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Analysis of blue fountain pen inks

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ABSTRACT

The forensic analysis of ink is of great interest particularly in the investigation of forgery cases relating to handwriting and signatures. As the documents are usually written with writing pens, it is therefore of interest to characterize the inks of different brands among the fountain pen inks. In this study the fountain pen inks components were separated by TLC and then separated components were analyzed by means of Ultraviolet visible (UV-Vis), infrared (IR) and NMR spectroscopy. UV-Vis analysis was successful in characterizing fountain pen inks of different brands. IR analysis revealed that each brands could be characterized and then differentiated by looking the pattern of each spectra. NMR spectroscopy has been useful for the comparison of ink brands.

Keywords: Fountain pen, TLC, UV-VIS, IR, NMR spectroscopy

INTRODUCTION

Inks comprise of pigment or dyes dispersed in a solvent either aqueous or organic [1]. Generally, compositions for writing ink consist of an inner portion of a metallic color and outer portions of a dye stuff based color [2]. 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 [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 and 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.

MATERIALS AND METHODS

Blue fountain pen ink of three different Indian brands was used to analyze in the study. The sample codes for the blue fountain pen ink used are as listed in table 1.

Table 1- Sample of blue fountain pen inks of different brands.

S. no.	Ink Brand	Code
1.	Camel Blue	A1
2.	Chelpark Blue	A2
3.	Parker Blue	A3

Thin Layer Chromatography

The separation of ink components will be carried out by TLC which includes preparation of silica gel glass plates in distilled water. All of the spots were approximately 0.5-0.8mm in diameter and the amounts of the ink applied were about 1.0-1.5µg. the origin were at1.0 cm from the bases of the plate. The developing solvents used were butanol/ethanol/water (50:10:15). Different colors of dye component will be eluted from plate and collected for further analysis. The retardation factor, R_f (the ratio of distance traveled by the compound to the distance traveled by the solvent) and color tones of the separated bands were recorded.

Spectroscopic Analysis

UV: Ink extract were used for UV–Vis analysis with ethanol used as a blank solvent. Absorbance spectrum was recorded in the wavelength range 200-800 nm. From the absorbance, the maximum absorbance from each sample was obtained. The spectra with regards to the maximum wave length and relative height of the components peak were compared for each sample.

IR: 10µL of ink sample were added to 100 mg of KBr powder. The sample extract were then grinded with KBr powder using mortar and pestle. The sample was totally dried and then pressed into KBr disc. Five tone pressures were applied to the sample to form a transparent disc. Infrared spectrum for each sample was recorded in the range of 450cm^{-1} to 4000cm^{-1}.

NMR: Ink extracts were used for NMR analysis by making NMR tubes. In NMR tubes, 4 drops of sample extract was mixed with approximately 4.0 ml solvent (chloroform) and finally closed tightly.

RESULTS AND DISSCUSSION

Table 2 shows the color bands and the R_f values of blue inks developed by solvent system used as such serially obtained on silica plate under normal incident daylight. From developed chromatogram ink samples of different brands A1, A2 and A3 showed four separated bands with R_f values given in table 2. The separated bands were analyzed using UV, IR and NMR spectroscopy.

Table 2- Separate color bands of different blue fountain pen inks and their R_f values.

Camel blue (A1)			Chelpark blue (A2)			Parker blue (A3)		
Color band	**code**	**R_f**	**Color band**	**code**	**R_f**	**Color band**	**code**	**R_f**
Pink	A14	0.4	Pink	A24	0.42	Blue	A34	0.58
Purple	A13	0.52	Purple	A23	0.55	Gray	A33	0.50
Light blue	A12	0.59	Blue	A22	0.69	Purple	A32	0.45
Blue	A11	0.72	Light blue	A21	0.74	Pink	A31	0.32

The inks of the three brands from fountain pen were examined by UV-Vis spectrophotometer in the wavelength range from 200-800 nm. Fig 1 shows the absorbance spectra from three brands of blue fountain pen samples. All of the ink samples showed one maximum absorbance peak in the wavelength range 210-280nm. A_3 ink samples showed the highest absorbance at wavelength 211.03 nm, A_2 at 296nm and A_1 at 297nm.

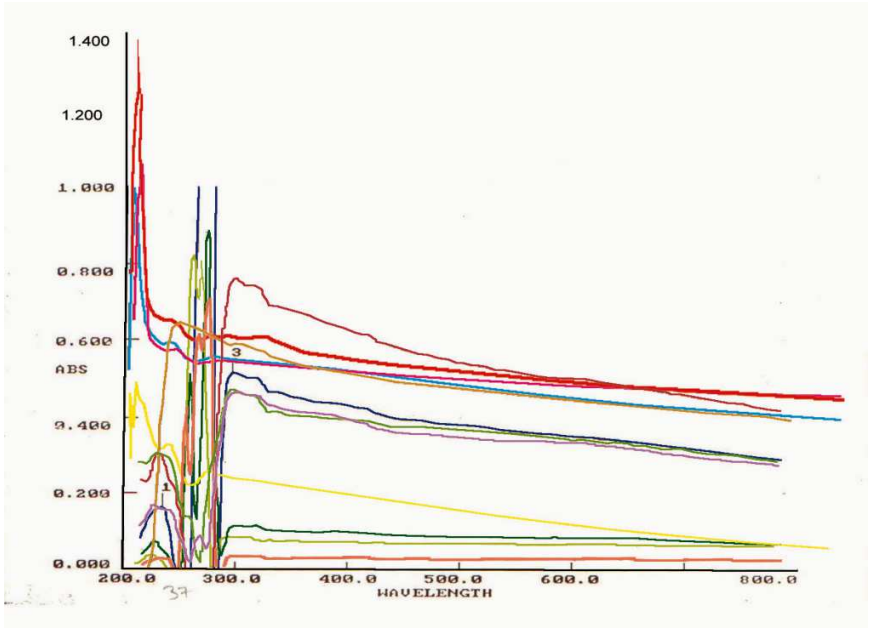

Fig.1- UV ofdye stuff obtained from A1, A2 & A3 blue fountain pen inks

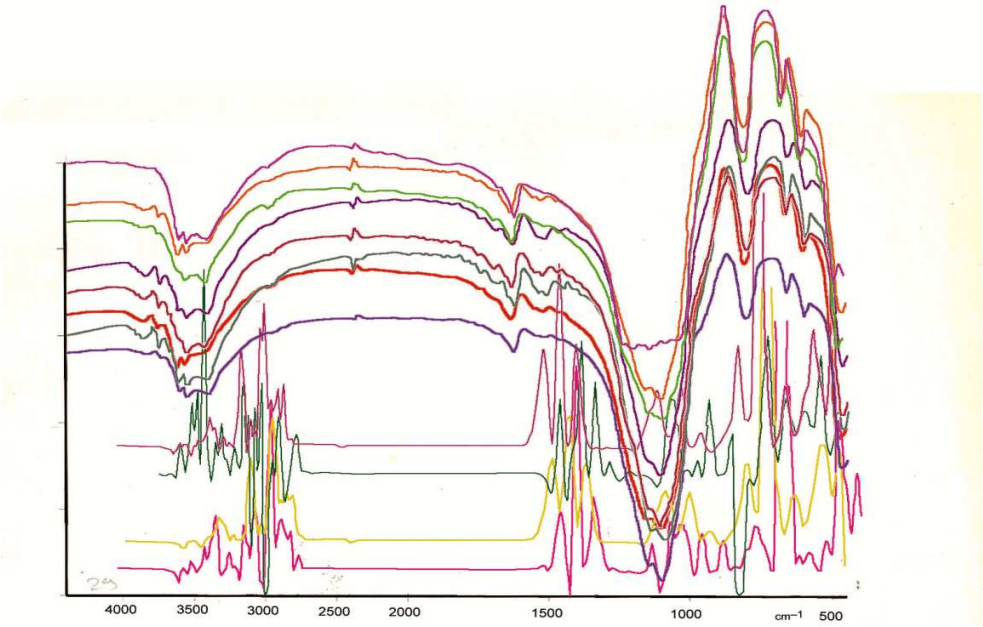

Fig.2- FTIR ofdye stuff obtained from A1, A2 & A3 blue fountain pen inks

The IR spectra for each brand generally showed a broad peak at 3000cm^{-1} to 3600cm^{-1}. This indicates the presence of the NH_2 group in the ink formulations. That was expected since fountain pen ink contained amine group. Three brands of the pens were analyzed in the region of 450cm^{-1} to 4000cm^{-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 graph the spectra of blue fountain ink from different brand A_1, A_2 and A_3 were quite similar. All spectra possessed a broad peak in the range 3000cm^{-1} to 3600cm^{-1} indicating the presence of CH_2NH_2 group in these inks and the presence of peaks in the range 1600cm^{-1} indicate the presence of aromatic compound or C=C or C=N group and peak in the range of 1100cm^{-1} indicate the presence of C-O-C bond. FIG2 shows the comparison of IR spectra of blue fountain pen inks. These spectra showed a broad peak in the range 3000cm^{-1} to 3600cm^{-1} indicating the presence of CH_2NH_2 group in these inks and the presence of peaks in the range 1600cm^{-1} indicate the presence of aromatic compound or C=C or C=N group and peak in the range of 1100cm-1 indicate the presence of C-O-C bond. Fountain pen ink of three brands showed peak in the range from 1000cm^{-1} to700cm^{-1}.

The NMR spectra presented in fig. 3 for each brand generally showed a peak at 7.0-7.5ppm. This indicates the presence of aromatic or CHX_3 and peak at 2.3-2.6ppm, it shows the presence of $(CH_3)_3N$ and 3.7ppm indicate the presence of CH_2X_2.

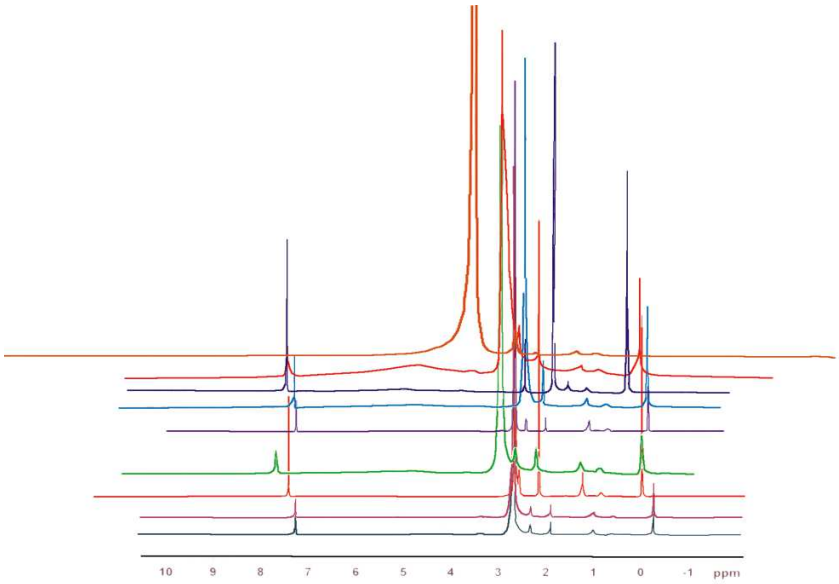

Fig.3- NMR ofdye stuff obtained from A1, A2 & A3 blue fountain pen inks

CONCLUSION

UV-Vis analysis showed that blue fountain pen ink samples that is A_1, A_2 and A_3 displayed only one peak at the wavelength in the range of 210 to 280nm. For IR/NMR analysis is not easy to discriminate these inks since all the samples have the same formulation. However the difference can be seen by looking at the intensity of main peak as well as the pattern of each spectrum.

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