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Forensic analysis on printer inks via chemometrics

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Forensic analysis on printer inks via chemometrics

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Abstract. Printer inks are becoming necessary for utilization for wide range of purposes by society in current times with rapid development in technology and digital media area. Thus, forgery and counterfeiting becoming easier for the criminals. It is dangerous as some criminals will misused the technology by mean of addition and adulteration of parts of text or numbers on document as the inks and document can be made as an evidence in the trial court. Thus, the characterization and differentiation of the printed inks in the suspected documents (civil or criminal cases) may provide important information about the authenticity of the printer inks. The focus of this study to differentiate the chemical component of three different types of sample inks by incorporation of FTIR spectrophotometer with principal component analysis. The unique features of the ink samples were unmasked from the score plots of the principal component analysis. Thus, the graphical representation provided by the FTIR spectra with principal component analysis enabled the discrimination certain chemical in the printer inks.

1. Introduction

Ink cartridges and inkjet printers are important technology for everyone daily uses whether for office or personal purposes. Inkjet printers can be used to print out many different types of documents. Consequently, the negative parts of this technology are criminals are able to manipulate this technology to commit several crimes such as forgery and counterfeiting. The crime of forgery generally concerns the making of fake documents (certificates or identification cards), false banknotes, stamps and checks, the changing of an existing document (e.g., prescription) or the creation of a signature without authorization (false stamps, false signs) [1 need to find fwd ref]. These documents also can be used as evidences in a court for some particular cases. The verification of the authenticity of these documents are crucial because if these documents are lacking in evidence of authenticity, the trial judge have the authority to dismiss the document as irrelevant evidence. Therefore, forensic chemists and forensic laboratories are increasingly engaged in the verification and examination of the documents and inks. Paper and printer inks can be used as a sample by the chemist to examine the authenticity by providing details with regards to the different types of chemical compound of the ink and when its manufacture with its sources [2]. This information can be related to examine in case a particular ink is counterfeit or authentic.

The utilization of ink cartridges with printer will never fade away anytime soon in the current time or foreseeable future because it can translate as a medium between people and digital world. The interesting and challenging parts about inks and printers is that anyone with access to low-cost scanners, printers, inks and personal computers are capable of generating forgery, counterfeit and unauthorized duplication of some particular documents [3]. The immediate progress of the printing technologies has given high advantage towards the criminals. The information about chemical formulation of each manufactured ink is unknown, therefore there is quite a challenge and can be out into question to identify the brand of the printing ink cartridges [4]. This project focusing on to differentiate the chemical components in the three different types of cartridge inks by developing a modeling of the inks by using multivariate data analytical techniques with FT-IR spectroscopy and MATLAB. The modeling will be functioning as a database for the chemists and examiners to aid their verification and authentication process by extracting the particular information about the inks rather than making the modeling from the scratch.

This study focuses on the three different types of authenticity of printer inks. The identification and characterization of printer inks can be performed based on the properties of functional groups exists in the sample. The samples in then analyzed by the FTIR spectrophotometer. The chemical bonds in the samples will vibrate once the infrared radiation that interacts with the matter is absorbed which produce the infrared spectrum. The correlation shows the infrared band positions and chemical structure becomes the fundamental information for the analyst to identify the unknown molecules or even the structural identification. After that, the dataset obtain from the FTIR spectra will be further analyzed using principal component analysis. Principal component analysis is one of the chemometric methods to recognize the similarities and differences of the chemical information by providing the pattern of the sample [5,6]. In addition, significant information about the samples also can be extracted from the principal component analysis [7].

2. Materials and Method

Six different types of inks were used in this study. The authentic and claimed as authentic printer inks of the same brand were bought separately at the local stores in Kuala Lumpur whilst the counterfeit printer inks were bought from Shopee online stores. The color of the printer inks used in this project is a yellow color. The samples were divided into *Group 1* and *Group 2* as shown in Table 1. *Group 1* consists inks that were printed on papers using a personal office printer followed by FTIR analyses whilst *Group 2* consists samples of inks which were tested directly by the FTIR spectrophotometer. The brand of the personal printer model used in this project was Epson printer model L100. Samples in *Group 1* were printed out on A4 sized papers (70 gsm) from a brand named Topvalu Multipurpose. Then the printed papers were cut into rectangular blocks with a size of 3.81 cm height and 5.08 cm width.

Table 1. Two groups of coloured and black printer inks representing the authentic, claimed as authentic and counterfeit samples.

Type of Ink	Brand	Colour/Black	Group 1	Group 2
Authentic	Epson T6641 (Yellow)	Colour	Sample 1	Sample 7
	Epson T6641 (Black)	Black	Sample 2	Sample 8
Claimed as authentic	Epson Refill Ink Compatible with T664 Series	Colour	Sample 3	Sample 9
		Black	Sample 4	Sample 10
Counterfeit	Universal Refill Ink for All CISS or Ink Tank Printer	Colour	Sample 5	Sample 11
		Black	Sample 6	Sample 12

The analysis process carried out using FTIR spectrophotometer which is located in International Institute for Halal Research and Training (INHART) laboratory at IIUM Gombak. The range of spectra is 4000 cm^{-1} to 400 cm^{-1} per one scan per sample. The generated dataset from FTIR spectrophotometer will be exported from Excel to MATLAB software version MATLAB® R2018b 7.10.0.499 produced by MathWorks company prior to performing principal component analysis (PCA). The PCA reduces the dimensions of a high dimensional data matrix onto a simple and interpretable PCA plots. In Figure 1, the data matrix X comprises by n by p matrix where 'n' represents the absorbance values of the samples and 'p' represent the number of spectral ranges. The score plots obtained from principal component analysis were further analyzed for the spectral characterization and identification of samples.

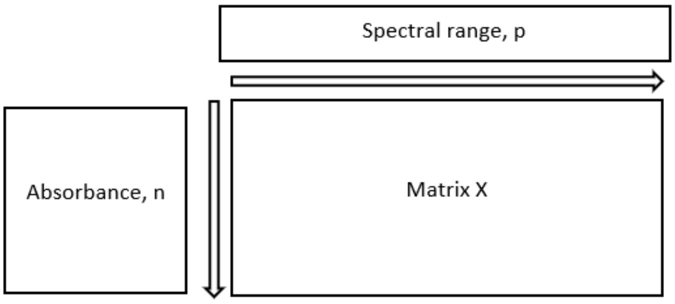

Figure 1. Two-dimensional data array, X.

3. Results and Discussions

The FTIR spectra illustrating the chemical structures of each type of printer inks used in this study were shown in Figure 2. The odd numbered samples represent the coloured printer inks (Samples 1, 3, 5, 7, 9 and 11) whilst the even numbered samples represent the black printer inks (Samples 2, 4, 6, 8, 10 and 12). Differences in the chemical arrangement and chemical composition in the inks result in distinctive spectra of each sample. When an organic compound interacts with infrared radiation, certain energy frequencies are absorbed while others are transmitted or reflected. The presence of functional groups in the substance determines whether the frequencies were absorbed or transmitted. To aid to the examination of the FTIR spectra, the spectra were assigned into four regions to determine the possible functional groups or chemical compounds in the inks (Figure 2).

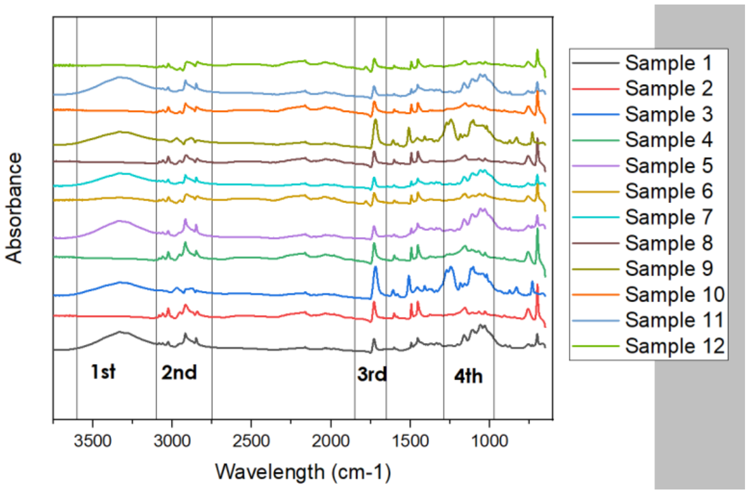

Figure 2. FTIR spectra for all printer ink samples and the four regions of analyses.

The first (1^{st}) region at wavelength of 3600 – 3200 cm^{-1} suggested the presence of hydroxyl group (O-H) with possible presence of compounds of carboxylic acid, alcohol and aldehydes. Clearly, all coloured printer inks showed strong absorption band in the first region due to presence of O-H group. However, weak absorption band was displayed by all of black printer inks samples at the wavenumber of 3600 – 3200 cm^{-1}. This suggested that O-H group is absent in the black printer inks. The second (2^{nd}) region at wavelength of 3200 – 2750 cm^{-1} corresponds to the C-H stretch with possible presence of compounds of alkenes, unsaturated rings (-CH=CH-) or aromatic compounds i.e., the aliphatic groups (-CH, $-CH_2$, $-CH_3$). One of the rapid diagnoses for the identification of chemical structure in the FTIR studies is the presence of single bond, double bond or aromatic ring formed by the C-H molecular stretch. The third (3^{rd}) region at wavelength of 1900 – 1700 cm^{-1} suggested the presence of ketones group i.e., C=O functional group with possible presence of acid halides, aldehydes, amides, anhydrides, and carboxylic acids. Finally, the fourth (4^{th}) region at wavelength of 1350 – 950 cm^{-1} corresponds to the presence of and sulphur (S=O), fluorine (C-F) and ether compound (C-O-C) functional group.

The principal component analysis (PCA) was performed on the spectra of twelve printer inks. The eigenvalues from the PCA decomposition showed that the first three principal components (PC) explain 94.78 percent variability in the printer inks, as shown in the scree plot (Figure 3).

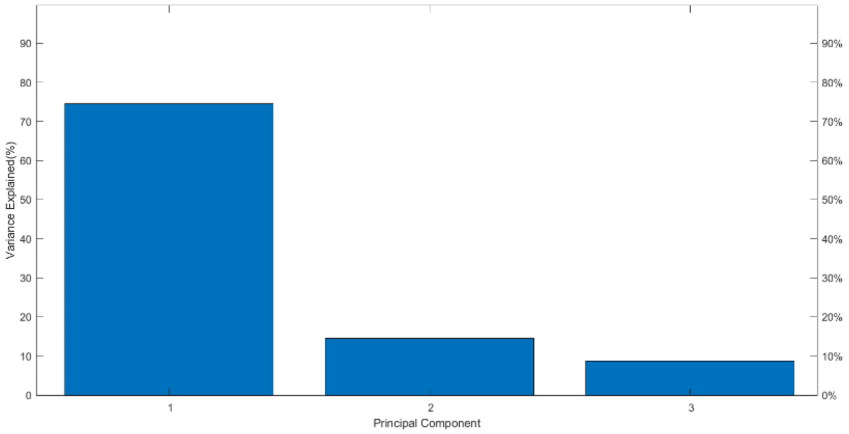

Figure 3. PC analysis of printer inks. Scree plot of the total variability explained by the first three PCs of the printer ink.

The score plot generated by performing PCA in the first region showed that PC1 successfully separates the black inks from the coloured inks due to the presence of the O-H functional group (Figure 4). The black inks were positioned on the right of PC whilst the coloured inks were positioned on the left of PC1.

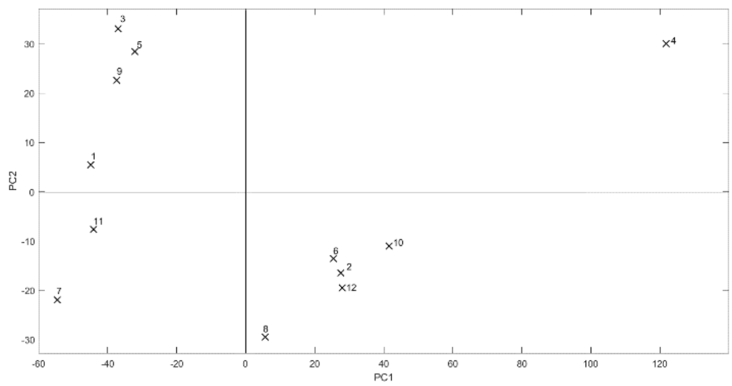

Figure 4. Score plot between first principal component and second principal component at region 3600 – 3200 cm^{-1}.

In the region 3200 – 3000 cm^{-1}, PC2 slightly separates the claimed to be authentic inks from the original and counterfeit inks as shown in Figure 5. The score plot divided into four quadrants which are quadrant 1 (located at positive region of principal component 1 and positive region of principal component 2), quadrant 2 (located at positive region of principal component 1 and negative region of principal component 2), quadrant 3 (located at negative region of principal component 1 and negative region of principal component 2) and quadrat 4 (located at negative region of principal component 1 and positive region of principal component 2).The samples in quadrants 1 and quadrant 2 the samples are displayed to have adsorption band below wavenumber of 3000 cm^{-1} while all the other samples in quadrant 3 and quadrant 4 shown to have peak above wavenumber of 3000 cm^{-1}. The score plot results show to distinguish between aliphatic and unsaturated compound in this project because any C-H stretch above 3000 cm^{-1} wavenumbers is the resulting from the C-H stretch of the aromatic, heteroaromatic, alkyne or alkene compounds meanwhile below than wavenumber of 3000 cm^{-1} indicates the compound is in aliphatic groups.

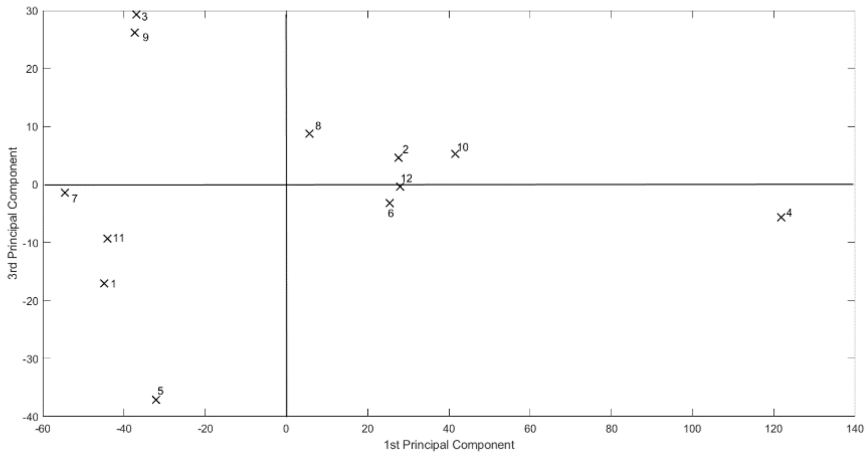

Figure 5. Score plot between first principal component and second principal component at region 3200 – 3000 cm^{-1}.

Figure 6 shows the score plot in the third region. The influence of ketone group or C = O in the spectrum compared to other functional groups such as O-H and C-H is the most intense due to the high intermolecular force or the difference in electronegativity shown by the oxygen with carbon bond. The wavelength of 1900 – 1700 cm-1, the present or absence of ketone functional group C=O can be detected. The other possible compounds are also aldehydes, carboxylic acid and esters. From the plot, only sample 4 were seen in the quadrant 4 meanwhile in the quadrant 3 there were only sample 5 and sample 11. In quadrant 1, there are 5 samples allocated which are sample 2, sample 6, sample 10 and sample 12. Sample 1, sample 3, sample 7 and sample 9 were in the quadrant 4. The score plot results show to distinguish between the samples with presence of ketone functional group and the sample with absence of ketone functional group.

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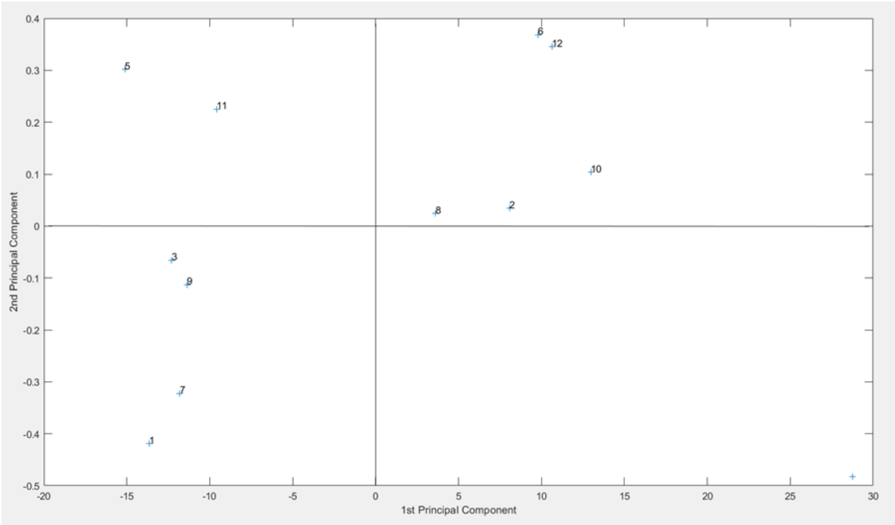

Figure 6. Score plot between first principal component and second principal component at region 1900 – 1700 cm^{-1}.

4. Conclusions

The implication of pairing between analytical method with chemometrics for the differentiation and characterization of several different types of printer inks were briefly discussed. The score plot of the principal component analysis enabled the discrimination of certain printer inks. The three proposed regions were significant to identify some of the compounds exist in the samples. The limitation of this study is that this study is applicable for same exact brands of samples used in this project only. Although there is no exact pattern to differentiate between counterfeit ink and authentic, some chemical component present in the printer inks can be identified and characterized. From forensic perspective, this situation may complicate the identification of the authenticity of printed ink deposited on a document. Thus, more research should be done to find out the other variables affecting the printer inks; hence producing a developing a printer inks database which can be used further for forensic purposes.

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