations, making it essential to develop more effective methods for forensic analysis and document authentication.

Currently, there are limited studies available, with no publications directly comparing stamp pad ink and printed ink using a combination of microscopy, TLC, and ATR-FTIR spectroscopy. Existing studies primarily focused on analysing stamp pad inks (Li, 2014; Ouyang et al., 2019; Rajagopal, 2019; Sharma et al., 2021), writing inks (Carvalho et al., 2019; Fatima, 2020; Fla´via et al., 2015; Guo et al., 2024) or printer inks (Tao et al., 2023; Zawawi et al., 2021) separately but not comparatively. This study sought to address this problem by developing forensic methods to accurately characterise and differentiate between black stamp pad and printed inks on paper, ensuring more reliable forensic verification in legal and investigative contexts.

1.3 Objectives of the Study

1.3.1 General Objective

The general objective of this study was to differentiate between stamp pad ink with printed inks produced from different printing technologies.

1.3.2 Specific Objectives

a) To examine the morphology of stamp pad ink and printed ink materials using microscopic analysis.

b) To determine the chemical composition of the inks using TLC analysis and ATR-FTIR spectroscopy.

c) To discriminate the stamp pad ink and printed ink materials based on their chemical data effectively using statistical techniques of HCA and PCA.

1.4 Significance of the Study

This study is significant for several important reasons, contributing to both forensic science and legal document authentication. First and foremost, it addresses the growing concern over document fraud, a critical issue in Malaysia, where counterfeit documents can lead to legal disputes, financial losses, and the erosion of trust in official systems. By focusing on the forensic characterisation of black stamp pad ink and printed ink, this study aims to provide reliable methods for distinguishing between the two, thereby improving the accuracy and reliability of document authentication processes.

The findings of this study are valuable to forensic document examiners, law enforcement agencies, legal professionals, and other stakeholders who deal with the verification of official documents. By employing chemical analytic techniques such as TLC and ATR-FTIR spectroscopy, the study will offer a robust methodology for identifying the unique characteristics of stamp pad ink and printed ink. This will enhance forensic capabilities in verifying the authenticity of documents, especially in cases where visual inspection alone is inadequate.

Moreover, this study fills a gap in existing study by providing a comparative analysis of stamp pad ink and printed ink. While previous studies have focused on individual types of ink, this study combined morphological and chemical analyses, offering a more comprehensive approach. The integration of these techniques provided new insights that can be used in forensic document analysis, ultimately strengthening the ability to combat document fraud and forgery.

In addition to advancing forensic science, the findings of this study would contribute to legal frameworks by offering reliable methods for distinguishing genuine documents from forged ones. Since many legal processes and institutions rely on the authenticity of original documents, this study helps protect the integrity of these processes, ensuring that the documents used in legal and business transactions are legitimate. Ultimately, this study aimed to mitigate the risks associated with document forgery, protecting individuals, organisations, and society from the adverse effects of fraudulent activities.

CHAPTER 2 : LITERATURE REVIEW

2.1 Rubber Stamps

Rubber stamps are widely recognised as tools for imprinting designs or information onto various surfaces. They are a specialized form of crafting and communication, made using diverse types of inks that contain dyes or pigments combined with other chemical compounds. The process begins with the preparation of a specific image or pattern, which is either moulded, carved, vulcanized, or laser-engraved onto a rubber sheet (Chayal et al., 2019). This rubber sheet, once shaped, acts as the medium for transferring the image.

To use the rubber stamp, the ink, which composed of pigments or dyes, is evenly applied to the raised surface of the rubber design. When the rubber is pressed onto a writing medium such as paper, the ink transfers, producing a clear, coloured impression of the image or text. This method ensures that the details of the pattern are replicated accurately on the target surface. Rubber stamps are commonly used in official settings for authentication purposes and in creative contexts like arts and crafts.

2.2 Manufacture of Inks

2.2.1 Stamp Pad Ink

Stamp pad ink is a chemically complex formulation designed for efficient and durable stamping on various surfaces. It typically consists of pigments, synthetic resins, vegetable or mineral oils, and high-boiling-point solvents (Ouyang et al., 2019). The pigments used vary widely and include colours like pink, fast bright red BBN, Pigment Scarlet Powder 808, Everbright Bronze Red C, and phthalocyanine blue, among others (Ouyang et al., 2019). These pigments are key to defining the ink's colour, intensity, and durability. Synthetic resins and oils act as binding agents, ensuring the ink adheres effectively to surfaces, while high-boiling-point solvents control the ink's viscosity and drying characteristics. The Material Safety Data Sheet (MSDS, 2013) for Artline stamp pad ink (MSDS No. EHJ) lists its components as water, glycol solvent, dye stuff, and additional ingredients. Stamp pad inks are available in a variety of colours, including black, blue, red, green, and violet.

A significant challenge with stamp pad ink is achieving quick drying without compromising usability. The primary formulation of stamp pad ink uses glycerol and water (Waters, 1938). Glycerol, a non-volatile component and hygroscopic component, prevents the ink from drying on the pad but slows its absorption into paper (Waters, 1938). When applied to paper, the ink dries through absorption rather than evaporation. On highly absorbent paper, this occurs quickly, but on well-sized paper, the process may take longer, increasing the risk of smudging during rapid stamping. To improve absorption rates, volatile organic compounds like alcohol can be added to the ink. Alcohol accelerates ink penetration into paper but is highly volatile, causing it to evaporate rapidly when exposed to air. Over time, this evaporation reduces the ink's quick-drying characteristics, necessitating frequent re-inking of the pad. A notable advancement in this area is the use of Butyl Carbitol, a slowly volatile ether of diethylene glycol. Butyl Carbitol offers the penetrative benefits of alcohol while maintaining ink fluidity over extended periods, even when exposed to air. It effectively balances the need for quick absorption into paper with the prevention of smudging and illegible impressions (Waters, 1938). This make them ideal for use on standard paper surfaces in official and professional settings, where documents need to be processed quickly without smudging.

2.2.2 *Printer Inks*

Printer models vary in their ink cartridge configurations and supported print technologies. Cartridges are categorised as black, colour, or a combination of both. For instance, a printer using a four-color process (cyan, magenta, yellow, and black) requires at least two cartridge slots, one for a three-colour cartridge and one for black ink. Some printers are limited to black ink, while others support interchangeable cartridges or solely utilize a three-color process (Doherty, 1998). These variations influence the microscopic differentiation between printer models and their applications.

Inkjet printers introduced in the 1990s are extensively documented, with data on their technology, cartridge configurations, and operational timelines. For example, the Canon BJC-70 employs a four-color process, while the Hewlett-Packard ThinkJet is designed for black ink only (Doherty, 1998). Printer introduction and discontinuation dates provide insights into market trends and technological advancements. Additional information, such as manufacturer details and compatibility, enhances the understanding of printer design and functionality.

Colour laser printers are now affordable and widely available. Although their cartridges are relatively expensive, they have a much longer lifespan compared to inkjet cartridges. For example, black cartridges typically need replacement only once a year, while colour cartridges can last up to three years. This longevity makes the overall maintenance costs comparable to those of inkjet printers. Colour laser printers can produce a glossy finish on plain paper, but using extremely glossy paper types should be avoided (Sinclair, 2011).

2.3 Printing Principles of Printers

2.3.1 Inkjet Printer

Inkjet printers operate by projecting ink droplets from tiny nozzles through a moving printhead onto a substrate (Doherty, 1998). Inkjet printing relies on the generation of sequences of droplets (Cummins and Desmulliez, 2012). Two primary technologies are utilized in directing these ink droplets, which are continuous inkjet (CIJ) and drop-on-demand (DOD). CIJ printers use electrostatic deflection to guide ink droplets through a single nozzle to the intended surface (Doherty, 1998). However, DOD technology is more widely adopted due to its efficiency and precise deposition capabilities because DOD printers release ink only when required.

DOD printing is further divided into two main processes: piezoelectric and thermal. The piezoelectric process employs a pressure pulse to expel ink from a chamber onto the substrate. This technology is commonly utilized in solid inkjet printers, which use solid blocks of ink that are melted and deposited onto paper, solidifying almost instantaneously (Cummins and Desmulliez, 2012; Doherty, 1998). An advanced variation of this method involves spraying molten wax onto a drum and transferring it to paper via rolling. Tektronics has been a prominent marketer of solid inkjet printers (Doherty, 1998).

In contrast, thermal inkjet technology or also known as bubblejet system relies on heat vaporization to propel ink onto a substrate. Ink is stored in cartridges within the printhead carriage. An electrical pulse heats the ink within the nozzle, causing vaporization and bubble expansion, which ejects ink onto the paper. The bubble's collapse creates a void that is refilled with new ink from the cartridge (Doherty, 1998). This process necessitates periodic replacement or refilling of the ink cartridge after extended use. During the 1990s, most inkjet printers adopted the thermal drop-on-demand process due to its cost-effectiveness and reliability. **Figure 2.1** shows the schematic diagram of a thermal inkjet print head.

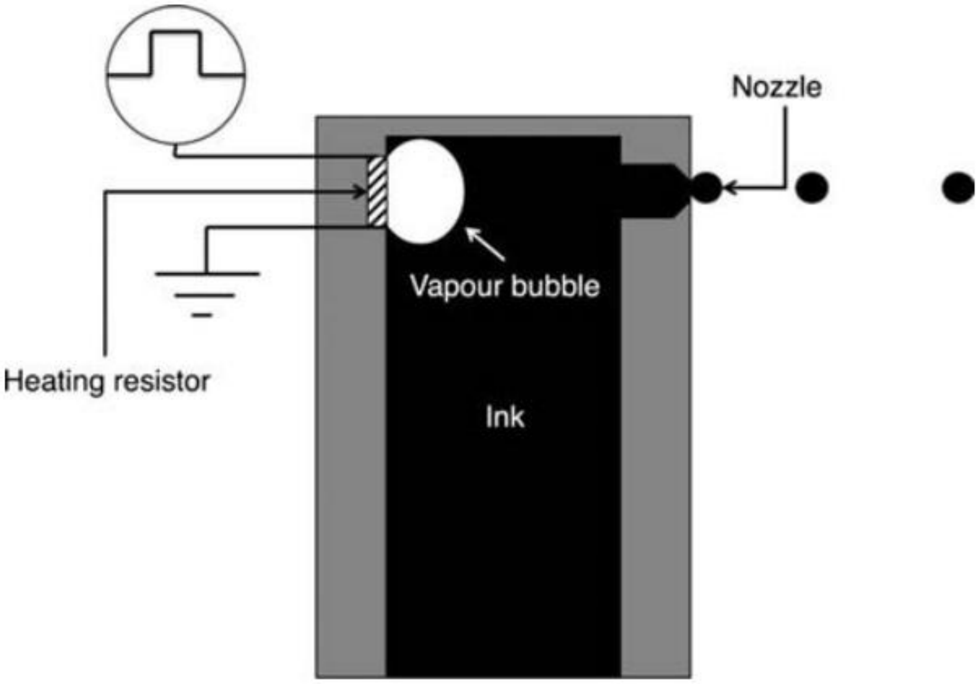

Figure 2.1*: Schematic of a thermal inkjet print head (Cummins and Desmulliez, 2012).*

Therefore, inkjet printing technologies, particularly DOD systems, have revolutionized printing by offering precision, cost-efficiency, and versatility. The ongoing advancements in piezoelectric and thermal processes continue to refine the quality and efficiency of inkjet printers, making them indispensable in both commercial and personal applications.

2.3.2 Laser Printer

Laser printers, which operate based on xerography, have become the go-to option for office printing due to their fast performance and quiet operation. These printers use a light-sensitive drum to transfer images onto paper (Sinclair, 2011). The drum, made from an insulating material, can hold an electric charge that is selectively neutralized in areas exposed to light. The core mechanism of a laser printer involves charging the drum, exposing specific parts to a laser beam, and thereby creating an electrostatic image. This process is controlled by a memory system capable of storing a full page of data. High-resolution graphics and colour printing require significant memory capacity, ranging from 2 MB for graphics to up to 64 MB for advanced colour printers.

Once the drum’s surface has been selectively charged, a powdered resin called toner is applied. The toner adheres to the charged regions of the drum to form the desired image. The toner application relies on two forces: magnetic attraction, facilitated by a magnetized developing cylinder, and electrostatic attraction, ensuring precise adherence of toner particles (Sinclair, 2011). Excess toner on the developing cylinder is evened out by a scraper blade.

The next step involves transferring the toner from the drum to the paper. A corona discharge places a positive charge on the paper, attracting the toner particles. After this transfer, a static-eliminator blade neutralizes the paper's charge to prevent it from sticking to the drum. To permanently affix the toner, the paper passes through heated rollers that melt the toner into the paper, producing the characteristic glossy finish of laser-printed material.

Maintenance and consumables are integral to the laser printer's operation. Toner, housed in replaceable cartridges, is a primary consumable. In some models, the photoconductive drum is part of the cartridge, as seen in Hewlett-Packard LaserJet printers (Sinclair, 2011). This design simplifies replacement but offers limited lifespan, typically supporting about 3,500 pages at standard print density. Drum replacement is generally required after 80,000 pages, while minor maintenance is needed every 20,000 pages (Sinclair, 2011). Additionally, some printers use a separate developer powder, which must be replenished alongside the toner. Paper costs for laser printing are relatively low, as most copier-grade paper is suitable. However, heavy paper may cause mechanical issues. Long-life cartridges and high-yield toner options are available for heavy-duty use, but extensive printing of dense graphics or fonts significantly reduces cartridge life. **Figure 2.2** illustrates the schematic layout of a monochrome laser printer.

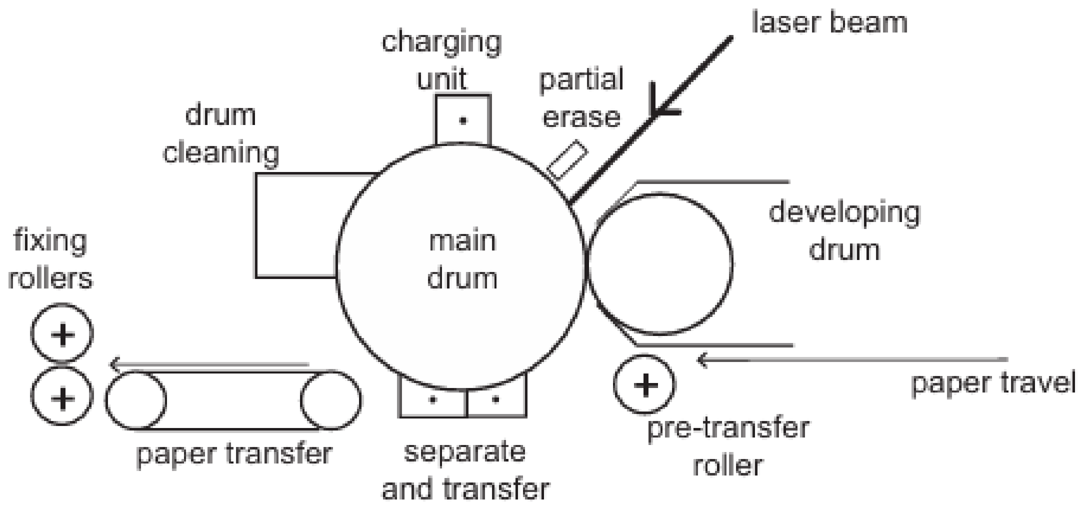

Figure 2.2*: The outline of a monochrome laser printer (Sinclair, 2011).*

2.4 Document Fraud and Forgery

Fraud represents a broad spectrum of illicit activities that can include theft, corruption, conspiracy, embezzlement, money laundering, bribery, and extortion (Hadi and Paino, 2016). These acts are typically driven by the intent to deceive, manipulate, or exploit individuals or organizations for personal gain or to inflict harm. Fraudulent activities often erode trust, disrupt operations, and can have far-reaching legal and financial consequences. In parallel, under common law, forgery refers to the fraudulent creation or alteration of any written document in a way that could cause harm or disadvantage to another party (Mohammed, 2002). Commonly, forgery involves private written instruments such as deeds, promissory notes, wills, or signatures.

In the context of document fraud, perpetrators use a variety of methods to alter, forge, or replicate documents, making it increasingly challenging to distinguish authentic documents from fake ones. Common techniques include tracing, which involves manually replicating signatures or text; the cut-and-paste method, where components of different documents are combined to create a fraudulent version; and the use of sophisticated technologies. Advanced tools such as image editing software (e.g., Photoshop), digital cameras, hardware tools, printers, and scanners allow fraudsters to manipulate documents with remarkable precision and realism. Such methods enable fraudsters to perform modifications that can include additions (e.g., adding fake details), deletions (removing legitimate information), substitutions (replacing genuine content with false data), or complete fabrication of documents (Chayal et al., 2019). These alterations often create tampered documents that appear genuine to the untrained eye, allowing fraudsters to use them for illegal purposes such as financial fraud, identity theft, or legal manipulation.

The growing accessibility of technology further exacerbates the problem. Image editing software and high-resolution printing and scanning equipment are now widely available, reducing the skill level required to produce convincing fraudulent documents. Consequently, even laypersons can be deceived by these counterfeit documents, making it critical to develop and implement advanced forensic techniques for document analysis. This highlights the need for effective detection methods, such as forensic examination of inks, paper, and printing technologies, to identify and combat document fraud.

2.5 Ink Analysis Methods

2.5.1 Non-Destructive Methods

Optical examinations are often the first line of analysis in forensic ink examination for detecting document forgery due to their non-destructive nature, affordability, simplicity, and ease of access, combining optical techniques with microscopic methods to assess ink properties. Microscopic methods provide visual examination into the physical characteristics of ink lines. Features such as striations, goofing, and fibre diffusion are frequently examined to determine the type of writing instrument and ink used.

Fatima (2020) examined writing inks, noting that ballpoint pen inks frequently exhibit striations and a glossy appearance due to their partial absorption into paper fibres. In contrast, gel pen inks create smooth and uniform lines without striations, though slight variations may occur depending on the writing pressure applied. Non-pen inks, such as those used in printers or typewriters, possess distinct microscopic features. For example, typewriter inks tend to appear dull with uneven edges, whereas offset and inkjet printer inks are characterized by evenly spaced dots or irregular splatters. These unique traits help establish a connection between the ink and its method of application.

Furthermore, Rajagopal (2019) conducted a microscopic analysis that revealed substantial differences in the physical and drying properties of skin-safe stamp pad inks, depending on their brand and type. Aero inks exhibited significant layer separation and unique drying patterns, particularly for invisible blue. Tattoo (visible) and ProColor (invisible green) inks demonstrated higher viscosities and resistance to drying, indicative of their oily compositions. W brand invisible inks stood out for their low viscosity, rapid drying, and minimal residue visibility.

Additionally, fluorescence microscopy has emerged as a valuable tool for non-destructive ink characterization. Khare et al. (2024) demonstrated the efficacy of fluorescence microscopy combined with ImageJ software for analysing the fluorescence properties of 125 blue, black, and red gel and ballpoint ink samples, emphasizing its utility in preserving the integrity of questioned documents.

2.5.2 Destructive Methods

Destructive analytical methods, such as TLC, paper chromatography, and capillary electrophoresis, provide detailed insights into the chemical composition of inks. TLC, in particular, is widely used due to its ability to separate soluble dyes and pigments, facilitating the identification of ink formulations. TLC is a form of liquid chromatography where the stationary phase consists of a thin layer of material, known as the sorbent, applied to a flat plate (Santiago and Strobel, 2013). The mobile phase, referred to as the developing solvent, moves the solutes through the stationary phase. The movement of solutes across the plate depends on two key factors: the ability of the mobile phase to dissolve and transport the solutes and the resistance of the sorbent, which pulls the solutes out of the solution and reabsorbs them.

The process involves a "stop-and-go" motion, where solutes are repeatedly absorbed into and desorbed from the sorbent. While only a small fraction of the solute moves at any given moment, each spot travels an average distance. Separation occurs as the solutes spread out due to random fluctuations, differences in particle movement, and variations in the uniformity of the sorbent layer (Santiago and Strobel, 2013).

Substances with a stronger attraction to the sorbent move more slowly, as they spend more time bound to the stationary phase. Conversely, those less attracted to the sorbent are more soluble in the mobile phase, allowing them to move more quickly

(Santiago and Strobel, 2013). This difference in interaction between the solutes, the sorbent, and the mobile phase enables the separation of compounds with varying properties.

Pagano et al. (2000) outlined the role of TLC in comparing modern imaging media, including jet inks and toners, underscoring its compatibility with various solvent systems and stationary phases. Also, Fatima (2020) has discussed about the application of TLC analysis in analysing blue ballpoint inks compositions.

2.5.3 Advanced Analytical Methods

Other advanced techniques, such as FTIR Spectroscopy, UV-Vis Spectrometry, and Raman Spectroscopy, have been employed for ink analysis. These methods provide molecular-level information about the colorants, resins, and other components in inks. Mass spectrometry techniques, including Direct Analysis in Real Time (DART-MS) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), further enhance ink differentiation by analysing organic and inorganic components (Khare et al., 2024).

FTIR spectroscopy is particularly useful in cases of forgery, counterfeiting, or document tampering, where ink examination can provide essential evidence. Inks used in documents, currency, and identification cards are often key in forensic investigations. FTIR is highly valued because it can determine the molecular structure of inks without damaging them. It works by exposing a sample to infrared light that induces molecular vibration and recording the wavelengths that are absorbed, producing a unique spectrum that serves as a chemical signature (Zawawi et al., 2021). This absorption provides valuable insights into bond strength and the presence of functional groups within a molecule.

Several factors influence vibrational frequencies, where the first key factor is the type of vibration. It involves stretching, bending, wagging, or twisting motions. Stretching vibrations generally occur at higher frequencies than bending vibrations, as stretching requires more energy to alter the bond length compared to altering the bond angle (LibreTexts, 2024a). Another crucial factor is bond strength or bond order, which directly impacts vibrational frequency. Triple bonds, such as C≡C and C≡N, vibrate in the highest frequency (2300-2000 cm^{-1}), following by double bonds, such as C=O and C=C (1900-1500 cm^{-1}), and weaker single bonds, like C-O (1300-800 cm^{-1}) (LibreTexts, 2024a).

The atomic weight also plays a significant role in vibrational behaviour, where lighter atoms vibrate at higher frequencies compared to heavier atoms (LibreTexts, 2024a). For instance, bonds involving hydrogen, such as C-H, N-H, and O-H, exhibit stretching vibrations at higher frequencies, typically above 2800 cm^{-1}. While electronegativity does not directly affect vibrational frequency, it influences absorption intensity (LibreTexts, 2024a). The polarity of a bond determines how strongly it interacts with infrared radiation. For example, C-C single and double bonds produce weak to moderate IR signals, whereas C-O single and double bonds generate strong signals due to their higher bond dipoles. As stretching vibrations occur, changes in the bond dipole enhance IR absorption intensity.

Figure 2.3 illustrates the main regions of the infrared spectrum where different types of vibrational bands are observed. The blue-coloured sections above the dashed line represent stretching vibrations**,** while the green-coloured area below the line corresponds to bending vibrations**.**

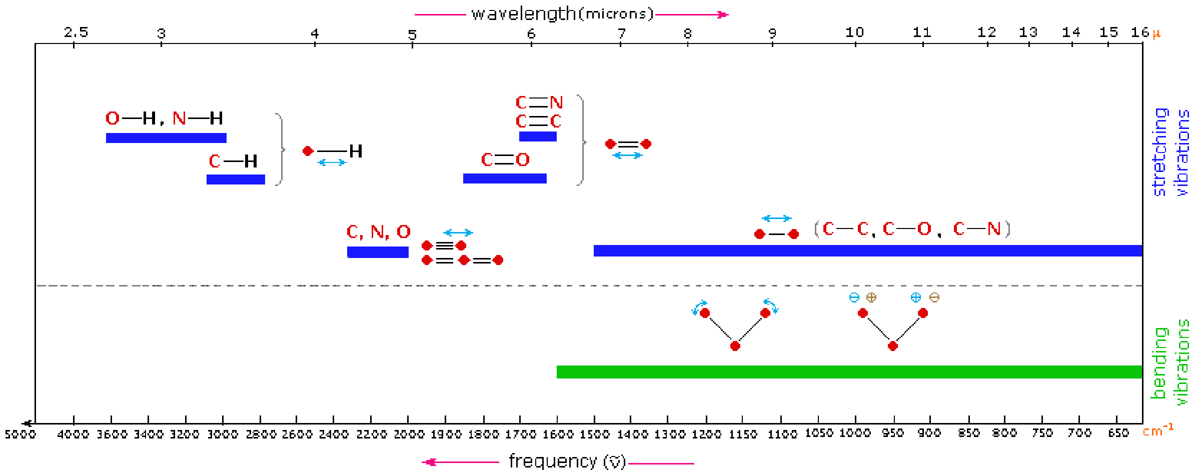

Figure 2.3*: The general regions of the infrared spectrum (LibreTexts, 2024b).*

Despite its advantages, FTIR has some limitations. The results are often specific to the inks studied, making it hard to generalize across different brands (Zawawi et al., 2021). Overlapping functional group signals can complicate the analysis, and the lack of comprehensive ink databases restricts its broader use. Future advancements should focus on building extensive ink reference databases and combining FTIR with other methods, like Raman spectroscopy or mass spectrometry, to improve reliability and accuracy. These developments would further establish FTIR as a vital technique in forensic ink analysis. In conclusion, FTIR provides a non-destructive way to examine ink composition, and ongoing advancements will enhance its ability to ensure document authenticity and integrity in legal cases.

Sharma et al. (2021) investigated various brands of red and blue stamp inks using a Bruker Alpha eco-ATR FT-IR spectrometer, employing several chemometric tools, including PCA, PCA-LDA, and PLS-DA. Similarly, Zawawi et al. (2021) analysed different types of printer inks, which are authentic, purportedly authentic, and counterfeit, through FTIR combined with PCA. In another study, Carvalho et al. (2019)

examined 37 brands of blue ballpoint pen ink and 27 brands of black ballpoint pen ink using ATR-FTIR spectroscopy, supported by HCA and PCA for data analysis.

Another study, such as that by Fla´via et al. (2015) investigated blue ballpoint pen inks using Raman spectroscopy combined with chemometric techniques. Also, Guo et al. (2024) focused on determining ink age by analysing the peak intensity of carbon black in neutral signature pens, utilizing both Raman spectroscopy and gas chromatography-mass spectrometry (GC-MS).

The physical and chemical properties of ink undergo changes over time, which are crucial for forensic examination. Studies like Ouyang et al. (2019) highlight the use of UV-Vis spectrophotometry to distinguish ink types and analyse aging processes. The absorbance ratio method correlates dye solubility with ink age, offering a reliable approach for relative dating within 10 weeks of stamping. Li (2014) further emphasized the significance of gas chromatography (GC) in analysing volatile components in stamp pad inks. The method effectively monitors solvent evaporation under natural and artificial aging conditions, enabling the determination of relative ink age up to three months. This approach is particularly useful for detecting document tampering when the purported date and the actual age of the ink differ.

2.5.4 Chemometrics Tools

PCA is a widely used statistical method in chemometrics for handling complex datasets with a large number of variables but relatively few samples (Sharma et al., 2021). PCA simplifies and interprets high-dimensional data by reducing its dimensions and representing it visually on PCA plots (Zawawi et al., 2021). PCA simplifies such datasets by reducing the dimensionality while preserving most of the original information. This reduction is achieved by transforming correlated variables into a new set of uncorrelated variables known as Principal Components (PCs). Each PC captures a specific proportion of the total variance in the data, with the first PC accounting for the largest variance, followed by subsequent PCs in descending order of variance contribution. In **Figure 2.4**, the data matrix X is an $n \times p$ matrix, where n corresponds to the absorbance values of the samples, and p represents the number of spectral ranges.

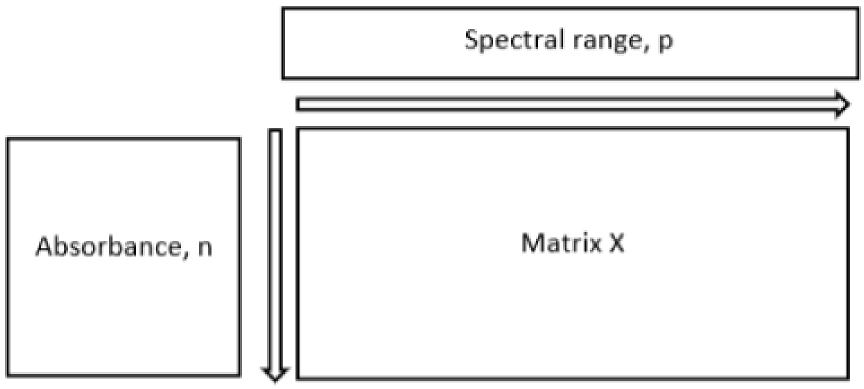

Figure 2.4*: Two-dimensional data array, X (Zawawi et al., 2021).*

The graphical representation of samples against their PCs provides insights into the relationships between samples, enabling classification and clustering. PCA also facilitates the detection of outliers and highlights similarities and differences among samples, making it a valuable tool for exploratory data analysis and pattern recognition in chemometrics. The method's ability to condense high-dimensional data into interpretable components with minimal information loss has established its importance in various applications, including spectral analysis and sample identification.

HCA is a clustering technique used to explore the organization of samples into groups and subgroups, revealing a hierarchical structure (Granato et al., 2018). The results of HCA are typically displayed as a dendrogram, a tree-like diagram that visualises the relationships and clustering of samples.

HCA employs two primary approaches for grouping: agglomerative and divisive as shown in the **Figure 2.5**. In the agglomerative method, each sample initially forms its own cluster, and clusters are progressively merged based on their similarities. Conversely, the divisive approach starts with all samples in a single cluster and recursively splits them into smaller clusters.

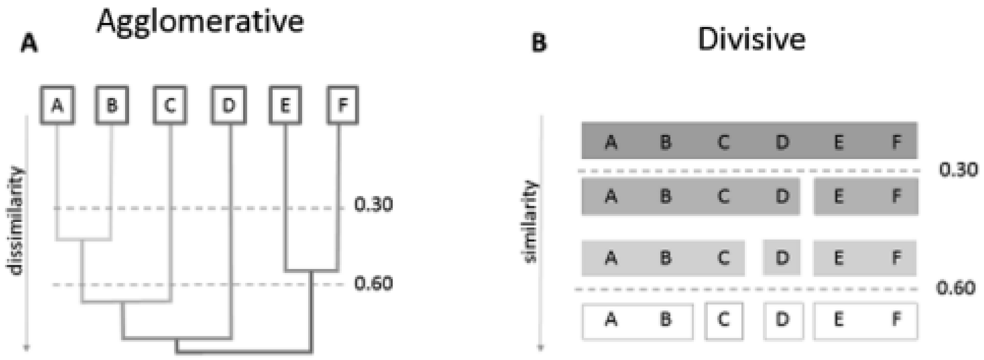

***Figure 2.5**: HCA dendrogram for agglomerative algorithm (A) and divisive algorithm grouping flow (B) (Granato et al., 2018).*

The clustering process relies on a chosen distance metric to measure the similarity or dissimilarity between samples, with commonly used metrics including Euclidean, Mahalanobis, and Manhattan distances (Granato et al., 2018). Additionally, the linkage criterion determines how clusters are merged or split, with popular methods being complete, single, average, and Ward's linkage. Ward's method, which optimizes a specific target function, is often selected for its effectiveness in minimising within-cluster variance.

CHAPTER 3 : METHODOLOGY

3.1 Research Design

This study investigated the forensic characterisation of black stamp pad ink and printed inks by analysing their physical and chemical properties. Methods included sample preparation, microscopic observation, chemical profiling using TLC analysis and ATR-FTIR spectroscopy were performed. Furthermore, chemometrical analysis such as PCA and HCA were applied to statistically interpret the data, providing insights into the compositional differences across the ink samples.

3.2 Apparatus and Materials

The materials and apparatus used in this study include iK Yellow unlined A4-size paper (80 GSM), Artline® black stamp pad ink (No. 00 EHJ-1) manufactured by Shachihata Inc., Japan, and a rubber stamp device with the word 'SAMPLE' (**Figure 3.1**). Printing was performed using inkjet printers (Canon Maxify MB5170 for CMYK and Ricoh Aficio MP 4002SP for black cartridge inks) and a Canon ImageRunner Advance C5051 laser printer for both CMYK and black cartridge inks.

Figure 3.1*: The rubber stamp with the word 'SAMPLE'.*

Analytical tools included a 3-in-1/2-in-1 X4 USB Digital Microscope and an ATR-FTIR Lumos spectroscopy (Bruker, Germany). TLC was carried out using aluminium plates, supported by additional laboratory equipment such as beakers, measuring cylinders, glass vials, aluminium foils, forceps, and droppers. For sample handling, gloves and haematocrit tubes were utilized.

The study also employed various chemical reagents, including ethanol (HmBG, Selangor), ethyl acetate (Merck, Germany), chloroform (Merck, Germany), hydrochloric acid (HmBG, Selangor), and n-butanol (Merck, Germany). 50 mL of 2N hydrochloric acid was prepared by adding 8.33 mL of hydrochloric acid to 41.67 mL of distilled water. These chemicals were stored in reagent bottles and used in the TLC analysis. Together, these materials and apparatus formed the foundation for conducting the forensic analysis of black stamp pad ink and printed inks.

3.3 Sample Preparation

3.3.1 Hand-Stamped Impressions

Seven black hand-stamped impressions were stamped on one piece of 80 gsm unlined A4 paper using the Artline black stamp pad ink, as shown in **Figure 3.2**. Six additional papers were prepared, each with one hand-stamped impression using the same ink and stamp device, as illustrated in **Figure 3.3**. All ink samples were stamped using the same rubber stamp device, under identical conditions, and by the same person to minimise variations in applied pressure. To eliminate any substrate variability, all A4 unlined white papers used in the study were sourced from the same batch.