Abstract— The analysis of ink is of great interest in the field of forensic, particularly in the examination of questioned documents. Forged documents relating to handwriting and signatures often appear in forensic cases. As these documents are usually written with writing pens, it is therefore of interest to discriminate between the colors of the inks and the brands among the ballpoint pen inks. This study comprised of analysis of inks utilizing spectroscopic methods. In spectroscopic methods, the inks were analyzed by means of Ultraviolet visible (UV-Vis) and infrared (IR) spectroscopy. UV-Vis analysis was successful in discriminating ballpoint pen inks of different brands. IR analysis revealed that each brands could be discriminated by looking the pattern of each spectra.

Keywords— Ballpoint Pen Inks, Ink Discrimination, Spectroscopic

I. INTRODUCTION

INKS comprise of fine pigment particles dispersed in a solvent. The pigment may or may not be colored, and the solvent may be aqueous or organic.

The earliest black writing inks, developed before 2500 BC, were suspensions of carbon in water stabilized with a natural gum or materials like egg albumen [1].

Generally, compositions for writing ink consist of an inner portion of a metallic color and outer portions of a dyestuff-based color [2]. Dyestuff-based color composition consists of a nonleafing metal powder pigment as a first pigment, an inorganic pigment or organic pigment as a second pigment, dyestuff, and solvent.

Ink analysis may be an important part of the investigation of questioned documents including forged checks, bills, contracts and others. Ink analysis does focus on a new chemical and analytical methods or techniques. It is a step to increase the discriminating power of ink analysis [3].

Government and private sector were using the ink examination as a method to ensure the authenticity or fake nature of the question document [4].

Ink analysis has been used by forensic scientist to identify inks on questioned documents. Examination and dating of inks on questioned documents has become common, and law enforcement agencies use this technique during their criminal investigations.

Ink analysis involved the examination of documents using the naked eye, oblique lighting conditions and using special optical filters. It can be performed using optical, spectroscopic and chromatographic methods [5].

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was utilized for the analysis of blue ballpoint pen ink samples on paper using KBr as a background. This analysis was found to give a poor discrimination between the ink spectra. Micro-ATR was found to be a simpler technique for acquiring spectra of the ballpoint pen ink samples [6].

FTIR was used to analyze different historical writing ink samples. The IR spectra were acquired using three different techniques of; KBr pellets, Si substrate and ZnSe cell. FTIR spectroscopic evaluation revealed the possibilities to identify the historical ink based on their chemical composition, and the nature of ingredients in different ink. However, only KBr pellet and ZnSe cell methods were successful [7].

Studied on multivariate chemometrics for the forensic discrimination of blue ballpoint pen inks based on their Vis spectra showed that the results of UV-Vis spectra of ink were difficult to compare. The ink sample size used was very small to overcome this problem. Each of the spectrums represents the average of the absorption from the same batch. The chemometric application such as cluster analysis (CA), principal component analysis (PCA) and discriminant analysis (DA) was successively used to calculate the discriminant model. UV-VIS examination may provide indications that the document has been stained by chemicals or other materials that may affect the ink analysis [8].

This study was undertaken to provide ink analysis data in order to assist question document examiners in their casework especially when it relates to the comparison of ink with that of a seized pen. This study is necessary since the usage of ballpoints pens are extensively used in documents.

II. METHODS

A. Sample Preparation

Ballpoint pens of three different brands were used in the study. Only blue and black pen inks were utilized. The sample codes for the pen used are as listed in Table 1.
Ink samples were prepared by shading the ink onto an area of 1 cm x 5 cm on a white A4 writing paper. The paper was then soaked in 100 mL of methanol in a test tube. The extraction of ink was done until entire ink on the paper totally dissolved in the solvent.

B. UV-Vis Analysis

Methanolic ink extracts were used for UV-Vis analysis with methanol used as the blank solvent. Absorbance spectrum was recorded in the wavelength range 400 nm – 700 nm. From the absorbance, the maximum absorbance from each sample been obtained. The spectra with regard to the maximum wavelength and relative height of the component peaks were compared for each sample.

C. IR Analysis

10 µL of methanolic ink were added to 100 mg of KBr powder. The sample extract were then grinded with KBr powder using mortar and pestle. The sample which was totally dried was then been pressed into KBr disc. Five tonne pressure was applied to the sample to form a transparent disc. Infrared spectrum for each sample was recorded in the range of 450 cm⁻¹ to 4000 cm⁻¹.

III. RESULTS

A. UV-Vis Analysis

The inks of the three brands from ballpoint pens were examined by UV-Vis spectrophotometer in the wavelength range from 400 - 700 nm.

Fig. 1 shows the absorbance spectra from three brands of blue ballpoint ink samples. All of the ink samples exhibited one maximum absorbance peak in the wavelength range 550 nm to 600 nm. Carera ink samples showed the highest absorbance at wavelength 584.14 nm followed by Papermate Kilometrico at 582.25 nm and Faber Castell at 577.40 nm.

UV-Vis profiles of black ballpoint pen inks are shown in Fig. 2. Carera exhibited three peaks whereas Papermate Kilometrico and Faber Castell only yield one peak. Papermate Kilometrico displayed the highest absorbance value at wavelength 590.09 nm followed by Carera at 594.92 nm, Faber Castell at 587.03 nm.

B. FTIR Analysis

The IR spectra of the two colors for each brand generally showed a broad peak at 3000 cm⁻¹ to 3600 cm⁻¹. This indicated the presence of the OH group in the inks’ formulations that was expected since ballpoint pen ink contained alcohol. Three brands of the pens were analyzed in the region of 450 cm⁻¹ to 4000 cm⁻¹. The discrimination of these inks by IR spectra is due to the presence or absence of a particular absorbance peak as well as the intensity of the peak.

Based on the Fig. 3, the three spectra of blue ballpoint ink from different brands; K-B-BP, C-B-BP and FC-B-BP were
quite similar. All spectra possessed a broad peak in the range 3000 cm$^{-1}$ to 3600 cm$^{-1}$ indicating the presence of CH$_2$-OH group in these inks, and the presence of peaks in the range 2880 cm$^{-1}$ to 2900 cm$^{-1}$ due to CH$_2$ and CH$_3$ stretching.

Fig. 3 IR Spectra for Blue Ink Samples of Ballpoint Pen (a) K-B-BP, (b) C-B-BP, (c) FC-B-BP

Fig. 4 shows the comparison of IR spectra of black ballpoint pen inks. These spectra showed a broad peak between the range 3000 cm$^{-1}$ to 3600 cm$^{-1}$ suggesting -OH group in these inks. The spectra also exhibited peaks at the region of 2880 cm$^{-1}$ to 2900 cm$^{-1}$ indicating the CH$_3$ and CH$_2$ stretching. Ballpoint inks of C-BLK-BP, FC-BLK-BP and K-BLK-BP showed peaks in the range from 1600 cm$^{-1}$ to 700 cm$^{-1}$.
IV. CONCLUSION

UV-Vis analysis showed that blue ballpoint ink samples that is K-B-BP, C-B-BP and FC-B-BP displayed only one peak at the wavelength in the range 550 nm to 600 nm. On the other hand, for the black ink samples, C-BLKP-BP exhibited three peaks yield two peaks and K-BLKP-BP and FC-BLKP-BP bring in only one peak in the spectrum. For IR analysis is not easy to discriminate these inks since all the samples have the same formulation. However, the different can be seen by looking at the intensity of main peak as well as the pattern of each spectrum.

REFERENCES


