COMPARISON BETWEEN BLUE BALLPOINT PEN AND BLUE GEL PEN INKS USING STEREOMICROSCOPY, VIDEO SPECTRAL COMPARATOR, ATR-FTIR, THIN LAYER CHROMATOGRAPHY AND CHEMOMETRICS TECHNIQUE

by

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List of Abbreviations

CCID	Commercial Crime Investigation Department
CD	Compact Disc
DP	Discrimination Power
FORAM	Raman Spectral Comparator
ATR-FTIR	Attenuated Total Reflectance- Fourier Transformer Infrared
GC-MS	Gas Chromatography- Mas Spectroscopy
HCA	Hierarchical Clustering Analysis
HCl	Hydrochloric Acid
HPLC	High Performance Liquid Chromatography
IR	Infrared
MALDI-MS	Matrix-assisted Laser Desorption/Ionisation-Mass Spectroscopy
OVD	Optically Variable Device
PCA	Principal Component Analysis
Rf	Retention factor
TLC	Thin Layer Chromatography
UV	Ultraviolet
VSC	Video Spectral Comparator

List of Symbols

RM	Ringgit Malaysia
%	Percentage
×	multiply
°	degree
nm	nanometre
g	grams
mm	millimetre
ms	millisecond
μL	microlitre
cm	centimetre
mL	millilitre
=	equals
-	substract
+	add
C-H	Hydrogen-carbon bond
C-O-C	Ether functional group
C=C	Carbon-carbon double bond
C=O	Carbonyl functional group
cm^{-1}	wavenumber

Abstrak

Pen telah digunakan sebagai alat untuk membuat perubahan pada dokumen semasa pemalsuan. Kemunculan dakwat pen hibrid yang mempunyai kedua-dua ciri dakwat pen gel dan pen mata bulat telah menyebabkan analisis diskriminasi dakwat tercabar. Oleh itu, kajian ini bertujuan untuk membandingkan ciri-ciri fizikal dan kimia dakwat pen mata bulat dan dakwat pen gel yang berwarna biru melalui profil dakwat mereka yang dihasilkan melalui empat teknik yang berbeza, iaitu mikroskopi, *Video Spectral Comparator* (VSC), ATR-FTIR dan kromatografi lapisan nipis (TLC). Sepuluh pen mata bulat dan sepuluh pen gel yang berwarna biru telah dipilih secara rawak tanpa mengira jenama. Pemeriksaan optik menggunakan mikroskopstereo dan VSC-6000, TLC yang menggunakan dua sistem pelarut yang berbeza dan spektroskopi ATR-FTIR telah digunakan untuk menganalisis semua sampel. Keputusan ATR-FTIR dan VSC microspectroscopy telah dianalisis dengan menggunakan *Principal Component Analysis* (PCA) dan *Hierarchical Clustering Analysis* (HCA) untuk membuat perbandingan dan diskriminasi. Keputusan menunjukkan bahawa profil dakwat pen yang dihasilkan dengan menggabungkan ciri-ciri mikroskope, pendarfluor, spektrum FTIR, kelarutan dakwat pen dan kombinasi bahan pewarna dakwat pen gel dan pen mata bulat berbeza walaupun pada semua pen ini kelihatan sama secara mata kasar. Ini menunjukkan bahawa gabungan teknik membenarkan diskriminasi yang lebih baik di kalangan sampel yang diuji.

Abstract

Pens have been used as tools to make alterations on documents during the act of forgery. The emergence of hybrid pen inks which exhibits both characteristics of gel pen and ballpoint pen inks has imposed challenges to ink discrimination. Therefore, this study aims to compare the physical and chemical characteristics of blue ballpoint pen inks and gel pen inks of similar hue through their ink profiles generated by four different techniques, namely microscopy, video spectral comparator (VSC), ATR-FTIR and thin layer chromatography (TLC). Ten blue ballpoint pens and ten blue gel pen inks were chosen randomly regardless of brands. Optical examination using stereomicroscope and VSC-6000, ATR-FTIR spectroscopy as well as thin layer chromatography using two different solvent systems were employed to analyse all ink samples. Results of ATR-FTIR and VSC microspectroscopy were statistically analysed using principal component analysis (PCA) and hierarchical cluster analysis (HCA) respectively to ease comparison and discrimination. The results show that the ink profiles of the pens which were created by combining the microscopical characteristics, fluorescent characteristics, FTIR spectra, ink solubility and combination of colourants used (dye or pigments) in gel pens and ballpoint pens vary despite the fact that all the pens visually appear to be of the same colour. This indicated that a combination of techniques provided better discrimination among the samples tested.

CHAPTER 1

Introduction

1.1 Background of Study

A document is any object which contains marks, symbols or signs which are intended to convey meaning or message to another person (Hilton, 1992). A document does not necessarily have to be written on a paper. Even graffiti art on walls, tattoos on skin, and carved letters on tombstones can be categorised as documents (Hilton, 1992). A document can be typewritten or handwritten with a pen, pencil or ink. Many documents are important in financial, legal, business, social and person affairs of an individual.

A questioned document is any document which its authorship or authenticity has been disputed (Koppenhaver, 2007). A document can be forged or altered to gain monetary profit or other illegal purposes. Alteration can be done by removing certain portions of the document, obliterating the contents using an opaque material, over-writing, extending or interlineating portions of letters on the documents and tampering (Hilton, 1992). An additional interlineation can change the details in a document. Usually, alterations are made carefully by the criminals in a way that does not instigate suspicion to the recipients or victims.

Various type of pens such as ball point pens, gel pens, and fountain pens have been used as a tool to write as well as to make alterations on documents. The pens used to alter a document may appear optically similar to the original pen ink entries on the documents when viewed under naked eyes. Hence, it is vital to discriminate pens of different entries to prove that alteration has been made on the documents. Therefore, determining the specific type of pen could be useful in investigations.

Ink of different pens has different composition of components (Brewer *et al.*, 2005). Various techniques are routinely used in forensic laboratories for ink analysis. Microscopic examination, optical techniques, chemical techniques and many analytical instruments can be used either alone or in combination to generate a 'fingerprint-like' profile that allows discrimination of inks from different entries on questioned documents. This present study employs four different techniques, namely microscopical technique, optical technique, thin layer chromatography and Fourier-transform infrared spectroscopy (FTIR) to compare ten blue ballpoint pen inks and ten blue gel pen inks of different and same brands which can be found in the market. The inter-brand variation and intra-brand variation of the inks are studied by comparing their profiles to each other.

1.2 Problem Statement

According to Commercial Crime Investigation Department (CCID), acts involving forgery and counterfeiting are categorised as commercial crimes and these type of crimes have been reported to have costed nearly RM1.755 billion in 2013 (Gannetion *et al.*, 2015). Department of Chemistry Malaysia (Jabatan Kimia

Malaysia) reported that handwriting, signature and ink analysis are the three most frequently encountered cases received by the Questioned Document Examination Unit. In 2012 alone, more than 400 cases involving ink and printer analysis were submitted to the department.

The emergence of hybrid pen inks having both the characteristics of gel pen and ballpoint pen inks has made differentiation of ink entries on altered documents difficult. Production of new writing tool could make activities of a forger more favourable (Morsy *et al.*, 2005). This poses greater challenge to document examiners. In order to minimise production cost, some manufacturers use the same ink but with different brand names (Neumann and Margot, 2009) making ink analysis and comparison even harder because it complicates both identification and comparison processes as two different entries may give the same analytical results.

Some gel pen inks are indistinguishable to most ballpoint pens under naked eyes (Houck, 2015) as they give similar luminescence characteristics when viewed under different light sources. Hence, a systematic forensic comparison between the profiles of gel pen inks and ballpoint pen inks is important. Optical and microscopical techniques may not be sufficient to distinguish the inks. Additional chemical and analytical tests shall be done in combination for a more defensible conclusion.

To date, most researches focused on the characterisation and analysis of ballpoint pen inks. Limited literatures found on studies involving gel pen inks examination. Thus, this study focuses on comparing the physical and chemical characteristics of blue ballpoint pen inks and gel pen inks that appears similar to the naked eyes by employing four different techniques.

1.3 Objectives

1.3.1 General objectives

To compare the ink profiles of blue gel pens and ballpoint pen inks using stereomicroscopy, video spectral comparator (VSC), ATR-FTIR and thin layer chromatography (TLC).

1.3.2 Specific objectives

1. To study the inter-brand and intra-brand variations of blue gel pen inks
2. To study the inter-brand and intra-brand variations of blue ballpoint pen inks
3. To create ink profile for effective discrimination of ballpoint pen inks and gel pen inks
4. To identify the differences in characteristics of blue ballpoint pen inks and blue gel pen inks of same and different brands.

1.4 Significance of this study

Ink is an important component in a document. Ink can be deposited on a document using various types of writing tools regardless of colour and brand. Additional marks can be made by forgers on a document to alter its details using a different similar looking ink as the original entry regardless of the type of pen.

Hereby, it is important to differentiate and discriminate the new ink entry with the original ink entry to prove alteration on the questioned document. This can be done by comparing their analytical profiles of the original and new ink entries. Comparison can be either done by comparing questioned ink profiles to database or comparing questioned ink profile to reference ink profile to establish its origin (Neumann and Margot, 2009). Different inks are expected to produce different ink profile as their composition varies. Hence, this study is very important to prove that inks can be easily discriminated by creating an ink profile which is merely a compilation of different analytical results regardless of pen type and brands.

CHAPTER 2

Literature Review

2.1 Questioned Documents

Documents are anything which has marks, symbols or signs that serve the purpose of conveying message or meaning to somebody (Kobilinsky, 2011). On a document, message or information occurs at two levels where the first level can be obviously seen whereas the second level is less obvious and it may need the assistance of a device or lighting source to view the information (Dat *et al.*, 2005). Documents can be found in different formats such as letters, envelopes, packages, calendars, diaries, ransom notes, suicide note, receipts, cheques, identification cards, contracts, wills, certificates, dollar notes, financial documents, CDs, stamps, graffiti, stamps and business records (Kelly and Lindblom, 2006a; Siegel, 2016). Documents which authenticity and authorship have been disputed are termed as questioned documents (Kelly and Lindblom, 2006a).

More often than not, questioned documents are linked with fraud, forgery, counterfeiting, impersonation, blackmail, threats, and murder (Kelly and Lindblom, 2006a). Alteration or obliteration of important document contents may inflict negative effect on a person's wellbeing, wealth, property, possession and reputation (Kelly and Lindblom, 2006a). On that account, determining the authenticity and authorship of a document is very important. In forensic science, questioned document examination caught the attention of many law-makers and forensic scientist after forgery was declared as a statutory offense in 1562 by the English Parliament (Levinson, 2001).

A typical document can be made from different types of papers, different combinations of ink entries and could also contain correction fluid, adhesives as well as stains (Kobilinsky, 2011). Hence, forensic questioned document examination can be divided into handwriting and non-handwriting analysis. Non-handwriting analysis focuses mainly on the composition of materials used in the making of the documents (Kobilinsky, 2011). Thus, one of the roles of a questioned document examiner is to determine the manufacturer of the documents, type of instruments or writing tools used to produce the documents, authenticity as well as the authorship of the documents in questioned and make necessary comparison with sufficient amount of reference standards (Siegel, 2016).

2.2 Ink analysis and its forensic Significance

In forensic document examination, instruments used to produce the document should be determined for investigation purposes. This includes the writing instruments used, entries of different types of ink, the type of paper used to create the document, and the seals on the document (Braz *et al.*, 2013).

Ink is a general aspect of documents (Jones and McClelland, 2013). For the past decades, ink analysis has assisted forensic scientists establishing authenticity of questioned documents (Morsy *et al.*, 2005). In forensic laboratories, ink analysis helps in criminal investigation by giving us information about possible alteration such as additions or overwriting on the document. If there are more than two entries applied on a document, ink chemical component determination, ink source determination, chronology of ink entries and determination of the approximate age are important information to assist the court of law in making decisions (Braz *et al.*, 2013; Jones and McClelland, 2013). This is based on the fact that, different inks have different compositions and formulations; hence, making them unique and useful in forensic case works (Brewer *et al.*, 2005; Senior *et al.*, 2012).

In general, if the ink on the suspected part of questioned document differs from the reference ink sample, it can be said that the document has been altered since the ink could not have originated from the same source (Tilstone *et al.*, 2006). Even if two inks appear similar in colour, their chemical compositions, constituents and substances used in their manufacturing processes may differ (Mohamed Izzharif *et al.*, 2013), which could be explored further using various analytical methods. In forensic laboratories, inks can be discriminated based on the differences in colour, luminescence, fluorescence, transmission, reflection, emission and absorption of radiation (Feraru and Meghea, 2014), especially in discriminating inks of similar colours. Combination of analysis output from several tests produces an ink profile to assist forensic investigation (Chalmers *et al.*, 2012).

Ink analysis was believed to have started by just observing and examining documents photographically using different optical filters for enhancement (Chen *et al.*, 2002; Morsy *et al.*, 2005). In the past, the chemical tests were done mainly to qualitatively test for the presence of metals such as copper, vanadium and chromium back then (Chen *et al.*, 2002). These metals can be usually found in fountain pen inks (Chen *et al.*, 2002). Few decades backward, when the forensic community was lacking research and advancement, only non-destructive methods and simple optical visualisation were used (Chalmers *et al.*, 2012).

Ink analysis can be done either by destructive or non-destructive techniques. Destructive techniques usually involve prior sample preparation, mainly to extract ink out of the questioned document (Allen, 2015). Hence, non-destructive methods are always prioritised to prevent inflicting damage on the evidence material (Tilstone *et al.*, 2006). Any test which may cause changes to the original condition of a document shall be avoided by examiners (Morsy *et al.*, 2005) to preserve the document. Visual examination, video spectral comparator, vibrational techniques (FTIR analysis), thin layer chromatography, high performance liquid chromatography, GC-MS and attenuated total reflectance (ATR)-FTIR microspectroscopy are examples of techniques routinely used for ink analysis (Braz *et al.*, 2013). The analyses mainly tests for colour, chemical composition and age of ink (Tilstone *et al.*, 2006).

In forensic analysis, every technique has its own drawbacks and do not provide stand-alone individual information to characterise and identify inks (Morsy *et al.*, 2005). Nevertheless, according to Hilton (1992), it is likely for a chemist or a document examiner to distinguish two different inks, but it is not likely to establish the source of the ink through forensic ink analysis.

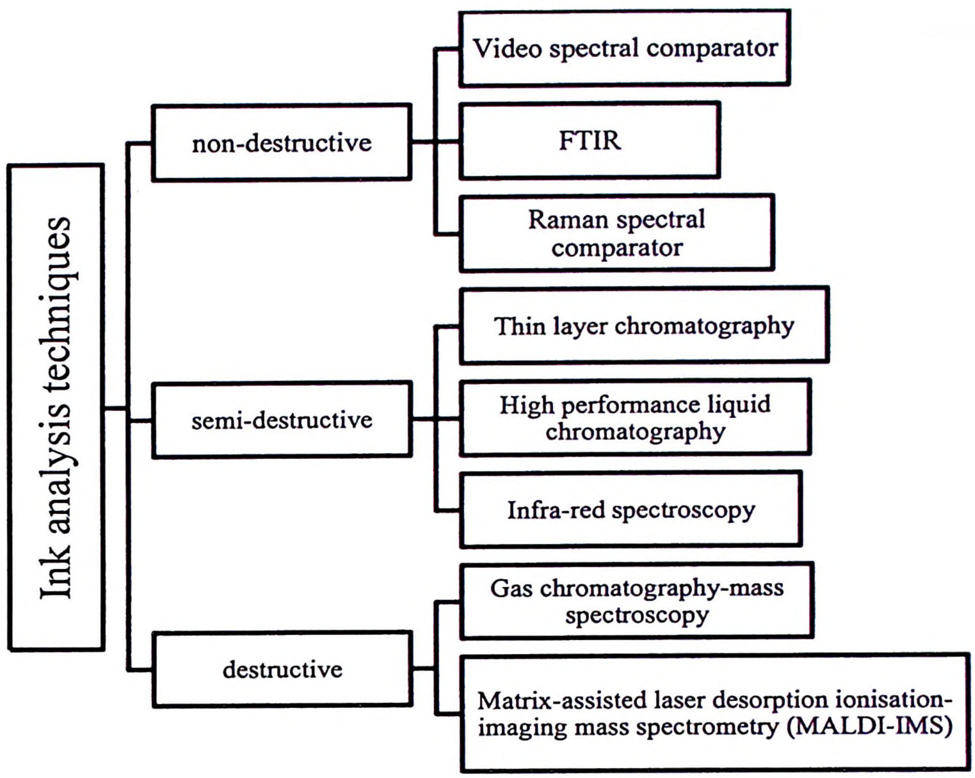

Figure 2. 1: Ink analysis technique classifications (Souza Lins Borba *et al.*, 2015)

2.3 Inks

According to Waite and Soanes (2007), ink is defined as coloured liquid which is used for writing, drawing and printing. Indian ink is the oldest ink produced using carbon black (soot from burnt oil) suspended in water along with additives like gums and varnishing components (Bell, 2008). Ink analysis focuses on determining specific chemicals contained in an ink (Brewer *et al.*, 2005). Dyes and pigments in the inks are responsible for their colour (Bell, 2013). Dyes dissolve in its solvent, whereas pigments remain suspended (Bell, 2013). When ink is deposited on a substrate, the solvent evaporates leaving behind the coloured particles (Bell, 2013).

Visually similar appearing inks differ from each other by a few physical properties including colour, density and intensity of colour, viscosity, surface tension, water fastness, light fastness, as well as fungal resistance (Claybourn and Ansell, 2000). Human eyes see colour when electromagnetic radiation from a particular region of electromagnetic spectrum reaches the sensory system (Bell, 2013). Colour of the inks perceived by human eyes is the product of absorption and reflection of light (Bell, 2013). Ink which comes with combination of different types of dyes and pigments may give different absorption characteristics.

There are nearly 12 classes of inks available in the market, but only four classes are commonly encountered in forensic caseworks (Tilstone *et al.*, 2006). The aforementioned classes of ink are ballpoint, liquid, printing and typewriter inks (Tilstone *et al.*, 2006). On some documents, different entries of pen can be differentiated by looking at the stroke width and defects on the strokes like gooping and striation within strokes (Hilton, 1992). Analytically, inks can be discriminated by looking at their composition of major (dyes and pigments) and minor constituents (impurities) (Liu *et al.*, 2006).

2.3.1 Ballpoint inks

Ballpoint pens were first invented in 1939 in Europe and were widely used in the United States in 1945 (Bell, 2008). The ballpoint pen inks in that era was only made of dye components in oil-based solvents like mineral oil, linseed oil, and recinoleic acid (Brunelle and Crawford, 2003). As the small steel ball at the tip of the pen rotates, ink flows out and spreads on writing material (Bell, 2008). The inks flow out via capillary action (Bell, 2008).

Ballpoint ink is a thick, quick-drying ink paste made-up of a complex mixture of dyes or pigments, solvents, resins, viscosity adjustors, ball lubricants (Dzulkiflee and Wan Nur Syuhaila, 2014). It may contain solubilisers, surfactants particulate material, fluorescers, glycols, antioxidants, glycerols, solvents and many other materials (Calcerrada and Garcia-Ruiz, 2015) to increase its desired properties. In general, the dyes usually makes up nearly 50% of ink composition (Houck, 2015) which are carried in the liquid portion of the ink known as 'vehicle' (Stefen, 2007). Additives can be driers, plasticisers, waxes, greases, soaps and detergents based on specific formulations (Djozan *et al.*, 2008) to prevent the ink from drying out too quickly while it is in the reservoir, do not spread out to the other side of page upon application, to fix the ink quickly on writing material after application (Dzulkiflee and Wan Nur Syuhaila, 2014), control the ink density or flow, and also to provide final appearance of the ink on the material (Calcerrada and Garcia-Ruiz, 2015). In short, the composition of ink components is adjusted to achieve desired characteristics such as the tackiness, drying, colour, cost, fluidity, and resistance to environmental factors such as light, heat, and moisture (Zlotnick and Smith, 1999). Although the previously mentioned components are commonly present in almost all ballpoint inks, their composition, ratio and amount differs (Chen, 2007). It is necessary for forensic scientists to know the composition of ballpoint inks to identify, characterise and compare inks during analysis (Calcerrada and Garcia-Ruiz, 2015).

Under low power microscope of 20× to 50× magnification, ballpoint pen inks gives glossy appearance with pasty-texture (Day *et al.*, 2005). Ink is only partly absorbed into the paper material due to its viscosity (Day *et al.*, 2005). During the process of writing using ballpoint pen, extra pressure is often applied, hence causing the ink to move to the edge of writings creating a halo in the middle (Day *et al.*, 2005). This is known as striation. Since, ballpoint pen inks are viscous and are not able to flow freely to feel the halo (Day *et al.*, 2005), striations can be seen in writings written using ballpoint pens under low power microscopes.

2.3.2 Gel pen inks

Gel pens are also common today that makes studies on the discrimination of gel pen inks of similar colour to be increasingly important in the field of forensic questioned document examination. Gel pens were first discovered in 1984 by Sakura Color Products Corporations in Japan who found a water-based pigment ink called Pigma (Mazella and Buzzini, 2005). Gel pen is smooth when writing and the manufacturing cost is not expensive (Brunelle and Crawford, 2003). Gel pen inks are water and solvent resistant (Bell, 2008), hence making it indestructible on paper material (Brunelle and Crawford, 2003). Gel pen inks are found to possess 'pseudoplastic' characteristics where it produces even ink lines or homogenous ink distribution upon writing (Brunelle and Crawford, 2003).

Unlike ballpoint inks, insoluble organic or inorganic pigments are used in the manufacture of gel pen inks (Brunelle and Crawford, 2003; Reed *et al.*, 2014). Therefore, thin layer chromatography is not a recommended analysis technique for ink discrimination (Weyermann *et al.*, 2012). Special pigments such as copper phthalocyanine (for blue inks), resins, water (60-80%), solvents, non-ionic surfactants, biocides, corrosion inhibitors, lubricants, emulsifying agents, pH buffers, polymerisation agents, pseudoplasticisers, sequestrants, and other additives make up gel pen inks (Liu *et al.*, 2006). Gel pen inks can be classified into three major groups, namely dye-based inks, pigment-based inks and hybrid-inks (Reed *et al.*, 2014) based on the colouring agent in its formulation.

In gel pen ink, the solvents used are water soluble (Brunelle and Crawford, 2003). Shear-thinning agents and plasticisers are additional additive components used in gel pen inks and this may make it to be different from ballpoint pen inks (Brunelle and Crawford, 2003). Li (2014) found that the chemical composition of gel pen inks resembles the composition of ballpoint pen inks.

Contrasting to the microscopic properties of ballpoint pen inks, gel pen ink does not appear glossy as it gets fully diffused into the paper material giving an evenly textured appearance (Day *et al.*, 2005). Since gel pen inks are free flowing, the ink fills the halo in writings (Day *et al.*, 2005). For this reason, striations are normally not seen in writings made using gel pens. Gel pen ink does not readily dissolve in water and solvents (Bell, 2008). This property of gel pen inks makes it suitable to create permanent writings. However, this can pose a challenge during forensic analysis as gel pen inks are difficult to be extracted out from the paper matrix prior to analysis (Bell, 2008).

2.4 Video Spectral Comparator

Video spectral comparator (VSC) is a imaging device mainly used to analyse inks, view security features on a document which are not normally visible to naked eyes or under normal lighting, and also to check for any visible evidence of alterations on a document (Mokrzycki, 1999). It is a multi-functional device (Aambo, 2010). The device is also called a comparator because it functions to compare the images or spectra of two or more different documents (Aambo, 2010).

The video spectral method is an *in-situ* non-destructive hyperspectral imaging method which uses IR absorbance, IR luminescence, UV and visible illumination to visually examine of questioned documents (Reed *et al.*, 2014). Lights of different wavelengths have different electromagnetic spectrum which can be distinguished by human eyes (Mokrzycki, 1999). VSC analyses ink entries based on their optical properties (Lacalamita, 2013). Inks appear differently at different light conditions depending on their optical properties (Lacalamita, 2013). Ink might absorb light and consequently appear darker, reflect light that makes it appears lighter, transmit light thus making it invisible or emit light at a different wavelength to cause fluorescent depending on its optical property (Lacalamita, 2013). VSC discriminates inks of similar colour based on these principles. In cases where ink entries are indistinguishable by VSC, chemical techniques such as thin layer chromatography (TLC) and high performance liquid chromatography (HPLC) can be employed for differentiation (Reed *et al.*, 2014)

VSC is equipped with different light sources like ultraviolet, infrared, spot light, and visible light which gives out light energy at different wavelengths. All these lightings may excite fluorescence or luminescence at different wavelengths with inks (Aambo, 2010). Modern VSC has a few types of build-in lighting system with varying positions; coaxial lighting, oblique lighting, transmitted, twin-side lighting or side-lighting and multi-angled lighting (Aambo, 2010). Table 2.1 shows the lighting directions in VSC and their functions.

Table 2.1: Table of lighting direction in VSC and their functions

Lighting	**Direction of illumination**	**Visualization**
Coaxial	Perpendicular	Retro-reflective features on documents
Side	Side (left or/and right)	Reveal different features on documents
Transmitted	Underneath/bottom	Reveal different features on documents (eg. difference in densities on a watermark)
Multi-angle/diffracted	Multi-directions	Optically Variable Devices (OVD)
Oblique	45°	Signs of indentations on documents

Spot lighting is high intensity lighting with narrow-band illumination which located directly above the document plate (Aambo, 2010). Filters can be used along with spot lamp to specifically define the desired wavebands for document examination (Aambo, 2010). The diffracted light or multi-angle LED light in VSC has the ability to illuminate light in different direction making it capable to visualise optically variable devices (OVD) such as pixelgrams, kinegrams and holograms (Aambo, 2010). At a suitable wavelength, VSC is capable of producing absorbance or reflectance spectrum which is useful in discriminating visually similar inks (Reed *et al.*, 2014). VSC is therefore described as a device which can differentiate inks effectively without sophisticated sample preparation step during analysis in forensic document examination laboratories (Reed *et al.*, 2014). Figure 2.2 illustrates the examination using video spectral comparator to detect alterations on documents.

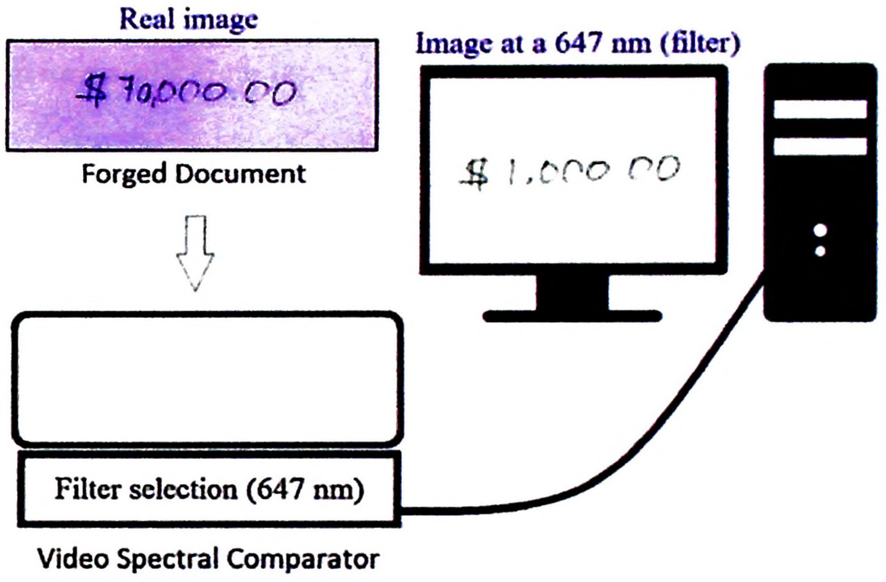

Figure 2.2: Examination using video spectral comparator to detect alteration of documents (Souza Lins Borba et al., 2015)

2.5 Raman Spectral Comparator (FORAM)

Raman spectral Comparator is a non-destructive technique for ink analysis which does not require prior sample preparation for analysis (Claybourn and Ansell, 2000). It can be used as a supplement to optical methods with advantage of being able to analyse even micro-regions of a document without damaging the original state of the document (Souza Lins Borba *et al.*, 2015). The resulting spectrum provides signature or fingerprints to inks of different entries allowing discrimination (Claybourn and Ansell, 2000).

In Raman spectroscopy, light is partially absorbed and partially emitted but at different wavelengths when light from a source is projected onto samples (Giles, 2016). The re-emission pattern of the light differs according to the molecular make-up of the ink components (Giles, 2016). The Raman Spectral Comparator is the improvised version of Raman spectroscopy which allows *in-situ* analysis of samples and this makes it a common instrument in forensic laboratories.

Fluorescence emitted by ink samples may affect the spectral quality to a certain extend (Souza Lins Borba *et al.*, 2015). To overcome this problem, baseline correction can be performed using lower power laser excitation wavelengths (Claybourn and Ansell, 2000) and helps to reduce signal-to-noise ratio (Feraru *et al.*, 2013).

FORAM is built with three different choices of laser wavelengths (532 nm, 685 nm and 785 nm), an adjustable stage to hold documents (A4 sized), special adjustments for laser probe alignment onto the documents which is about five microns in diameter, an integral video microscope also and software which allows multi-spectral visual comparison, peak-to-peak correlation and database cross-matching facility (*Questioned Documents*, 2015). The thin laser beam can be shone precisely onto to the part of document desired to be analysed (Giles, 2016).

2.6 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy is a non-destructive technique routinely used in forensic ink analysis. The spectroscopy works based on the interaction of infrared light with the samples to be tested (Smith, 1995). When matter receives electromagnetic radiation from the infrared (IR) region, the matter can be excited to a higher energy state after absorbing the radiation (Smith, 1995). The intensity of absorption strongly depends on the molecular nature of the matter (Smith, 1995). This results in an output called spectrum which consists of peaks and troughs (Allen, 2015). Each peak represents vibration frequencies of molecular bonds in the sample. If the chemical composition differ, different ink samples may give different, unique set of peak and troughs which acts like a 'fingerprint' allowing comparison (Allen, 2015).

An FTIR instrument consists of a IR light source, circular aperture, beam splitter, movable mirror, fixed mirror, sample holder, reference holder and a detector as illustrated in Figure 2.3.

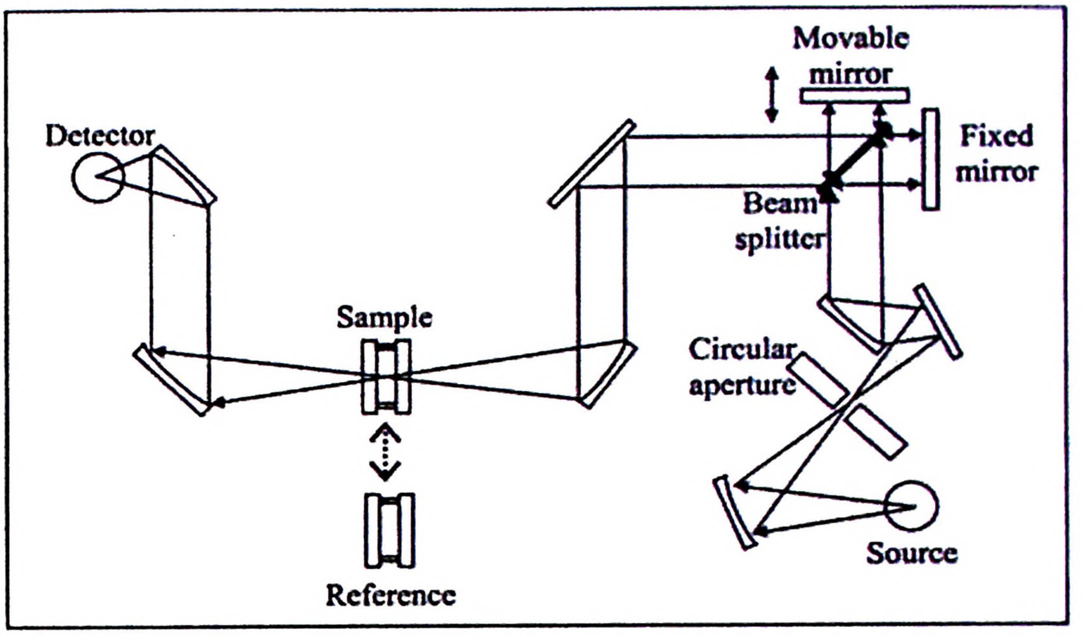

Figure 2.3: FTIR spectrometer component arrangement diagram (Gauglitz and Vo-Dinh, 2006)

The fixed mirror, movable mirror and beam splitter make up an interferometer (Gauglitz and Vo-Dinh, 2006). IR beam from its source will be divided into two parts with equal intensity and reflected back by the two flat mirrors; fixed and movable mirrors, which combines and gives rise to constructive and destructive interference (Gauglitz and Vo-Dinh, 2006). The product beam is called interferogram. The interferometer is also important in deciding the resolution of the spectrum produced by the spectrometer (Gauglitz and Vo-Dinh, 2006). Unlike the traditional IR spectrometer, the FTIR technique is useful in forensic document examination because it is non-destructive, precise, allows for quick analysis, and works fine on small samples.

2.7 Thin Layer Chromatography (TLC)

Thin layer chromatography employs a solid stationary phase and a liquid mobile phase (Pavia, 2005) to separate analytes. The technique was first used in 1966 by Tholl to analyse ink on questioned documents, which was proven to be an effective technique to separate dye as well as other volatile components in ink mixture (Morsy *et al.*, 2005). Ink samples are adsorbed on the stationary phase and separated into components by the upward bulk movement of mobile phase through capillary action (Sherma and Fried, 2003). The stationary phase of thin layer chromatography usually consists of an even layer of adsorbent material, usually silica gel, alumina or nitrocellulose on a supporting material like plastic, aluminium or glass plate (Pavia, 2005). The degree of sample separation highly depends on the affinity towards the stationary phase relative to mobile phase (Sherma and Fried, 2003).

In principle, higher the polarity of the analyte, the stronger the affinity of the analyte towards the plate, the longer time it takes to migrate to the other end of the plate. Therefore, suitable solvent system should be used as the mobile phase to ensure good resolving power during chromatography (Tilstone *et al.*, 2006). Polarity of the solvent system can often be adjusted by using different ratios of solvents of different polarities to attain separation of the best resolution (Djozan *et al.*, 2008).

Albeit its lack of automation, thin layer chromatography is still a preferred technique in ink analysis (Brewer *et al.*, 2005). However, TLC is a qualitative method making quantitation components present in the ink samples impossible (Djozan *et al.*, 2008). In routine ink analysis, the technique is used to separate coloured and non-coloured components which make up the ink mixtures (Tilstone *et al.*, 2006). Prior to analysis, ink samples are scraped out from the questioned document and extracted using suitable solvent like methanol and pyridine (Djozan *et al.*, 2008).

Upon TLC, comparison is made by calculating the retention factor (Rf) of the separated components (Djozan *et al.*, 2008), thus distinguish similar coloured pen inks, paints, fibers and other materials found in the crime scene (Djozan *et al.*, 2008). Previous literature has shown that forensic discrimination of gel pen inks using thin layer chromatography technique is extremely difficult (Brunelle and Crawford, 2003), especially when pigments are used as colourants instead of soluble dye components (Brunelle and Crawford, 2003).

CHAPTER 3

Methodology

3.1 Research Design

This research is an experimental study. The experiment was done using two types of analytical techniques, i.e. destructive and non-destructive techniques. A straight horizontal line of 1 mm thick was drawn on a 70 g PaperOne brand white A4 paper using ten blue ballpoint pens and ten blue gel pens (refer Figure 3.1 and Figure 3.2). All the pens were given specific labels as stated in Table 3.1. The gel pen inks and ballpoint pen inks were written on separate papers and labelled as 'GEL PEN INKS' and 'BALL POINT INKS'. Lines were drawn at least 15 mm apart. Each ink entries of ballpoint pens and gel pens were labelled according to their respective brands (refer Figure 3.3 and Figure 3.4). Papers of the same type and brand were used throughout the experiment to avoid matrix interference.

Figure 3.1: Ballpoint pen samples used in this experiment. From left, BGS1, BGS2, BP1, BP2, BPM1, BPM2, BPM3, BFC1, BFC2 and BS1

Figure 3.2: Gel pen samples used in this experiment. From left, GFC1, GP1, GP2, GP3, GC1, GC2, GC3, GM1, GT1 and GR1