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Evaluation of Organic Solvents Efficiency for Ink Samples Extraction

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ABSTRACT

Questioned document examination becomes a great interest and one of the broad fields in forensic science. It involves the analysis of ink, handwriting and signature examination, paper's physical structure analysis and the ageing of a document. Ink analysis in forensic document examination is a challenging process. Questioned documents examiners are dealing with unknown source of ink and minute sample size. Ink extraction needs to be done before the ink analysis. 17 gel pen ink samples were chosen in this study. Solubility test has been done to determine the degree of solubility of ink in a variety of organic solvents. Extraction solvent optimization is a process to evaluate the efficiency of organic solvents to extract ink samples. Ethanoic acid showed the ability to dissolve most of the ink samples and displayed maximum absorbance of UV-Vis spectra.

Keywords: *gel pen ink; ink analysis; ink extraction; organic solvent; questioned document examination.*

1. INTRODUCTION

Advancements of technology today required all transactions or documentation to be digitally executed. Despite this paradigm shift, paper and handwritten documents are still utilised in many legal transactions like medical records, diaries, receipts, letters, contracts, cheques and others. Besides, people's signature is required for the legalities of these formal documents [1]. Varieties of pen have been chosen as the editorial medium on documents. The foremost conventional ink formulations used today come from ballpoint pen, rollerball pen and gel pen [2].

Documents will undergo physical and chemical changes once the ink was deposited on the surface of the paper. The changes include solvent evaporation, hardening polymerization of resin and dye degradation. The longer the ink has been deposited on the document, the more changes will occur. Hence, the method of ink extraction will take an extended time. Any documents associated with crime cases that raise doubts in authenticity and authorship are called as questioned documents [3]. It is also named as any object bearing handwriting or typing material. Any writing on the wall, door, windows or any objects are also classified as a questioned document [4]. Question document examination becomes a good interest and among one of the broad fields in forensic science. It involves analysis of ink, handwriting and signature examination, paper's physical structure analysis and also the ageing of documents [5].

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The ink may be a liquid or semi-liquid material used for writing, printing or drawing. Generally, the ink contains fine pigment particles dispersed in a solvent. The pigment may or might not be coloured and also the solvent could also be aqueous or organic. Today ink formulations are very complex. The ink is made up from three basic components: (1) carrier solvent which allows colourants to flow on the surface, (2) colourants which consist of pigments or dyes that give colour to the ink. There are two sorts of colourants, natural and artificial. In addition, the last component (3) is additives like resins, lubricants, solubilizes, surfactants, particulate matters or fluoresces. The standard and quantity of additives used will be varied and be determined by the ink manufacturer [6],[7].

Nowadays, gel pen has become famous. It had been first manufactured by Sakura Colour Products Corporation from Japan in 1984. Its popularity is because of its low cost, smooth writing characteristic and environmental friendly [8]. Many manufactures produced their brand of gel pen. Hence, each brand will have its unique composition of ink recipe.

Gel pen inks written in a questioned document must be extracted before analysis. Ink extraction could be a crucial step within the forensic field which involves the ink analysis. Sharma and Kumar claimed that ink extraction is incredibly important within the accuracy of date estimation of ink [9]. The extraction process could be a simple process with the acceptable organic solvents used. However, questioned documents examiners face an issue to settle on the acceptable solvents for ink extraction as inks from different brands will have their uniques composition. It will result in more solvent consumption and therefore the extraction process will become tedious. Besides, documents examiners must consider the ink sample size provided as the inks written in questioned documents exist in minute quantity.

The objectives of this study are to classify the type of blue gel inks and to evaluate the efficiency of organic solvents to extract the ink from varieties of blue gel pen inks. Extraction process provides a degree of ink solubility in organic solvents. The data obtained can help questioned document examiners to choose the appropriate organic solvent for ink extraction in real crime cases.

2. METHODOLOGY

2.1 Solubility Test

Solubility test was done to determine the solvent that has the ability to extract the ink line drawn on paper. Solubility was measured based on the ability of the ink to dissolve, the colours of extraction and the presence of precipitate in the extract. 17 blue gel pens (Figure 1) were randomly chosen in this test. The sample codes of blue gel pen inks are as listed in Table 1.

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Figure 1: Varieties of gel pen ink samples

Table 1: Samples code for blue gel pen ink

Brand	Tip Size	Pen Description	Sample Code	Number of samples
Faber Castell	0.7	Fast Dry Air Gel	FCAG	2
	0.7	True Gel	FCTG	
M&G	0.7	R5	MGR5	2
	0.5	Y Gamma	MGYG	
Pilot	1.0	Signature Pen G3	PG3	2
	0.5	Wingel	PWG	
Paper Mate	0.7	Gel	PMG	2
	0.7	Ink Joy	PMIJ	
Uniball	1.0	Broad Waterproof	UB	1
Exan	0.5	G383	EX	1
Zebra	1.0	Sarasa Clip	ZB	1
Monami	0.5	Jeller Pen	MNJP	2
	0.4	Jell Line	MNJL	
Pentel	1.0	Energel BL110	PT110	2
	0.7	Energel BL417	PT417	
Stabilo	0.5	Palette	STP	1
Unicorn	0.38	Ultra-Fine	UNC	1
			TOTAL	**17**

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Each ink samples were prepared by writing 10 cm ink line on 80 gsm white paper. These papers were then soaked in 60 mL of variety solvents (Figure 2) such as methanol, ethanol, acetone, acetonitrile, acetic acid, chloroform, dichloromethane, n-butanol and ethyl acetate. The time for all the ink samples to dissolve was set at 15 minutes in room temperature.

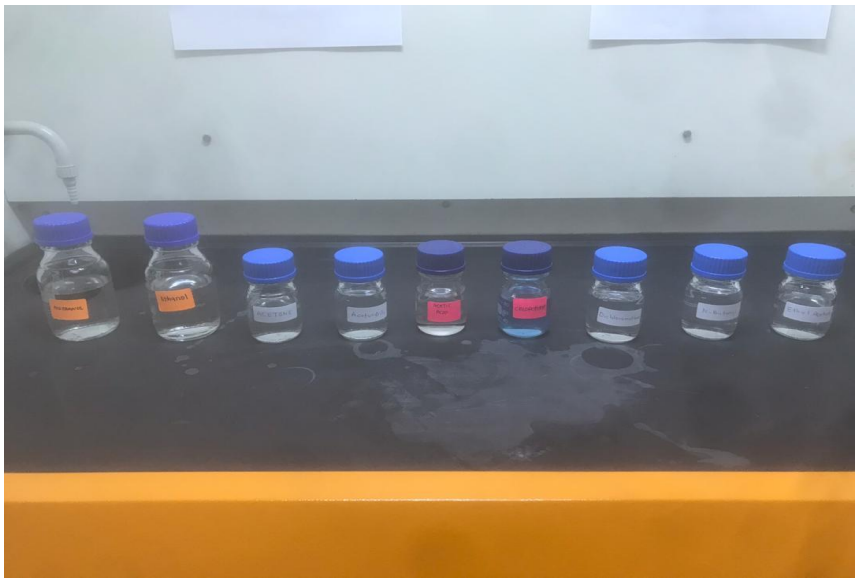

Figure 2: Organic solvents for ink extraction

2.2 Extraction Solvent Optimization

The selection of suitable solvent is very crucial as the amount of sample in real crime cases received by the forensic document examiner is in minute size. Solvent opmitization was done to attain the solvent that displayed the maximum absorbance value of UV-Vis spectra. Solvent optimization was done using UV-Vis spectrophotometer Lambda 35 Perkin Elmer. Extraction of PMIJ and PT110 were randomly chosen in five solvents from previous solubility tests such as methanol, ethanol, acetone, acetonitrile and acetic acid. Absorbance spectrum was recorded in the wavelength range 300 nm – 800 nm.

3. RESULT AND DISCUSSION

Table 2 shows the result of the solubility test with different solvents. Figure 3 shows the degree of ink solubility.

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Table 2: Solubility test result for the blue gel pen ink samples

Organic Solvents / Ink Samples	Methanol	Ethanol	Acetone	Acetonitrile	Acetic Acid	Chloroform	Dichloromethane	n-butanol	Ethyl acetate
FCAG	1	1	0	1	1	1	0	1	0
EX	0	0	0	0	0	0	0	0	0
PG3	2	2	1	1	2	1	1	1	0
MGR5	0	0	0	0	0	0	0	0	0
MGYG	0	0	0	0	0	0	0	0	0
PM	0	0	0	0	0	0	0	0	0
UB	0	0	0	0	0	1	0	0	0
PMIJ	2	2	1	1	2	1	0	1	0
STP	2	1	1	1	1	1	0	0	0
UNC	2	1	1	1	2	1	0	0	0
PT110	2	1	1	2	2	1	1	1	0
ZB	0	0	0	0	0	0	0	0	0
FCTG	0	0	0	0	0	0	0	0	0
MNJP	2	1	1	1	1	1	1	0	0
PT417	2	2	1	1	2	0	1	1	0
MNJL	0	0	0	0	0	0	0	0	0
PWG	2	2	1	1	2	1	1	1	0

Based on Table 2, the results show two gel inks from Pilot (PG3, PWG) and Pentel (PT110) dissolved in all solvents provided except ethyl acetate. PMIJ, STP and UNC ready to dissolve in seven solvents excluding dichloromethane and ethyl acetate. PT417 was able to dissolve in all solvents except chloroform and ethyl acetate. Conversely, EX, MGR5, MGYG, UB, ZB, FCTG, PMG and MNJL were unable to dissolve in all solvents provided therefore these ink samples will not be selected for further analysis. The ink composition was one of the factors that influenced the solubility. According to Liu *et al.*, 2006 dyed based ink is able to dissolve in organic solvent compared to pigment-based inks [8].

The observation from this solubility test able to separate 17 blue gel pen ink samples into two groups, 9 dye-based gel inks and 8 pigment-based inks. This result complemented the findings of Liu *et al.*, 2006 as they were able to classify black gel pen ink into pigment-based ink and dye-based ink from solubility test [8].

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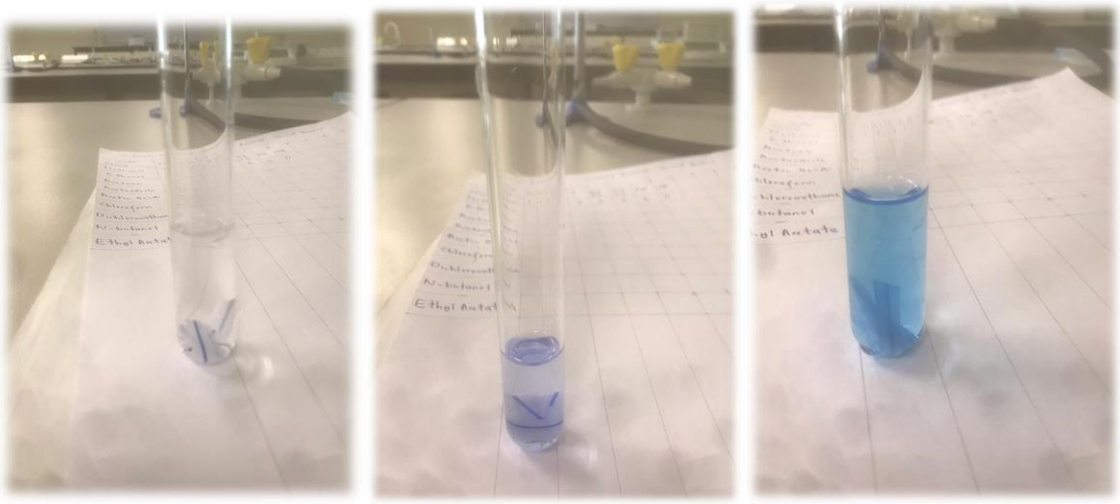

0 – Insoluble 1 - Partially Soluble 2- Completely Soluble

Figure 3: Degree of ink solubility

As we can see from Table 2, all the ink samples could not be dissolved in ethyl acetate. Gel pen inks used water as a carrier. Ethyl acetate is slightly soluble in water due to limited hydrogen bond formation. Hence it is unable to extract all the gel pen ink samples. Only 5 and 6 samples were able to dissolve in dichloromethane and n-butanol respectively. Hence, these three solvents were classified as inefficient for ink extraction and be excluded for extraction solvent optimization.

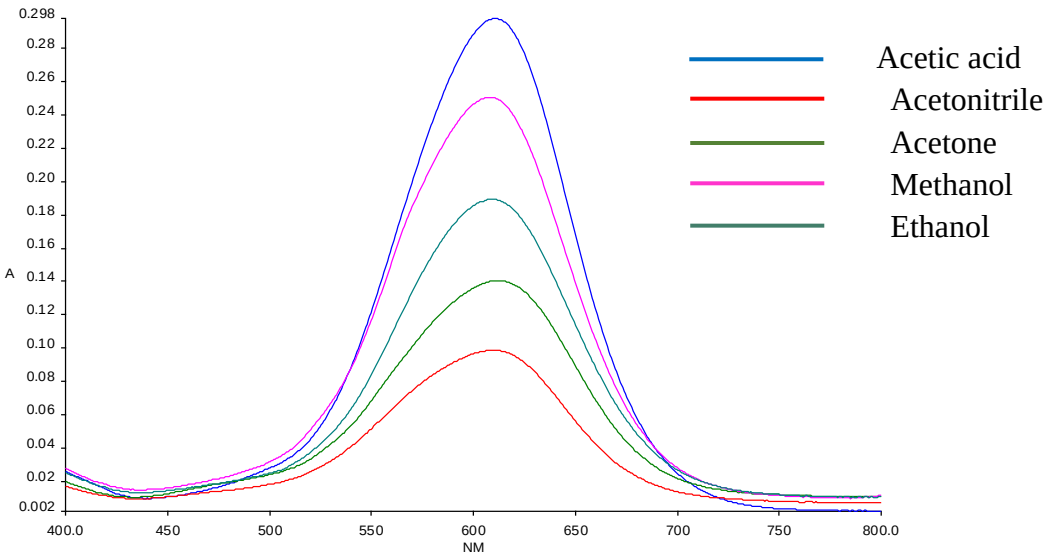

Figure 4: UV-Vis spectra of PMIJ blue ink sample extracted using different solvent

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From the observation, there is no precipitation formed for every sample in the solubility test. The degree of the solubility was done based on human eye judgement and observation. Therefore, the solvent which extracts the maximum amount of ink from the writing samples can only be verified by UV-Vis spectroscopy analysis [10]. This task is achieved by comparing the absorption value of extracted inks from UV-Vis spectra.

Figure 4 and Figure 5 show the overlay spectra of PMIJ and PT110 in selected organic solvents from solubility test done before. PT110 and PMIJ sample displayed a prominent peak at the range 550 nm to 650 nm and 600 nm respectively. The result has shown that the ink extraction for PMIJ and PT110 in acetic acid is the most efficient followed by methanol and ethanol. Acetic acid shows the highest absorbance for both ink samples, indicating that it is effective to extract the maximum amount of ink from the writing samples.

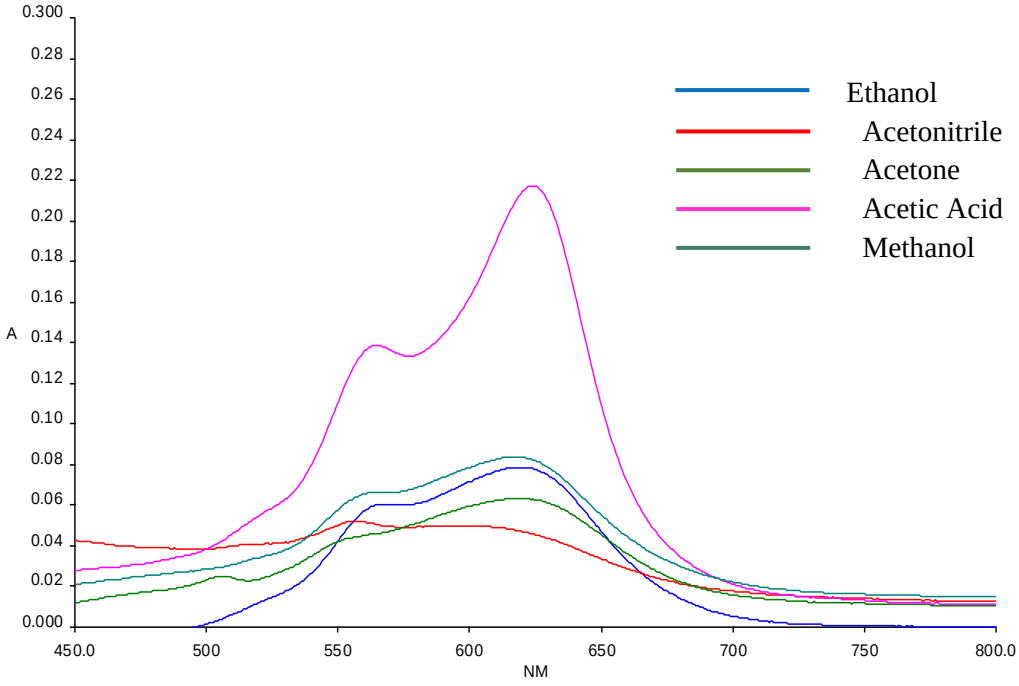

Figure 5: UV-Vis spectra of PT110 blue ink sample extracted using different solvents

4. CONCLUSION

Five organic solvents; methanol, ethanol, acetone, acetonirtile and acetic acid are able to dissolve most of the samples with the highest degree of solubility. The result obtained showed that acetic acid was the effective solvent to extract most of the ink samples from the paper. Ink extraction in acetic acid displayed maximum absorbance of UV-Vis spectra. However, in real cases, acetic acid could be a corrosive chemical. Hence, questioned document examiner can consider ethanol as the best solvent for ink extraction. Further study should be done by including a large form of gel pen brands and different colours such as black or red.

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