Original Article

STUDY ON THE EFFECT OF AGEING TO GEL PEN INK ON PAPERS USING ATTENUATED REFLECTANT MODE FOURIER TRANSFORM INFRARED (ATR-FTIR) SPECTROSCOPY .

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ABSTRACT

Forensic analysis of writing ink ageing on document is one of the most challenging parts in forensic investigation. It can significantly prove to be useful in forensic document examination as it helps to build a timeline of an event or provide link to investigation. The objective of this study was to study the effect of ageing to gel pen ink on different papers i.e. A4, envelop, newspaper and manila card using Attenuated Reflectant Mode Fourier Transform Infrared (ATR-FTIR) spectroscopy. Inks were deposited on four different types of papers and subsequently subjected to ageing at different interval (7, 14, 30, 60 and 90 days). The aged and fresh inks were compared through visual examination and statistical evaluation using paired t-test was then carried out based on their mean absorbance. The results showed that the gel pen ink deposited on different types of papers subjected to ageing could not be differentiated from their fresh counterpart using ATR-FTIR and statistical analysis. As a conclusion, under the experimental parameters used in this study, the writing inks deposited on different types of papers subjected to ageing could not be differentiated from their fresh counterpart using ATR-FTIR and statistical analysis.

INTRODUCTION

In forensic science, document associated with criminal cases in which its authenticity and author-ship are questionable or dubious are termed as questioned documents (QD). They can be prepared either manually using writing instruments such as ballpoint pen, gel pen, marker pen, fountain pen and pencil or automatically using computer, commonly on paper although other materials are also possible. In forensic science, careful analysis of QD could reveal useful information regarding the authorship, authenticity and type of writing instruments being used to prepare the documents. Writing ink on paper is particularly important because of the significance of signatures and handwritten records. The paper document is the most popular writing medium in daily life until today.

In 2007, a study [1] had shown that Solid Phase Micro-extraction (SPME) technique can be employed to determine the volatile components of ball point inks quantitatively by direct analysis on paper prior to Gas Chromatography-Mass Spectrometry (GC–MS) [1]. The aim of SPME technique used was to monitor the evaporation of ink's volatile components as the ink ages on document [1]. A previous study [2] also reported that SPME extraction was capable to monitor the ink ageing analysis. SPME have high sensitivity and limit of detection. However, this technique requires sample preparation and time consuming.

Gel pen inks

Gel ink pen is a popular writing material due to its smooth and interesting writing appearances [3]. They are used in daily activities to sign contracts, checks, loans and other documents. Gel pen inks are water-based inks which contain dyes or pigments as colorants, water as vehicles, resins, nonionic surfactants and other additives [4]. Acid dyes and related organic compounds containing several sulphonic groups generally used as the colouring agents in gel pen inks [4][5]. Nowadays, the growths of modern techniques allow easy and efficient way to analyse and identify gel pen inks.

Previous study [6] showed that Ion Pairing High Performance Liquid Chromatography (IP-HPLC) was capable to detect the composition changes in blue gel pen ink deposited on paper stored at different lighting conditions and also in natural environment. Chromatograms were developed to interprete the ageing mechanism of ink to establish the differences between natural and artificial ink aging [6]. Besides, it also provided an explanation on the changes the relative component of the dyes in the blue gel pen ink [6].

The aim of this study were to analyse fresh and aged writing inks on the different papers using ATR-FTIR, to manually evaluate the spectra of fresh and aged gel pen ink on the different papers and to determine the most optimum IR spectra region for statistical comparison of aged inks with their fresh counterparts.

MATERIALS & METHODS

Sample collection

Gel pen, fountain pen, marker pen, white A4 paper (70 gsm), envelope, newspaper and manila paper where purchased from a book store located in Kubang Kerian area. Table 1 shows the list of samples used in this study and their respective reference code.

Sample preparations

Each of the paper was cut into small rectangular square with dimension of 1 cm x 1 cm using a pair of scissors. The inks from the ballpoint pen and gel pen were transferred onto the paper by scribbling ensuring that the whole area of the papers were covered with inks. The paper cuts were secured onto a board using hair pins and then left to age at room condition for 90 days. For the purpose of sampling identification of the paper cuts, they were given reference codes according to the list in Table 2.

FTIR Spectral acquisitions

The spectra of the inks were acquired using a Bruker Tensor 27 (Bruker Optics, UK) FTIR spectrometer equipped with a diamond ATR sampling attachment. Prior to acquiring the spectra of the inks, a standard polystyrene film was scanned to ensure that the ATR-FTIR was working correctly. Spectral measurements were taken over the entire spectral range of 4000 cm^{-1} to 600 cm^{-1} with resolution of 4 cm^{-1}. Within this ageing period, spectra of the inks were acquired at 0 day (i.e. immediately after preparation), 7 days, 14 days, 30 days, 60 days and 90 days interval.

Spectral evaluations by direct visual comparisons

The effect of ageing to gel pen ink on the different papers was evaluated by directly comparing the spectra of aged inks to the spectra of their fresh counterparts which were acquired immediately after preparation (i.e. 0 day). This method was necessary in order to narrow down the selection of infrared region to perform statistical analysis.

Statistical analyses

Paired t-test was performed to statistically evaluate the effect of ageing using IBM SPSS statistical software (SPSS 2.0, IBM, USA). Data pre-processing (i.e. standardisation) was performed prior to statistical test in order to overcome 'one-to-one' variation within a large data set. To assess the effect of selection of spectral region to ageing evaluation, the paired t-test was first performed to the frequency region and then to the fingerprint region (1500 cm^{-1} – 600 cm^{-1}). The

Table 1: List of samples used in this study and its respective code

Sample	Reference code
Gel pen	B
A4 paper	a
Envelope	b
Manila paper	c
Newspaper	d

Table 2: List of sample cuts with their respective reference code

Sample description	Reference code
Gel pen on white A4	Ba
Gel pen on white envelope	Bb
Gel pen on white manila paper	Bc
Gel pen on newspaper	Bd

parameters set-up for the paired t-test is shown in Table 3. Null hypothesis will be accepted when the computed p-value exceeded the α value, and vice versa.

RESULTS

Repeatability and reproducibility studies

Repeatability and reproducibility studies were performed prior to performing the ageing study of the writing inks on the different papers to evaluate the intra and inter precision or robustness of the techniques employed. The repeatability and reproducibility were measured by calculating the percentage (%) Relative Standard Deviation (RSD) of the absorbancies of six prominent bands or peaks was selected from the resultant spectra of the writing inks on the papers. The selected bands are as shown in Figure 1.The %RSD calculated for both repeatability and reproducibility studies were less than 5% and less than 20% respectively which indicating good intra and inter precision of the techniques.

Visual examinations of the infrared spectra

Figure 2 to 5 displays the spectra of the gel pen ink on the different papers after being aged in the environment for 7, 14, 30, 60 and 90 days. The 0 day spectrum was obtained from the writing ink immediately after its deposition on the paper. It acted as reference spectrum where the spectra of aged inks were compared.

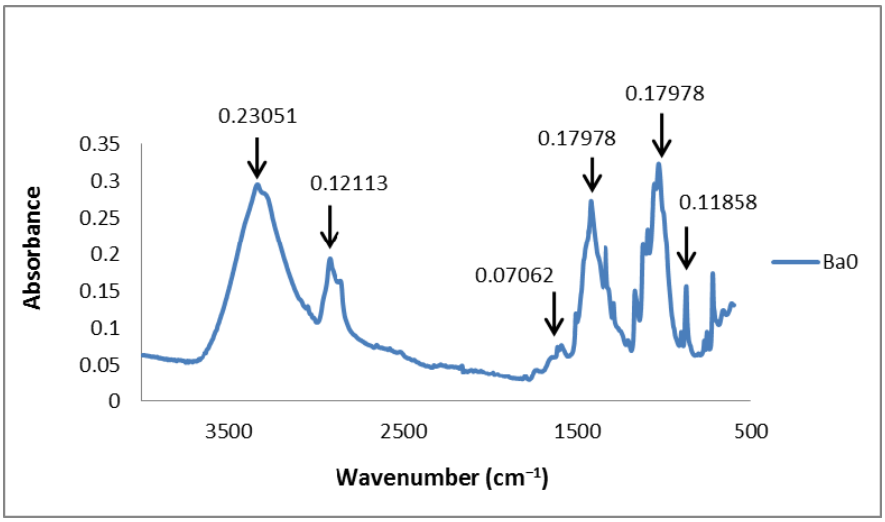

Figure 1: The infrared spectra of gel pen ink on A4 paper. The arrows show the six prominent bands used to calculate the %RSD for repeatability and reproducibility studies.

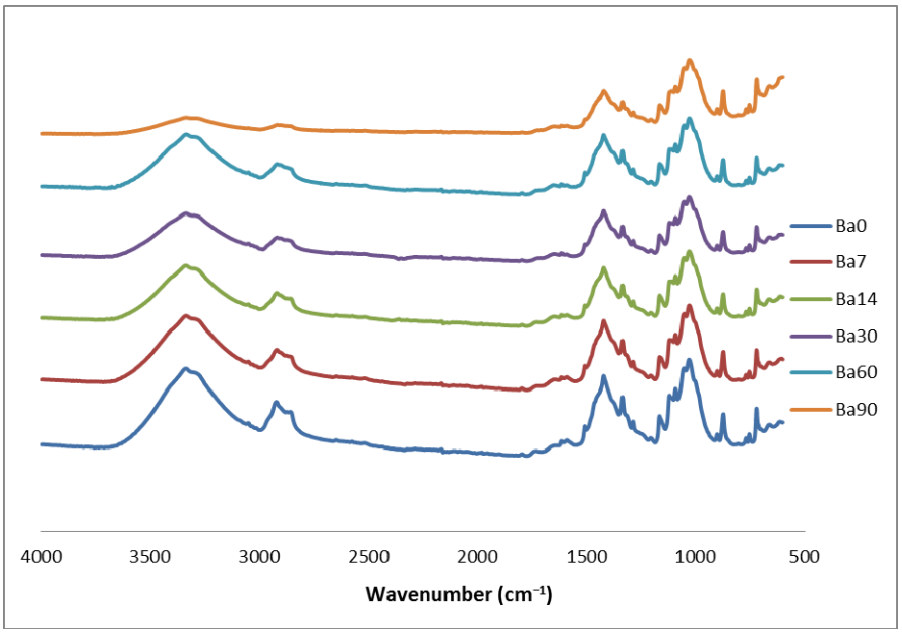

Figure 2: Infrared spectrum of gel pen ink on white A4 paper

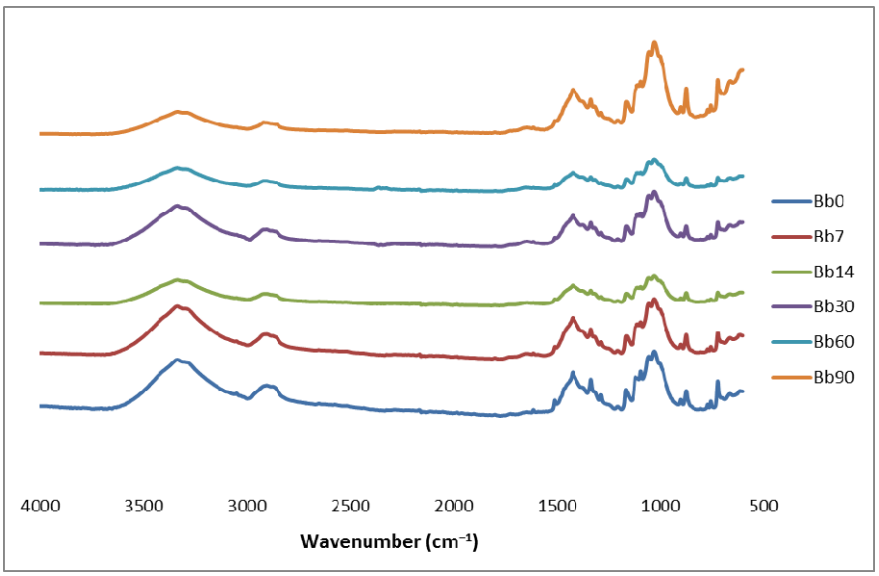

Figure 3: Infrared spectrum of gel pen ink on white envelope

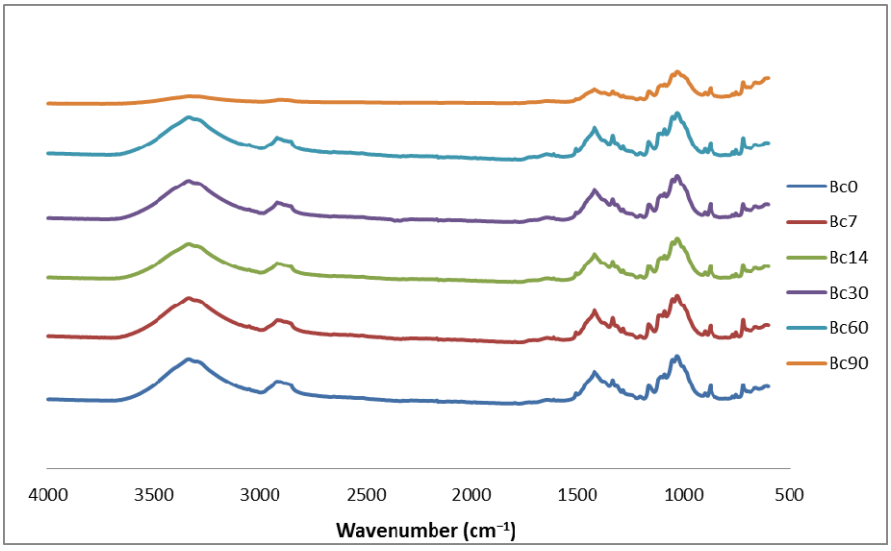

Figure 4: Infrared spectra of gel pen ink on manila paper

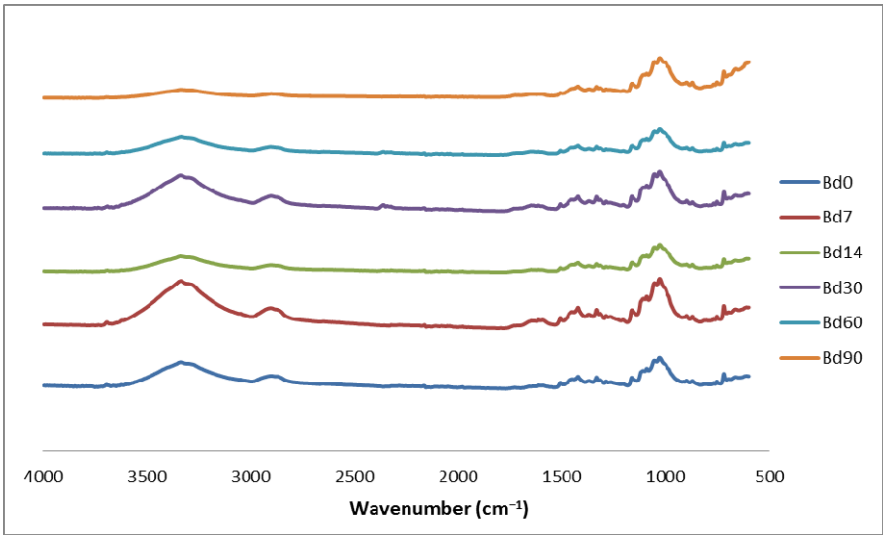

Figure 5: Infrared spectra of gel pen ink on newspaper

Statistical analyses
Paired t-test was used to evaluate the effect of ageing of writing inks on different papers to the environment. This particular statistical test was chosen to assess pre and post treatment effect, in this case, before and after ageing in the environment. The frequency and fingerprint regions were tested separately. The main reason was to see which regions can successfully capture the ageing effect. The frequency region at 3700 cm^{-1} – 3000 cm^{-1} was selected as this corresponds to the O-H group region that had shown remarkable changes over 90 days of exposure from visual examinations. Table 4 shows the outcomes of paired t-test for gel pen inks on white A4 paper.

DISCUSSION

Repeatability and reproducibility studies
The %RSD calculated for both repeatability and reproducibility studies were less than 5% and less than 20% respectively which indicating good intra and inter precision of the techniques.

Visual examinations of the infrared spectra
In general, the spectra of the gel pen inks on the different papers did not show any remarkable changes especially at the fingerprint region, in other words were quite consistent except for O-H group within the group frequency region which showed marked decrement particularly after 90 days of ageing. This is because ink components could oxidise, cross-link, polymerise, and evaporate when exposed to the environment [7].

Based on visual examinations alone, it was extremely difficult to conclusively judge or said that the writing inks had experienced significant changes after 90 days of ageing. These situations hence justify the use statistical technique to evaluate the effect of ageing. In this study, paired t-test was used and its outcomes are further discussed in the following section.

Statistical analyses
Table 4 showed that the p values of the paired t-test for all conditions at fingerprint region were greater than 0.05. This means that there was no significant difference before and after ageing. In other words, no changes in terms of organic components of ballpoint pen inks. Samples deposited on the different papers after 7, 14, 30, 60 and 90 days of exposure p value was equal to 1.000 (p = 1.000).

However, it showed different outcomes of p value of the paired t-test for all conditions at frequency region (3700 cm^{-1} – 3000 cm^{-1}) where p <0.05 for all conditions. This means that there was no significant difference before and after ageing. Similar results can be observed for gel pen ink deposited on envelope, manila and newspaper.

The significant difference occurred at O-H absorption band was due to moisture of environment and from the solvent within the ink component. Besides that, it was also influenced by behaviour of solvent that contain O-H group was easily evaporated when the ink affixed on paper. This change was not necessary that the ink component changed over 90 days because at fingerprint region, it composed of other ink components. Thus, it was conclusively judge the profile of ink does not change over 90 days.

CONCLUSION

From the result obtained, visual examinations could not objectively evaluate the effect of ageing to gel pen inks. On the other hand, statistical analysis i.e. using paired t-test can objectively evaluate the effect of ageing to writing inks as demonstrated in the present study. The statistical results suggested that there were no significance

Table 4: Results of paired t-test of gel pen on A4 paper.

Sample	IR region			
	3700 cm^{-1} – 3000 cm^{-1}		1500 cm^{-1} – 600 cm^{-1}	
	t-stats (df)	p value*	t-stats (df)	p value*
Ba0-Ba7	-35.575 (364)	0.000	0.000 (467)	1.000
Ba0-Ba14	-50.750 (364)	0.000	0.000 (467)	1.000
Ba0-Ba30	45.961 (364)	0.000	0.000 (467)	1.000
Ba0-Ba60	-49.240 (364)	0.000	0.000 (467)	1.000
Ba0-Ba90	45.983 (364)	0.000	0.000 (467)	1.000

difference between aged inks with their fresh counterparts on after 90 days of exposure to the environment. Meanwhile, the paired t test calculated using the frequency region (3700 cm^{-1} – 3000 cm^{-1}) showed that there were significant changes between aged inks with their fresh counterparts. However this could not conclusively reflect on the overall change to inks compositions since this region corresponds to O-H which might due to solvent used in the manufacturing of the inks for example phenoxyethanol or perhaps moisture absorbed from the environment.

Needless to say, evaporation of these substances is inevitable process as such could not be used to judge changes experienced by the inks. Fingerprint region is suggested to be the region to study the effect of ageing because it composes of more complex ink's components. These findings also infer that organic components in writing ink might be stable and did not change significantly up to three month of exposure to the environment.

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