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CHARACTERISATION OF BALLPOINT PEN INK USING VSC

DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT FOR THE DEGREE OF BACHELOR OF SCIENCE (HONS) IN FORENSIC SCIENCE

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List of Abbreviations

CE	Capillary electrophoresis
EB	Binding energy
FC	Faber- castell
G	G-soft
FDE	Forensic document examiner
FTIR	Fourier infrared spectroscopy
GC/MS	Gas chromatography/mass spectroscopy
HPLC	High performance liquid chromatography
IR	Infrared
LCD	liquid crystal display
P	Pilot
PM	Papermate
S	Stabilo
SEM	Scanning electron microscopy
TLC	Thin layer chromatography
UV	Ultraviolet
UV-Vis	Ultraviolet visible
UV-Vis-NIR	Ultra-visible-near infrared spectrophotometry
VIS	Visible
VSC	Video spectral comparator
QD	Questioned document
XRF	X-Ray fluorescence

List of Symbol

%	Percent
/	Divide
=	Equal
Cm	Centimeter
N	Number of possible samples pairs
Nm	Nanometer
TM	Trade mark
X	Times

Abstrak

Analisis dakwat adalah salah satu fokus utama dalam peperiksaan dokumen forensik. Keupayaan untuk membezakan satu jenis dakwat dari yang lain sangat berguna dalam pelbagai kes seperti "document alteration" iaitu pengubah suaian terhadap sesuatu dokument. Pelbagai jenis teknik telah dibangunkan untuk menghasilkan keputusan yang cemerlang dalam membezakan dakwat yang mempunyai warna yang sama. Kajian ini memberi tumpuan terhadap mendiskriminasikan dakwat dengan kaedah tidak memusnahkan yang merangkumi pemeriksaan optik di bawah sumber cahaya yang boleh dilihat dan ultraungu (UV) dan mikro-spektrometri dengan menggunakan Video Perbandingan Spektra (VSC) 6000. Kuasa diskriminasi (DP) telah digunakan untuk meningkatkan kualiti VSC dalam membezakan visual dakwat warna yang sama.

Melalui perbandingan spektrum, warna dakwat yang sama iaitu biru dapat dibezakan mengikut ciri-ciri dakwat yang diperolehi dari setiap jenama yang berbeza. Spektrum dibandingkan dan DP yang diperolehi ialah 93.33%. Melalui perbezaan spektrum, dakwat pen mata bulat dari model dan jenama adalah sama dalam corak keseluruhan mereka. Penampilan fizikal mereka menunjukkan beberapa ciri-ciri yang sama di antara jenama yang sama dan juga pelbagai jenis jenama yang lain dalam pemeriksaan mikroskopik. Walaupun begitu, dakwat warna yang sama sukar untuk dibezakan di bawah cahaya UV kerana semua pen ini tidak berkilau. Kesimpulannya, untuk kaedah yang tidak memusnahkan, VSC adalah teknik yang paling lebih baik, bukan sahaja kerana ia adalah mudah untuk dikendalikan, ia juga tidak mengambil masa yang lama untuk memproseskan data.

Abstract

Inks analysis is one of the main focuses in forensic document examination. The ability to differentiate one kind of ink from another can be quite useful in many cases such as document alteration. Many kind of technique has been developed in order to produces an excellent result in differentiating similar colour inks. This research will be focus on the ink discrimination by non-destructive method which includes optical examination under visible light source and ultraviolet (UV) and micro-spectrometry by using Video Spectral Comparator (VSC) 6000. Discrimination power (DP) was used to improve quality of VSC in differentiating visual of similar colour inks.

The characteristic of ink was able to discriminate similar colour ink which is blue from different brands by means of differences in spectra. The spectra were compared and DP of 93.33% was obtained. The spectra of ink from different individual ballpoint pen of the same model and brand were similar in their overall pattern. Their physical appearance shows some similar properties between same brands as well as different kind of brands in the microscopic examination. Despite that, similar colour ink is hard to be differentiating under UV light because all of these pens do not fluoresce. As a conclusion, for non-destructive method, VSC would be most preferable technique, not only because it is easy to handle, it is also time efficient.

Chapter 1

Introduction

1.1 Why ink analysis?

Ink source identification on a variety of documents is very useful in forensic document examination. The ability to differentiate certain kind of ink from others can be very useful for many reasons. One of the examples is document alteration by writing with a pen of similar colour. The composition of ink dye can therefore help to discriminate the types of pen used. Not only that, by comparing inks between an original and a copy or two documents believed to have the same author can determine the relationship between two samples in a forgery case. By analysing the raw colourant material which is available during a specific historical period, sample authentication can also be done and tested (Egan *et al,* 2005). The ability to differentiate between inks can therefore allow the forensic scientist to evaluate the authenticity of a suspicious document (Feraru & Meghea, 2014).

In the area of forensic questioned document (QD), inks analysis is mainly focused on comparing, identifying and discriminating the ink obtained from writing instrument used to write on a document (Ismail *et al,* 2014). One of the aims during forensic examination is to obtain as much information regarding the document as possible without altering or damaging the document if possible so that the documents are not destroyed in the course to identify fraud, by forging documents (Rankin, 2005).

This research focuses on the part of ink analysis by comparing and further discriminating the ink samples of ballpoint pen with similar colour. Visual examination under normal condition might not be able to detect the minor differences on writing that are produced by pens of similar colour. Using suitable analytical methods, forensic document examiners attempt to discriminate between them i.e. the original and added writing.

1.2 Advancement of pen technology

Over the years, technological developments have rapidly expanded the range of pen designs and ink composition used throughout the world. Quill and nib pens have given way to other classes of writing instruments such as the ballpoint, roller ball and gel pens. The newer pens have different requirements for the properties of their writing inks. These inks may contain many substances aiming to improve ink characteristic, thus improve the quality of the pen as a writing tool (Halim *et al,* 2013).

Among different types of pens, the most widely used and thus frequently encountered in forensic document examination is probably ballpoint pen. This might be due to its availability and popularity in the market compared to the other pens (Causin, *et al.*, 2008). Hence, this study was conducted based on the discrimination of ink from ballpoint pens. Although many companies are offering different model of ballpoint pens in Malaysia, only five types of models from five different firms were chosen for this study as they appeared to be the major brands. These are Faber-Castell, G'soft, Kilometrico, Pilot, and Stabilo as they are mostly available in markets. Three basic colours, i.e. black, blue and red were selected in this study.

1.3 Composition of Inks

In forensic science, there are many area of study regarding question document, one of the important aspects is the analysis of ink, paper, and their interaction. Its main purpose in document identification is to prevent adulteration. Currently, the inks used in modern pens contain many chemical substances including colourants, vehicles, and additives, which are adjusted in composition to produce the desired writing characteristics (Hunger, 2003).

Generally, the most important component is the colouring material or also known as colourant which consists of dyes and pigments or a combination of them. Colourants are compounds that give ink the desired colour and can include any or all of the following chemical classifications: pigments and/or acidic, basic, azoic, direct, disperse, reactive, and solvent dyes. In ink analysis, colourant is often being focused on because of their properties of light-absorption and emission which can be detected by multiple analytical methods.

Both dyes and pigments are not the same; dyes are compounds that are solubilised in the ink vehicle while pigments are insoluble multi molecular granule which are finely ground in the vehicle. The fluidity as well as the drying characteristic of the ink will change if the composition of the vehicle is adjusted. Basically vehicle consists of oil, solvent and resins. The solvent in the vehicle allow the ink to flow and carry the colourants to the material surface. In date-of-origin investigation, solvent are the primary ingredient to be analysed (Egan *et al,* 2005).

Not only that, other substances are also used to adjust the characteristics of the ink, such as driers, plasticisers, waxes, greases and surfactants in which called additives (Silva *et al,* 2014). Additives can serve as flow (viscosity) modifiers, surface activators, corrosion controllers, solubility enhancers, and preservatives. Detection of these additive compounds can greatly aid forensic examiners because the compounds can be manufacturer-specific. Their identity is often a highly guarded secret in ink formulations, as are the colourants themselves (Egan *et al,* 2005).

1.4 A Brief History of Ballpoint Pen

The ballpoint pen we used today was invented by a man named Ladislao Jose Biro and commercialised in Hungary in 1938. The principle of the ballpoint pen was originally patented by John Loud in 1888 and in 1916 by Van Vechten Riesberg, but neither of these products was exploited commercially (ASME, 2005).

1.4.1 Ballpoint pen

Ballpoint pens work by utilising tiny metal ball bearings present at the tip of a pen. The ball is commonly made from tungsten carbide, which is often used to make armor piercing bullets. After the material has been shaped, it is then get polished (Smallwood, 2014).

The polished ball is then loaded into a socket. Due to the fact that the space available between these two parts is supposed to be virtually, they need to be accurate to within a thousandth of a centimetre on the ball (Smallwood, 2014). If any flaws are present, the ink would not flow properly, risking also the ink being exposed to the air which can dry it out. By gravity, the ink will be pulled down onto the ball which transfers ink as it is dragged along or pressed against paper or a comparable surface. This allows ballpoint pens to write around 100,000 words each (Smallwood, 2014).

1.5 Ink Analysis

A ballpoint pen ink consists of synthetic dyes (acidic and/or basis), pigments (organic and/or inorganic) and a range of additives. Inks of similar colour may consist of different dye composition and are frequently the subjects of forensic examinations. Other focus beside ink is the detection of alteration and addition to a document when it was written. When two inks are compared, both chemical and physical examination are needed in which a various kind of technique was used such as optical microscopy, infrared reflectance and luminescence, ultraviolet, fluorescence, solubility tests, and thin-layer chromatography (Chen *et al,* 2002).

In forensic analysis, inks can be discriminated by either non-destructive methods or destructive method depending on whether a sample needs to be taken from the document, in which destructive methods is a process that will consumed some part of the document. Destructive method include high performance liquid chromatography (HPLC), thin layer chromatography (TLC), capillary electrophoresis (CE), gas chromatography/mass spectroscopy (GC/MS) and Fourier transform infrared (FTIR) spectroscopy. Therefore, in forensic laboratory, non-destructive methods such as visual or optical examination, microscopic examination, scanning electron microscopy (SEM), video spectral comparative (VSC) and Raman Spectroscopy are often the initial choice (Halim *et al,* 2013).

Feraru *et al,* (2014) suggested that non-destructive analytical method for example microscopic and other optical technique would be more preferable method. In ink examination, these methods allow a chosen parameter of ink such as its colour, luminescence and absorption of radiation to be analysed thus provide useful information to the analyst.

Most of the cases faced by document examiner are differentiating and identifying of inks with almost similar colours. Thus, observation of document under visible light and infrared is a method which generally used for non-destructive while for destructive method would be thin layer chromatography (TLC) (Fabiańska & Trzcińska, 2001).

1.6 Aim and Objective

1. To observe the visual different in ink colour from ballpoint pen of similar and different brands.

2. To discriminate the ink sample of similar ink colour under UV light (365 nm).

3. To study the ballpoint pen ink by micro-spectroscopy comparison using VSC.

4. To evaluate the possibility to discriminate among the samples of provided from various manufacturer.

Chapter 2

Literature Review

2.1 Question document

According to Kumar *et al,* (2012) alteration and addition to valuable data on paper documents are among the fastest growing crimes around the globe. The loss due to these crimes is huge and is increasing at an alarming rate. For example, alteration done onto a piece of cheque, with the same colour on ink can change the amount of money receive or transfer. The techniques, which are used by Forensic Document Examiners (FDEs), to examine such cases, are still limited to manual examination of physical, chemical and microscopic when the ink of similar colour is involved (Kumar *et al,* 2012).

Questioned document examination involves a combination of many techniques for the characterization of inks (ChemImage Corporation, 2010). In actual forensic cases, forensic document examiners are seldom provided with prior information of the evidence at hand and it is solely up to the expertise, extent of knowledge and experience of the forensic document examiners to decide on the origin of the evidence (Ismail *et al,* 2014). The examination of inks is often performed to evaluate the authenticity of these documents (Halim *et al,* 2013). The aim of most analyses is to determine whether two pieces of written text originated from the same ink (Senior *et al,* 2012).

2.2 Why ballpoint pen?

In the United States, at least four out of five people use a ballpoint pen for routine writing rather than a fluid ink pen (Crown *et al,* 1961). That shows majority of people used ballpoint pen in their life rather than other kind of pen, not only because it is cheaper, it is also popular among people.

Although a pen of ink comes from the same brand, the ink analysis done might turn out to be different because some ink will evaporate and some will not depending on the composition itself. Other substances used for finely tuning the characteristics including driers, plasticisers, waxes and greases (Senior *et al,* 2012). Tests based upon the presence or absence of various types or varieties of these constituents would allow ballpoint pen ink differentiation to be more definitive and less empirical (Crown *et al,* 1961).

2.3 Examinations of inks

Forensic document examination often requires establishing whether or not a particular pen was used to write a document and whether or not the inks from a questioned document and a known document are the same.

2.3.1 Destructive vs non-destructive approach

Ink analysis is an important forensic procedure that can reveal useful information about questioned document. Modern inks contain many substances that can improve ink characteristics (Senior *et al,* 2012). The techniques regarding the analysis of inks can be divided into non-destructive and destructive methods. The non-destructive method, such as VSC, is preferable because it does not alter the document but it is limited to the used of forensic examiner (Senior *et al,* 2012).

The first one involves techniques, which do not damage the content of the document (non-destructive approach) and the second one gives a solution although there may be some damage to the original documents due to the chemicals used (Destructive approach). Research on non-destructive approach is based on conventional and modern physical and microscopic examination. Destructive approaches use conventional as well as sophisticated chemical and analytical methods (Kumar *et al,* 2012).

2.3.2 Visual Comparison Method

For non-destructive method, human eye is one of the best tools in visual comparison although some limitation does arise during colour discrimination. Unfortunately, this method is subjective in nature as the observers are defining the colour based on their perception and colour sensitivity. In addition, human eyes have its limitation to detect small differences in colour and thus it is normal for one who is unable to differentiate between two or more visually similar colours. Visual examination also prone to errors as the results may be easily influenced by many factors including metamerm which is a phenomenon that happens when colours change when observed under different light source (Pfeffferli, 1963).

2.3.3 Visible Examination under Ultra-Violet light Source

When light is absorbed onto a surface, a photon gives all of its energy to an electron and then disappears. As an electron leaves its orbital, there will be a vacancy which will be filled by another electron from a higher orbital than where the exited one came from. When the electron from the higher orbital makes this transition it will emit a photon. The energy of this photon will be the amount of energy the electron loses in the transition. This energy is the binding energy (EB) of the first electron subtracted from the binding energy of the electron which fills its place. This value will always be lower than incident photon used to excite the first electron. When the reemission of energy is in the visible region, this phenomenon is called fluorescence (Aambø, 2011).

Visual examination of ink can be accomplished under ultraviolet (UV) with the wavelength of approximately 190 to 380 nm, visible (VIS) with the wavelength of approximately 380 to 800 nm as well as near-infra that has the wavelength from 780 to 2100 nm. Some inks fluoresce under UV such as heterorotaxane whose fluorescent color changes along a spectrum of red to yellow to green, while some will luminescence under IR light depending on the chemical properties of the ink. UV light examination is used in this study and the parameter chosen to classify them is their capability of fluoresces. The ink which is bearing fluoresce material in its formulation is able to fluoresce and thus can be separated from the other samples if there is any.

2.3.4 Video Spectral Comparator (VSC)

The Video Spectral Comparator 6000 (VSC) is a machine made by Foster and Freeman. An example is shown in Figure 1.

Figure 1: The image of Video Spectral Comparator 6000 (VSC).

Normally used by forensic document examiner to validate a document. The instrument has a different kind of light sources to examine document. Police used it to check that passports and other documents are real and not forgeries while in the cultural heritage sector; they evaluate inks and looks for deterioration in documents. The instrument is a comparator, and it is often used to compare one set of images or spectra up against another (Aambø, 2011).

A VSC is capable of investigating infrared absorption, infrared luminescence, ultraviolet fluorescence, and transmitted light to determine inks (Ellen, 2006). Good understanding of the basic principles of light is needed in order to comprehend the working principle of VSC. Visible light is a form of radiant energy which ranged from 400 to 700 nm within electromagnetic radiation. When it is directed toward an object, different effects occur as a result of emitted wavelength and the composition of the object (Mokrzycki, 1999). The effects are as follows:

i. All or part of the light reflected off the object making it appear white or lighter
ii. All or part of the light absorbed by the object making it appear black or darker
iii. Part of the light reflected while part of it absorbed producing colours in the VIS region of the radiation
iv. Light transmitted through the object
v. Light strike the object, be absorbed and then reemitted a longer wavelength-luminescence

The VSC acquires the combination of cameras, lights and filters to create each of these effects (Mokrzycki, 1999). These effects also occur in the radiant energy that is not visible to human eye *i.e.* UV and IR regions. Furthermore, installed software enable images of examined document to be recorded and manipulated (rotate, flip, and render negative). It also incorporates function to mix different images which enabling distinct images to be overlaid or compared side by side. The VSC 6000 has the ability to enhance, contrast, and superimpose images of different documents, and facilitates for spectrometry of reflectance and luminescence, thus making it the most useful instrument in questioned document examination.

2.3.5 Discrimination Power (DP)

According to Smalldon and Miffat (1973), the discrimination power is the probability that two distinct samples randomly selected from the parent population would be discriminated in at least one attribute if the series of attribute were determined (Smalldon & Moffat, 1973).

The distribution of each attribute over the population is assumed to be known from a study of a large number of samples (Smalldon & Moffat, 1973). Furthermore, according to Smalldan and Moffat (1973), if an attribute x_i is subject to measuring error it is assumed that a definite quantity E_i can be agreed so that samples differing in the attribute by an amount which exceeds E_i are discriminated while those which are within E_i are termed the error factor. Since samples must be either matched or discriminated, the probability that two randomly selected samples will be matched in all the k attributes (PM_k) is related to DP_k by the equation

$DP_k = 1 - PM_k$

If PMi is the probability of a match in attribute x_i and all the attributes are uncorrelated then the Discrimination Power (DP) for a series of k attributes (DP_k) is given by

$DP_k = 1 - k \ \pi \ i = 1 \ PM_i$

The DP is used to compare the result obtained using optical methods, (such as Video Spectral Comparison (VSC) and Micro Spectrophotometry (MSP) in the ink comparison study. The DP of the technique is calculated according to the following equation:

$DP = 1 - 2M/n(n-1)$

Where M is the number of non-discriminated pairs of samples and n is the total number of samples. The DP is a measurement of the selectivity of the method to differentiate the ballpoint pen inks analysed. The main objective in the comparison of ink samples was to minimise the number of false negative. On the other hand, it is also important to minimise the false positive rate in order to obtain an optimal DP. When attempting to increase the DP, the risk of false differentiation increased rapidly (Weyermann *et al,* 2012).

2.3.6 Studies on forensic ink analysis

Although ink can be differentiated by a number of non-destructive methods, determining some inks are so similar in chemistry that their absorbance and reflectance properties display little, if any, differences when utilizing today's most common types of imaging technology (ChemImage Corporation, 2010). In the study of Ismail (2014), ballpoint pen inks that were difficult to discriminate previously on the basis of their UV-Vis spectra alone, were successfully discriminated and resolved after undergoing chemo metrics treatments (Ismail, 2014).

Literature search could not retrieve any work on the application of pattern recognition techniques for the detection of an alteration made with ballpoint pen strokes, although there are some literatures available on ink analysis using image processing and pattern recognition techniques (Kumar *et al,* 2012). Since the colour of the ink is similar, it is very difficult to make out the difference between the altered and the original strokes (Kumar *et al,* 2012).

Samples may be differentiated on the basis of transmission, reflection and fluorescence spectra obtained for inks deposited on the surface of paper. However, in order to identify the ink, it is necessary to determine its type and composition, using methods of physic-chemical analysis. Among these methods, thin-layer chromatography and capillary electrophoresis were applied most often (Feraru & Meghea, 2014).

Ultra-visible-near infrared spectrophotometry (UV-Vis-NIR) and Fourier Transform Infrared Spectrometry (FTIR) can also be used to pen brand differentiation. Identification of an ink formulation may be important for questioned document examination. Knowledge of ink formulae can help to determine the authenticity of a document, including age and the presence of any change to the document (Feraru & Meghea, 2014).

X-ray fluorescence spectrometry as an analytical technique which examines the elemental contents of a small sample and provides information about pigments and filler, is more sensitive to higher atomic weight elements than Scanning Electron Microscopy (SEM). Nevertheless the depth of X-ray penetration as well as the beam diameter influence on the results obtained for multilayer materials (Feraru & Meghea, 2014).

Many works have been published aiming to propose and optimize methodologies for analysing inks on documents. Bell *et al* compared the results obtained by Raman, surface-enhanced Raman spectroscopy (SERS), video spectral comparator model 2000 (VSC 2000) and thin layer chromatography (TLC) for analysis of 26 different pen inks on questioned documents. The result indicated that DP of Raman spectroscopy was better as compared to standard visual technique using VSC 2000 (Silva *et al,* 2014).

In order to study the composition of inks for blue and black ballpoint and gel pens, Zieba-Palus and Kunicki uses micro-Fourier transform infrared spectroscopy (micro-FTIR), Raman spectroscopy and X-Ray fluorescence (XRF) to compare (Silva *et al,* 2014). The author concluded that micro-FTIR provides satisfactory information for the analysis of the in composition, but a complete information is obtained only when the three technique are combined. Causin *et al* also proposed the same conclusion which the best results are obtained through the joint observation of all the techniques evaluated (Silva *et al,* 2014). Causin *et al* stated this after comparing the discriminant power of UV-Vis, FTIR spectroscopy and TLC techniques in forensic analysis of 33 inks from blue and black ballpoint pen of different models. However, most of these techniques present a high cost, require the sampling/destruction of part of the document and are usually not available for all forensic laboratories.

Zimmerman and Mooney (1988) compared twenty-two black, eight blue, and seven red inks were compared using laser examination, and proving that laser examination is an option for non-destructive method of ink differentiation (Zimmerman & Mooney, 1988).

Sree (2011) used fifteen blue ballpoint pens with similar hue from 5 brands to draw straight lines and wavy word samples on A4 white paper known samples were then subjected to visual examination, stereomicroscope examination and UV observation. The ink was also extracted using methanol and subject to TLC analysis using ethyl acetate, ethanol and water (70:35:30) as the solvent system (Sree, 2011).

The results of Sree (2011) show that the visual examination has its limitation to distinguished ink colours. The 15 samples can be grouped into blue, light blue and dark blue. Visual examination under stereomicroscope could further characterise the visual characteristics including better colour discrimination and the appearance, both straight and wavy lines (Sree, 2011). Ultraviolet (UV) light examination can further subgroup the lines into black and light blue, thus provide further classification among the inks. When inks were subjected for TLC analysis, both band colour and Rf values could further subgroup the inks even from the same brand (Sree, 2011).

Kuh (2014) conducted an analysis of similar coloured inks using non-destructive techniques namely optical examination under ultraviolet (UV) light, microscopic examination, and micro-spectrometry by using Video Spectral Comparator (VSC) 6000 (Kuh, 2014). The author found out that the micro-spectrometry was able to discriminate similar coloured inks from different brans by means of differences in spectra. The DP for blue ink pen was 100%, black ink pen was 90%, and red ink pen was 70%. The spectra of ink from different individual ballpoint pen of the same model and brand were similar in their overall pattern. The author found that different brands were not able to be discriminated under UV because all do not fluoresce (Kuh, 2014).

An experiment done by Zeichner *et al* (1988), shows there is an inherent advantage of transmission method over the reflectance method. In addition, the deviations from Beer-Lambert Law may be considerably lower when transmission Microspectrophotometry was used instead of nondestructive transmission method (Zeichner *et al*, 1988).

Chapter 3

Methodology

3.1 Sample Collection

In this study, 15 numbers of blue ballpoint pens from five different of brands were purchased from the market. They are Faber-Castell, Stabilo, Papermate, Pilot and G'soft. These brands were chosen for the study as they are widely found in Malaysia market. The labels of the samples used in this study were as follows: FC for Faber-Castell, S for Stabilo, PM for Papermate, P for pilot, G for G'soft. The details of manufacturer name, brands, and code of sample number acquired are shown in Table 3.1.

Table 3.1: Information of blue ballpoint pen used in the study.

Manufacturer	Brands	Sample code
Faber castell	CX7 supersmooth 0.7mm fine	FC1
	Ballpen 1423 1.0mm medium	FC2
	Clickball 1422 0.7mm fine	FC3
G'Soft	BP-GS-56 0.7mm	G1
	GS-5566 0.6mm	G2
	PDA 1 0.7 fine	G3
Pilot	BP-S medium 1.0mm	P1
	Super-GP 1.0mm	P2
	Rexgrip 0.7mm	P3
Papermate	KV2 fine blue	PM1
	Kilometrico 100 LV ink fine	PM2
	Kilometrico 80% recycle F	PM3
Stabilo	Linear 308 ML 41	S1
	Excel 828 N F	S2
	Galaxy 818 F	S3

The research was conducted using several non-destructive techniques in differentiation of similar colour ink samples. It started with the visual examination under UV light, then proceeded with microscopic examination and finished with spectrometry technique.

3.2 Optical examination under UV light

Fifteen straight lines in about seven centimetre (cm) were drawn on a piece of 70g A4 white IK YELLOW™ using respective pen brands and models. The lines were examined under the illumination of UV light at 365 nm. This examination aims to see inks fluorescence feature. The observation was recorded.

3.3 Microscopic examinations – VIS light

Upon in UV light examination, the same 15 samples were examined using VSC 6000 (Foster and Freeman, Worcestershire, United Kingdom), version 6.6 produced by Foster and Freeman Ltd (see Appendix 2) under VIS light. The samples were observed under the same range of magnification (34.07x) to better examine the discriminating points between them. This magnification is sufficient enough to reveal its physical details. The magnification power and source of lighting were used for the rest of the ink sample.

A few class characteristics of the ink samples were noted down for comparison purpose. These are colour, appearance, smoothness and special ink characteristic such as gooping, skipping, glossy and striation of the produced samples.

3.4 Reflectance spectrometry in VIS light

The examination of ink samples by means of reflectance spectrometry in VIS light were carried out by VSC 6000 (Foster and Freeman, Worcestershire, United Kingdom), version 6.6 produced by Foster and Freeman Ltd (see Appendix 2).

3.5 VSC 6000 components

The VSC consists of a main unit and a PC system. The main unit consists of high resolution charge-coupled device (CCD) colour camera with sensitivity from 360 nm to 1100 nm, different filters as well as a translight panel. Underneath the panel are light sources which illuminate the document from below. The camera of VSC equipped with zoom lens which can be magnified up to 130x. There is also software to ensure compatible combinations of illumination and imaging filters automatically to prevent light leakage. Instrumental functions are selected and controlled through a simple graphical user interface and the Windows operating system. In addition, there is an integral micro-spectrometer that allowing for rapid measurement of absorption, reflectance, transmission and fluorescence spectra. These spectra can be measured from VIS to IR wavelengths (400 to 1000 nm) within electromagnetic radiation (Foster and Freeman, 2014).

3.6 Spectral measurement of known ink samples

A horizontal line of approximately three cm in length was drawn on the piece of A4 white paper. They were grouped according to their brands and colours (see Appendix 1). All measurements for the ink samples were taken in relation to a blank.

Prior to analysis, VSC was calibrated: The camera was zoomed in with a high magnification as possible. Fine focus was adjusted until it produced a clear image. Then a white tile was placed in the crosshair (arrow) to use it as white references.

The paper with the ink sample was placed under an imaging system of VSC 6000- FireWire digital five Megapixel CCD colour camera. The image of the sample was displayed on a flat screen colour liquid crystal display (LCD) monitor that is connected to the imaging system. The image was brought into focus and adjusted to suitable magnification. Next, the crosshair was moved to the unmarked part of the white paper in order for measuring the white reference. Then, the crosshair was moved to the sample for spectrum measurement. Finally, the spectra were recorded in spectrum screen and labelled with a code. Table 3.2 shows the parameters used during spectral measurement.

Table 3.2: Parameters for spectral measurement.

Mode	Reflectance
Illumination	Incandescent filament lamps (400-1000 nm)
Main Sources	Flood lighting
Filters	Off
Magnification	X34.07
Iris	60%
Brightness	60

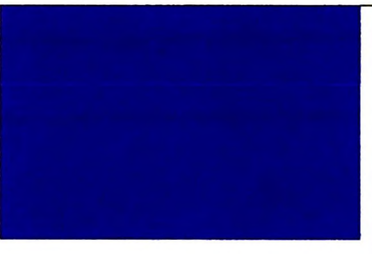
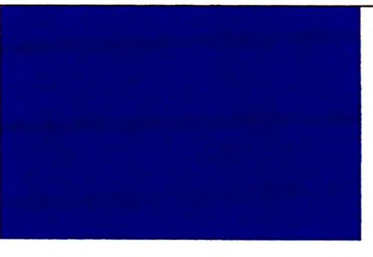
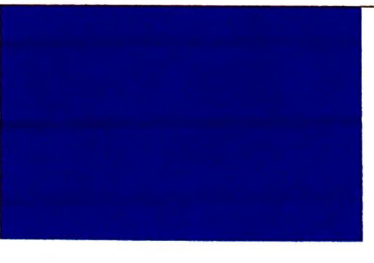
Chapter 4

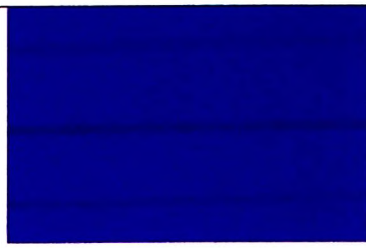
Result and Discussion

4.1 Optical examination under UV light

UV radiation was used to screen the ink samples in order to classify them into fluorescent or non-fluorescent class. Based on Table 4.1, all ink samples showed no fluorescent signal.

Table 4.1: Observation of fluorescence properties of ink samples.

Manufacturer	UV visualization	Sample no.	Fluorescence
Faber castell		FC1	No
		FC2	No
		FC3	No
G'Soft		G1	No
		G2	No
		G3	No
Pilot		P1	No
		P2	No
		P3	No
papermate		PM1	No
		PM2	No
		PM3	No

Stabilo		S1 S2 S3	No No No

The ability of ink to fluorescent is based on the fact that certain materials absorb the energy from UV and then undergo electronic transition to higher energy state. The energy that falls back to its original energy level causes the extra energy to produce in the form of a light photon. The wavelength of the emitted light depends on how much energy is released, which depends on the particular position of the electron under our experimental conditions, the samples did not fluoresce and this did not allow the ballpoint pen inks to discriminate.

4.2 Microscopic examination under VIS light

Ink sample was examined using VSC to determine the colour and morphological characteristics of the ink. Some unique characteristic were observed. There was skipping of ink caused by insufficient flowing of ink from the ball socket. Striation of pen also occurred where the imperfection of ball or ball housing to function properly as seen in the left image of Figure 4.1.

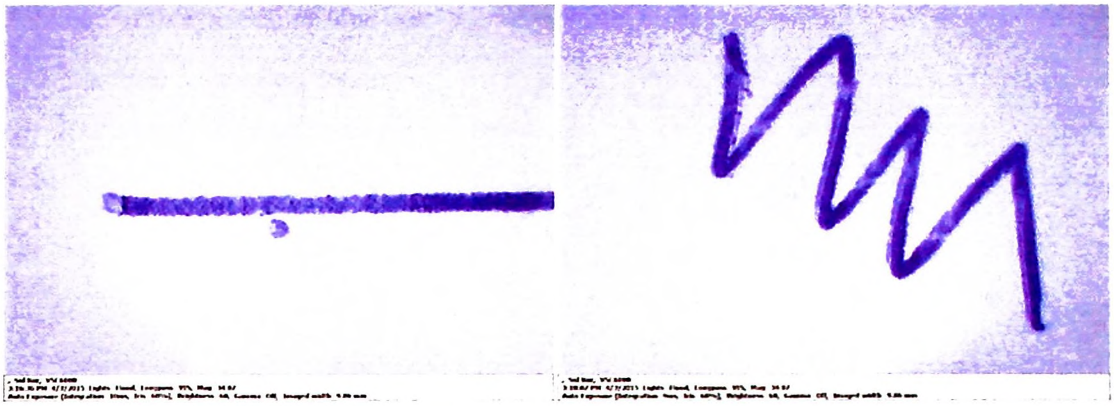
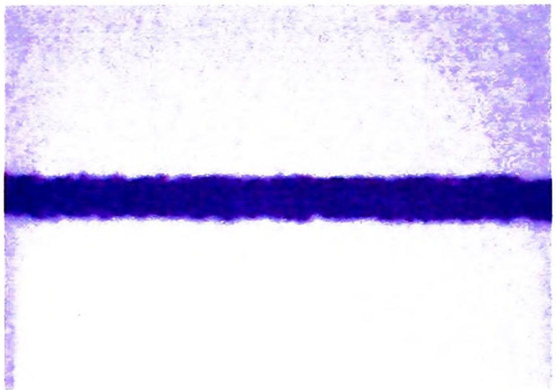
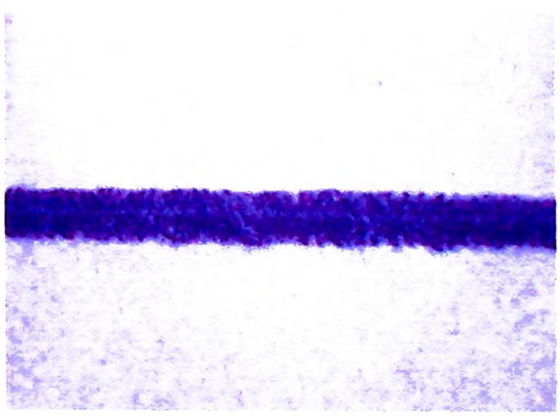


Figure 4.1: skipping (left) and striation (right)

The physical appearances of ink such as smoothness, glossy, striation and colour saturation were examined. Visual examination using VSC shows that most of the colour can be grouped as dark blue, blue or light blue. Most of the ink looks similar in colour deposited onto the paper. However, a few samples from Faber-Castell, G'soft, Papermate and Stabilo showed inter variation differences in colour as shown in Table 4.2.

Due to the partial absorption of the ink into the surface of the corresponding paper, glossy appearance may differ from less glossy, glossy or very glossy. The less ink absorb will lead to very glossy appearance. The striation on the other hand may produce individualistic evidence whereby the imperfection of ball or ball housing may cause this. Striation was observed as the production of non-inked area in a line (Ink Analysis, 2005). Smoothness on the other hand depends on the ink produce when it transfer onto the ink, sometimes ink will not deposit uniformly when written on a paper thus does not produce a smooth line.

Table 4.2: Observation of blue colour ink from five different brands.

Manufacturer	Sample no.	Image	Colour	Appearances
Faber castell	FC1		Dark blue	Smooth Less glossy No striation
	FC2		Blue	Smooth Glossy No striation
	FC3		Blue	Unsmooth Very glossy Striation present