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Identification of Different Inks Using FT-IR

Dissertation submitted in partial fulfillment for the
Degree of Bachelor of Science in Forensic Science

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CERTIFICATE

This certify that the dissertation entitled

"Identification of Different Inks Using Fourier Transform-Infrared Spectroscopy"

is a bonafide record of research work done by

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During the period from 26th December 2005 to 23rd April 2006 in my supervision

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ABSTRACT

Infrared spectroscopy is one of the powerful techniques used in the characterization of materials. The vast majority of the molecules in universe possess vibration energy within the mid-infrared region, which extends from 4000-400 cm^{-1}, so it is defined as fingerprint region for most of the materials particularly those polymeric materials that incorporate chemical functional groups as part of their structure.

In this project, three types of inks were used for analysis of the components: ballpoint inks, marker pen inks and fountain inks. Each type has different brands and color. The focus of this study was to assign the major absorption bands and try to differentiate the types of inks. This aspect of studies is important from the forensic point of view.

On the basic of spectral bands, the fountain pen, ballpoint pen and marker pen inks, were easily identified and discriminated; mainly the dyes components.

CHAPTER 1

INTRODUCTION

Ink analysis is one of the important aspects of the departments of police, customs, immigration and other agencies that deal with documents as their routine work. Some people alter documents for their own benefit or plan. It is important for forensics scientists to verify the document whether it is original or forged.

Analysis of ink can be divided into 2 categories, destructive method and non-destructive method. Non-destructive methods for ink analysis involve visual examination, microscopy and Raman spectroscopy. On the other hand, these methods also involve the observation of ink on the document by means of a reflectance technique that allows the recording of spectral characteristics of inks without removing the sample from its support. The destructive methods for ink analysis include thin layer chromatography, high performance liquid chromatography, Fourier Transform Infrared spectroscopy and gas chromatography. By these methods, a portion of the ink has to be removed from the document prior to the analysis.

The visual examination of ink only detects the obvious alteration on the document, e.g., the document altered by using different color of pen. If the alteration of the document is done using a same color of pen, it is impossible to examine using naked eyes.

Simple microscope, such as, compound microscope also can be used for ink examination. This microscope can reveal a microscopic characteristic of the ink such as dot or granules. These characteristics can be used to compare questioned and standard inks in the same pages or from different pages.

Other non-destructive method for ink analysis is Raman spectroscopy. It can directly identify and characterize specific inks found on the paper surface (Mazzella & Buzzini, 2005). Questioned and standard inks will show similar Raman spectrum if they come from a same source.

Most of the inks in the market are not made by single color but with the combination of various colors to form desired color. Black ink, which is used to write the ransom note, is often a combination of several colors. Black inks from different manufacturers are composed of different combinations of colors. Thin layer chromatography can be used to reveal the combination of this color. If the question sample and standard sample is run on the same TLC plate, each component of the inks from each sample will travel at different rates. This allows mixtures of the compounds to be separated and allows different samples to reveal the different colors used in their manufacture.

Another technique used to detect inks is FT-IR, which is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can also be applied to the analysis of solids, liquids, and gasses.

Inks are the mixture of three components, which can be adjusted in composition to produce the desired writing characteristics. These components are colorants, vehicles and additives (Egan et al; 2005). Colors of inks can include any of the several chemicals. Chemical classifications that can be used are pigments and/or acidic, basic, azoic, direct, disperse, reactive and solvent dyes. In common inks analysis, colorants are the most important that can be used because the light-absorption and emission properties that can be detected by various analytical methods. Vehicles or carriers are usually solvents that can allow the inks to flow from the tip and carry the colorants to the material surface. Solvents are the typical ingredients analyzed in date-of-origin investigations because of their gradual evaporation from a document (Egan et al 2005; Aginsky 1994; Brunelle 1992; Brunelle and Cantu 1987; Brunelle et al. 1987; Cantu 1996; Cantu 1991; Cantu 1988). In the last components of inks, additives are the one that can serve as flow (viscosity) modifiers, surface activators, corrosion controllers, solubility enhancers and preservatives (Egan et al. 2005; Brunelle and Reed 1984; Leach and Pierce 1993). This component can be the manufacturer specific and can greatly aid forensic examiners.

In the ballpoint pens, felt-tip marker and fiber-tip pen (fountain inks) contain solutions of dyes in water or organic solvents like propylene glycol, propyl alcohol, toluene or glycol-ethers. They are used as resins preservatives and wetting agents.

The fountain inks commonly contain these three types of compounds. Dyes in the fountain inks are derived from aniline salts, which impart various colors. However, in some other types of fountain inks, the dyes are derived from vegetable dye formulas. To control the flow resistance of inks, the thickening agent like ethylene glycol, glycerine or some other chemical agents are commonly used in the manufacturer of fountain inks. The detergents or surfactants are used to reduce the surface tension of the ink for better wetting. Phenols or some other mild fungicides are used to keep mold from growing in inks. As in the common inks, the additives are also present in the fountain inks. They can control the acid base balance (pH) of ink. However, these additives will not effect the pens.

Ballpoint pen inks contain a variety of components such as dyes, additives and solvents. Dyes in the inks are used to detect the age of the inks. The analysis of age in inks was important in the forensic document examination. The common dyes used in the compositions of ballpoint pen inks are methyl violet or crystal violet (Weyermann et al. 2005). Ink vehicles are used to dissolve the dyes or disperse the pigments in inks. To control the viscosity of the inks and to serve as fillers, various resins and polymers were used (Wilkinson et al.).

The marker inks for writing board are manufactured by blending a colorant, a resin and a mixed solvent consisting of a good solvent for the resin possessing a high speed of vaporization and a non-solvent for the resin possessing a lower speed of vaporization than that of the good solvent. It forms on the writing board, marker traces which can be readily wiped-off.

In this work, different inks are used to identify the component that constitute ballpoint pen inks, marker pen inks and fountain inks.

OBJECTIVES OF THE STUDY

- To identify the composition of the inks
- To differentiate the inks.
- To characterize different ink using FT-IR
- To compare the composition in each ink

CHAPTER 2

REVIEW OF LITERATURE

Vogt et al (1997) reported the separation, comparison and identification of fountain pen inks by capillary electrophoresis with UV-visible and fluorescence detection and by proton-induced X-ray emission. The studies were targeted at testing the applicability of capillary electrophoresis to separate blue and black fountain pen inks in the original liquid form and dried on different substrate materials. After the optimization of the separation conditions, diode array and UV-Vis, detection with two excitation wavelengths was applied to collect information from the electropherograms, in order to compare the ink extract with the original inks. In addition, nondestructive proton-induced X-ray emission (PIXE) spectrometry was used to characterize the elemental composition of dried inks on different substrate materials. Finally, all the information content from CE and PIXE analyses of original and dried inks has been integrated and used for the reliable identification of fountain pen inks.

Zlotnick & Smith (1998) reported the separation of some black roller ball pen inks by capillary electrophoresis. This demonstrated the potential of CE to discriminate between liquid black roller ball inks. CE provided high resolution, requiring a minimal amount of sample. Lewis & Chen Wang (1998) applied infrared spectroscopy that is the most widely used technique for the determination of molecular structure and for the identification of compounds.

Derivative spectroscopy has also applications in many areas where interpretation of conventional spectra was difficult, because of a high background signal or where the superimposing of two or more spectral bands causes interference. In their study, 12 dyes having similar structure were synthesised and their FT-IR spectra recorded. They studied the state of hetero-bifunctional reactive dyes. Dyes with the same chromophore but with different branched substituted alkylsulphone groups are complex conjugated molecules; it is thus difficult to recognise every characteristic frequency in the FT-IR spectra.

Roux et al (1999) investigated the evidential value of blue and black ballpoint pen inks in Australia. The different ballpoint pen inks of different brands, models and batches were analyzed by using three techniques. Those techniques are filtered light examination (FLE), reflectance visible micro-spectrophotometry (MSP) and thin-layer chromatography (TLC).

Kiss et al (2000) in a paper published on color pigments of *Trichoderma harzianum* used TLC. FT-IR and HPLC with diode array and mass spectrometric detection has also been employed. The investigations were motivated by the supposition that the measurement of the quantity and distribution of color pigment of *Trichoderma harzianum* may contribute to its chemotaxonomic evaluation.

Brunelle & Speckin (2001) compiled a technical report with case studies on the accelerated aging of ballpoint inks. This includes the results of several actual case examinations in which accelerated aging was used to estimate the age of ballpoint inks on questioned documents. The results obtained using accelerated aging were verified either by the examination of known dated writings, examination by another examiner, or by the identification of dating tags in the inks. This technique has been routinely accepted in court throughout the United States, as well as in Israel, and Australia.

Ko et al (2002) have reported the novel synthesis and characterization of activated carbon fiber and dye adsorption modeling. They prepared activated carbon fibers (ACF), analyzed synthesis mechanism of those fibers, and developed a new dye adsorption model. The surface chemical structures of the synthesized viscose rayon phosphates and ACF were analyzed using time-of-flight secondary ion mass spectrometry (TOF-SIMS) and attenuated total reflectance FT-IR spectroscopy (ATR FTIR). Surface images were obtained with an atomic force microscope (AFM) and a field emission scanning electron microscope (FE-SEM).

Thanasoulias et al (2003) studied multivariate chemometry for the forensic discrimination of blue ballpoint pen inks based on their visible spectra. The multivariate chemometry is a powerful tool for multi-component systems and allows the extraction of maximum information from complicates datasets. In this study, they used 50 blue ballpoint pen inks from five different brands. The samples were dissolved in absolute ethanol and their absorbance values in the range of 400-750 nm, after appropriate transformations, were used as variables in the multivariate statistical techniques of cluster analysis (CA), principle component analysis (PCA) and discriminant analysis (DA). These techniques were successively used to establish an effective and meaningful discriminant model.

Hofer (2004) studied the dating of ballpoint pen inks by HPLC with electrostatic detection (ESDA); blue ballpoint pen ink in the cashbook was analyzed. If the questioned document contains an intersection between two or more lines, it can be important to find out which of the lines has been produced first. The analysis of ink dyes is recommended to determine the documents.

Siegel et al (2005) used laser desorption or ionization mass spectrometry to analyze inks in questioned documents. They used technique to determine the age of handwriting and printed documents. The age of the inks can be determined by studying the chemical behavior of dye that make-up the inks. The laser desorption mass spectrometry is a valuable tool for elucidating the structures of dyes used in inks and tracking the change in their chemistry as they age. The most important consideration in implementing an artificial aging technique is that it causes the same chemical changes in the ink that natural aging do. The natural aging is a complex process that involves light, heat, oxygen and paper.

Maind et al (2005) analyzed Indian blue ballpoint pen inks tagged with rare-earth thenoyltrifluoroacetonates by inductively coupled plasma-mass spectrometry and neutron activation analysis. They studied the efficacy of homogeneous mixing of inorganic taggants with blue ballpoint pen ink with the objective to establish linear relation of intensity against concentrations or amounts of taggant and to derive the minimum detection limit. Tagging of ballpoint pen ink with suitable taggant is a unique method to come out with definitive inferences on the detection of forgery in documents written with ballpoint pens. Aliquots of such tagged ink having varying amounts of taggants were analyzed by ICP-MS and NAA. The tagging of ink with suitable organic or inorganic constituents is a useful method for the characterization of ink. If the ink contains a unique organic or inorganic taggant, different from the other components present in normal varieties of ink, it can serve as a unique identification index. This study can allow drawing various combination options based on different rare-earth chelates as suitable materials for tagging of ballpoint pen inks for absolute or relative age determination to aid in document related crime examination.

Mazzella & Buzzini (2005) analyzed blue gel pen inks by using Raman spectroscopy. In forensic science, Raman spectroscopy has become a tool of major importance for the analysis of gel pen inks. It is a non-invasive, non-destructive analytical method allowing samples to be examined without any preparation.

Senvaitiene et al (2005) reported the spectroscopic evaluation and characterization of different historical writing inks. FTIR spectroscopy was used to perform the historical writing ink samples. The samples were analyzed by using three different techniques. Those techniques are KBr pellet, Si substrate and ZnSe cell. The KBr method was used for the characterization of evaporated to dryness ink samples, while Si substrate and ZnSe cell techniques were used for the analysis of aqueous solutions or suspensions of ink. FT-IR has been used to determine the identity of historical inks based on their chemical composition. In addition, the evaluation of the results obtained from IR spectroscopy offers the possibility to identify effectively the nature of various ingredients in different ink samples. The KBr method used to characterize historical writing ink samples was successful, as was the ZnSe cell method, but the Si substrate method was unsuccessful.

Egan et al (2005) used capillary electrophoresis for forensic analysis of black ballpoint inks in the lab to measure the components like dyes available in the ballpoint inks. They used two different capillary electrophoresis instruments to perform ink and dye separations. A Beckman Coulter (Fullerton, California) P/ACE MDQ Series capillary electrophoresis system equipped with a photodiode array detector measured the basic dye components present in black ink formulations and dye standards. Another type of capillary electrophoresis was a Hewlett Packard/Agilent 3D (Palo Alto, California) also equipped with photodiode array detector. One advantage of performing capillary electrophoresis separation of dyes is the ability for effectively narrowing of the compound candidates responsible for a particular peak. Forensic analysis of ballpoint pen inks was the driving force in developing capillary electrophoresis buffers that adequately separate dye compounds for identification. Ink extractions were subjected to capillary electrophoresis buffer methods, as well as thin-layer chromatography and laser desorption/ionization- mass spectrometry analyses to characterize the dyes present in the pen inks studies. Both the techniques were used to compliment the capillary electrophoresis analysis and to search for dye components that might not be detected with capillary electrophoresis.

Kher' et al (2006) investigated about the forensic classification of ballpoint pen inks using HPLC and IR with principal components analysis and linear discrimination analysis for the evolution of forensic analysis. It is revealed that the components of ballpoint inks like dyes, additives and solvents could be assayed by a number of analytical techniques like HPLC and IR. The ability to differentiate between inks can allow the forensic scientist to evaluate the authenticity of a suspicious document. Chromatograms of blue inks were collected at four different wavelengths: 254 nm, 279 nm, 370 nm and 400 nm to enable better resolution by including the three dimensions of the wavelength, array detector measured the basic dye components present in black ink formulations and dye standards. Another type of capillary electrophoresis was a Hewlett Packard/Agilent 3D (Palo Alto, California) also equipped with photodiode array detector. One advantage of performing capillary electrophoresis separation of dyes is the ability for effectively narrowing of the compound candidates responsible for a particular peak. Forensic analysis of ballpoint pen inks was the driving force in developing capillary electrophoresis buffers that adequately separate dye compounds for identification. Ink extractions were subjected to capillary electrophoresis buffer methods, as well as thin-layer chromatography and laser desorption/ionization- mass spectrometry analyses to characterize the dyes present in the pen inks studies. Both the techniques were used to compliment the capillary electrophoresis analysis and to search for dye components that might not be detected with capillary electrophoresis.

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Weyermann et al (2006) investigated the photofading of ballpoint dyes on paper by LDI and MALDI MS. They characterized the degradation processes of methyl violet and ethyl violet, the two typical ballpoint dyes by using laser desorption/ionization (LDI) and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (MS), and evaluated the possible application of the method to forensic examination of documents. The degradation of the dyes methyl violet and ethyl violet in stroke from a ballpoint was studied under laboratory conditions influenced by different factors such as light, wavelength of light, heat and humidity.

Zięba-Palus & Kunicki (2006) reported the application of micro-FTIR spectroscopy, Raman spectroscopy and XRF method examination of inks. They evaluate the possibility of discrimination between inks by the use of spectrometric methods. They revealed that infrared spectroscopy makes it possible to analyze the ink composition. It provides the information on the main dyes, resins and oily liquids. The main pigments are easily detectable using the infrared spectra of inks. Raman spectrometry enables direct, non-destructive analysis and comparison of ink samples and can be a valuable complementary technique to infrared examination. In case when IR and Raman spectra are not sufficient to differentiate between the samples, elemental composition should be carried out. X-ray analysis provides information about pigments and enables to discriminate between ink samples.

CHAPTER 3

MATERIALS AND METHODS

3.1 Chemicals

All the chemicals were of analaR or spectroscopic grade. They were used as such, or stated otherwise.

3.2 Glassware

The glass slides were obtained from Sail Brand that made in China. Other glassware was from Brand (Germany).

3.3 Apparatus and accessories

The vacuum desiccator was used to keep KBr moisture free, after drying in a thermostatically controlled oven at 110°C.

3.4 Ink samples

The ink samples or pens and markers (Table 1; Fig. 1), manufactured by local companies were obtained from Kota Bharu supermarkets.